**Colorado State University**

**Department of Chemical and Biological Engineering**

**CBE 333: Chemical and Biological Engineering Lab I**

**Binary Distillation**

**Fall 2016**

OBJECTIVES

For the binary-distillation experiment, the goals are:

1. To demonstrate the applications of material and energy balances in the analysis of a distillation column.

2. To investigate the effects of operating conditions on the temperature and composition profiles within the column, and on the overall separation achieved.

3. To explore the effect of heat loss on column performance.

Working with teams from the other lab sections, students will systematically vary the thermal quality of the feed, the reflux temperature, the reflux ratio, and the feed tray location to determine the effects on the separation of a mixture of isopropanol and water.

INTRODUCTION

Distillation is a very common industrial separation process. Applications abound in the refining of petroleum and in the production of both commodity and specialty chemicals. It is an operation used to separate the components of a liquid mixture whenever the components differ in volatility. In such cases, when vapor-liquid equilibrium is achieved, the more volatile components concentrate in the vapor phase and the less volatile ones in the liquid phase. In a distillation column, rising vapor has multiple opportunities to equilibrate with descending (reflux) liquid. Thus, a much greater separation is achieved than is possible with a single equilibrium stage. The vapor-liquid contacts may be done continuously in a “packed” column or in discrete units in a “tray” column.

One reason for the popularity of distillation as a separation process is that heat is the “separating agent” in distillation. Since no foreign substance is introduced to bring about separation by distillation, there is no need to subsequently remove the separating agent in another separation process. Thus, distillation is sometimes referred to as an “ideal” separation, in contrast to “non ideal” separations such as absorption and extraction in which foreign substances are added to the feed.

Most industrial applications of distillation involve multi-component mixtures. However, most of the principles involved in multi-component distillation can be demonstrated with a binary mixture.

BACKGROUND

**Basic Mathematical Description**

To evaluate the performance of a particular distillation column when operated at a given set of conditions, it is necessary to develop a model of the system in terms of

(a) thermodynamic vapor-liquid equilibrium relationships

(b) total mass balances

(c) individual-component mass balances

(d) energy balances

and to obtain a mathematical solution of the resulting set of equations either analytically or graphically.

**Material and Energy Balances**

A mathematical analysis of continuous binary distillation under steady-state conditions begins with an overall column material balance equating input and output. Using the notation of Figure 1 (which counts plates up from the reboiler), this may be written as

 (1)

where F is the molar flow rate of the feed, D is the molar flow rate of the distillate and B is the molar flow rate of the bottoms. The corresponding balance for the more volatile component is

 (2)

where *zF,* *xD*, and *xB* are the mole fractions of this component in the feed, distillate and bottoms streams, respectively.

Making similar balances around the column top and the “n+1th” plate above the feed, as shown by the upper dotted line in Figure 1, one obtains

 (3)

and



 (4)

Here Vn and Ln+1 refer to the molar flow rates of vapor and liquid entering and exiting the section, respectively, and y and x are the vapor and liquid mole fractions of the more volatile component in these streams. Upon rearrangement, we obtain

 (5)



Making similar balances around the lower section of the column (see the lower dotted line in Figure 1), one obtains the analogous equations

 (6a)

 (6b)

and

 (7)

Equations (5) and (7) are the system operating lines.

In addition to the material balances written above, to completely define the system, an energy balance around each section is required along with a thermodynamic expression describing the vapor-liquid equilibrium relationship. Often, however, it is possible to make a simplifying assumption that uncouples the heat and mass balance equations. This assumption, known as constant molal overflow, requires that the liquid and vapor flows in each section remain constant (though not necessarily equal). This condition is achieved if:

(a) molar latent heats of the components are equal,

(b) sensible heat effects are negligible when compared to latent heat effects,

(c) the mixture forms a thermodynamically ideal solution (no heat or volume changes upon mixing), and

(d) heat losses from the column are negligible.

For many common situations encountered in simple binary distillation, these assumptions are reasonable.

**Vapor-Liquid Equilibrium**

In order to complete the mathematical system of equations, it is necessary to obtain the vapor-liquid equilibrium relationship. First, the relative volatility α for a binary mixture is defined as

 (8)

Equation 8 can be rearranged to yield

 (9)

which can be used to construct the “equilibrium curve” provided that a value for α is known. For cases in which modified Raoult's Law holds (i.e., when the vapor behaves as an ideal gas, and the liquid not necessarily as an ideal solution),

 (10)

and

 (11)

Using the above relations in (8) gives

 (12)

where P is the total pressure.  and  are the vapor pressures of pure components A and B, and values can be calculated with the Antoine equation. The liquid activity coefficients,  and , can be calculated using a variety of thermodynamic approaches, but for binary distillation the semitheoretical correlations developed by Margules, van Laar or Wilson are sufficient..

**Analytical Solution**

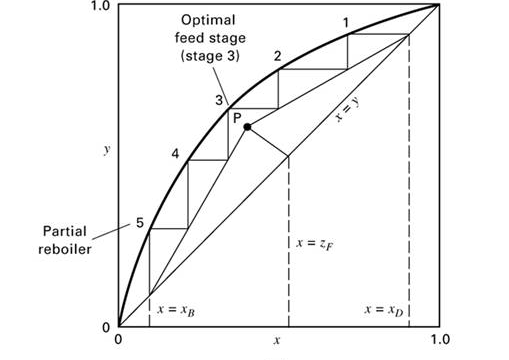
If the relative volatility, α, in equation (8) may be considered constant, a stage-by-stage analytical solution of the material balance equations (equations 1, 2, 3, 5, 6, 7) is feasible. For total reflux conditions, a shortcut procedure called the Fenske method, outlined in Appendix I, has been developed.

**Graphical Solution**

Often, however, it is difficult to express the vapor-liquid equilibrium relationship mathematically in a convenient form. Under these circumstances, a relatively straightforward graphical solution, known as the McCabe-Thiele Method, is available. This technique is essentially a step-by-step construction of the previously-developed material balance equations plotted on a y versus x (vapor-liquid) equilibrium diagram. In Figure 2, such a construction is demonstrated. The equilibrium line shows the thermodynamic vapor-liquid relationship for a typical simple binary mixture of two volatile liquids. Equations (5) and (7) are plotted as the rectifying and stripping operating lines, respectively.

Note that with the usual simplifying assumptions previously listed, constant molal overflow is obtained and the quantities  are all constants. Furthermore, if the product compositions xD and xB are fixed, then it is clear that equations (5) and (7) are both of the linear form: 

Thus, they yield lines when graphed on the McCabe-Thiele diagram. They intersect at the overall feed composition as shown in Figure 2.



**Figure 2:** McCabe-Thiele Graphical Method for solving simple binary distillation problems [2, pg. 267].

Starting at the top of the column, the vapor from the top plate is condensed. This implies that y1 = xD. Since the exiting vapor and liquid are assumed to be in equilibrium on an ideal stage, x1 is then found from the equilibrium curve of the diagram. A solution of the operating line expression for y2 in terms of x1 is readily obtained either mathematically or graphically by dropping a vertical from (x1, y1) to the rectifying line and reading the ordinate at this intersection.

In a similar fashion, one steps alternately between the equilibrium and operating lines to determine compositions of succeeding ideal stages in the column. After passing through the feed composition, the stripping operating line replaces the rectifying operating line as one terminator of each step. The procedure is continued until the bottoms composition xB is reached or passed. For the example shown in the preceding diagram, 5 ideal stages are required to obtain the indicated separation.

It should be noted, however, that in actual practice equilibrium between the exiting vapor and liquid streams is not usually attained; hence, the ideal stage represents only a theoretical goal. Stage efficiencies (defined as a function of the percentage approach to equilibrium between the two streams) for actual systems can range roughly between 30 and 80% of the theoretical value. Efficiencies can vary widely for any one particular stage, depending on the operating conditions and the physical and chemical properties of the mixture being distilled.

When the assumption of constant molal overflow cannot be made, the operating lines become curved and the material and energy balances must be solved simultaneously. A graphical procedure (Ponchon-Savarit Method), which requires enthalpy-composition data for the saturated vapor and saturated liquid, is available [2, pg. 286], but many software packages (e.g.,ASPEN) are able to model such cases.

FLUIDS

Water and isopropanol (2-propanol) are used in this experiment.

DESCRIPTION OF THE SYSTEM

The distillation column is pictured in Figure 3. The following is a brief description of the main pieces of equipment:

1. Feed Tank Reservoir - a 10-gallon, stainless-steel welded tank with a sloping bottom for proper drainage. The reservoir is fitted with a liquid-level slight-glass, a lockable safety filler cap, a return line from the boiler, and an outlet header that supplies two feed pumps.

1. Still Boiler - a 5-gallon, cylindrical, stainless-steel tank with dished heads. The main heating element is a stainless steel, sheathed-bayonet-type element with explosion-proof electrical fittings. This element has a continuously-variable control and is rated at 2500 Watts. Precise liquid level control is obtained by means of a float-type control element that actuates a solenoid-operated valve that recycles excess liquid from the still boiler to the feed reservoir. The boiler also has a drain valve and a temperature gage.
2. Condenser - Pyrex and stainless steel shell-and-tube type heat exchanger containing a spiral tube coil. The heat transfer area of the coil is 1.5 ft2. The flow of cooling water through the coil is measured and controlled with a rotameter, and the inlet and outlet water temperatures are measured with thermocouples. The shell side is equipped with a pressure-relief valve set for 1.0 psig.

1. Distillate Receiver - a 3-inch O.D. by 12 inch long Pyrex tube with stainless steel caps at the top and bottom. The top is equipped with a pressure-relief valve set for 1.0 psig. Condensate enters through the top. On the bottom there are three outlet lines: a sample/drain line, a reflux line that returns the condensate to the top of the column, and a distillate line that returns the condensate to the feed tank.
2. Feed and Reflux Immersion Preheaters - Cartridge-type heaters rated at 250 Watts and sealed in a stainless steel enclosure. Each unit has a thermocouple and a temperature control element (rated for 100°F to 275°F).
3. Instrumentation and Control Panel
   * Main system power is controlled by means of a circuit breaker, on/off switch, and indicator light.
   * Automatic controllers supply power to the boiler heater and to the feed and reflux preheaters at setpoints dialed in by the operator. The boiler is equipped with a thermal-overload indicator, and the total power being supplied to the system is indicated with voltmeter and ammeter readings.
   * The boiler-level-control switch activates the system’s automatic level controller.
   * On/off switches and indicator lights are placed on circuits for the centrifugal feed pump and the centrifugal reflux pump. Separate variable speed controllers are used for the diaphragm feed pump and the diaphragm distillate pump.
4. Thermocouples – twelve are connected at strategic points throughout the system These include one in the still boiler, six in the column (one for each sieve plate tray), two on the condenser water inlet and outlet lines, one for the distillate line, and one for each preheater. Outputs are monitored with a digital pyrometer with a selector switch.
5. Rotameters - used to meter the feed, reflux and distillate flows. Calibrations are provided in Appendix II.
6. Plate Column - consists of 6 sieve plate sections. Each is assembled from a 5-inch-long, 3-inch I.D. glass pipe section, a stainless steel process ring with four connections, and gasketed flanges and bolts.

SAFETY

Isopropanol is flammable and toxic, so handle it carefully and use the waste bottle provided to dispose of isopropanol/water solutions. Wear protective eyeglasses, long pants and closed-toe shoes in the lab. Locate the first aid cabinet, the fire extinguisher and the eye-wash station before running this experiment.

Note that the boiler heater and the feed and reflux preheaters can be extremely hot.

Pressure relief valves are located at the top of the distillate receiver and on the shell side of the condenser. These are set to open at approximately 1.0 psig.

W-1

R-2

R-4

R-3

R-5

C-1

F-1a

F-3

B-2

B-1

F-2

F-4

F-1b

Feed Pumps

T1

T2

T3

T4

T5

T6

T13

T12

T8

T10

T11

B-3

T9

PRV

PRV

T7

Feed Reservoir

Overheads

Receiver

Reflux

Pump

Distillate Pump

QF

QB

QL

R-1

Cooling

Water

**Figure 3:** Piping and instrument diagram (P&ID) for the binary distillation column.

LABORATORY PERFORMANCE

**Team A: Total Reflux**

1. The column will have been prepared by the Instructor following the startup procedure given in Appendix III.

2. While the total reflux run is coming to steady state:

* 1. Measure the refractive index (RI) of the isopropanol/water mixtures previously prepared. Refractometry procedures are given in Appendix IV.
  2. Convert the sample concentrations from v/v % isopropanol to mole fractions of isopropanol. Plot the RI versus mole fraction of isopropanol to obtain a calibration curve, and fit the data with an analytical expression that will be used later to convert RI readings to isopropanol mole fractions.

3. Run at total reflux.

* When the system has been stable long enough, take samples of distillate and bottoms through valves R-3 and B-1. Measure the refractive index of both samples by following the procedures given in Appendix IV.
* Take liquid samples from each tray in the column by inserting syringes through septum ports on the trays. Measure the RI of each sample.
* Record the temperature readings, power readings, rotameter readings and pump settings for the run on the electronic data sheet provided.

**Team B: Distillation Runs with Reflux**

1. The column will have been prepared following the startup procedure given in Appendix III.

2. Attach the feed line to the assigned tray. Adjust the feed preheater to obtain the assigned feed condition (saturated, subcooled). Adjust the reflux preheater to obtain the assigned condition (saturated, subcooled). Adjust the reflux and distillate flows to obtain the assigned reflux ratio while keeping the liquid in the overhead vessel stable. (The bottoms valve must be periodically clicking, indicating that there is actually product flow from the bottom of the column.)

2. Wait for the system to reach steady state at the assigned conditions.

* Monitor system temperatures and flow rates. Once no additional adjustments are required, wait for the composition of the overhead receiver to stabilize.
* When the system has been stable for 15 minutes, take samples of feed, distillate and bottoms through valves C‑1, R-3, and B-1. Measure the refractive index of each sample, and use the calibration curve obtained last week to determine the composition of each stream.
* Take liquid samples from each tray in the column by inserting syringes through septum ports on the trays. Measure the RI of each sample, and determine the liquid composition at each tray
* Record the temperature readings, power readings, rotameter readings and pump settings for the run.

3. Keeping the feed tray and feed flow rate constant, repeat the process with a reflux ratio of 1.

**Table 1:** Summary of run conditions for the distillation experiments.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Lab Section | Reflux Ratios | Feed Tray # | Feed Temperature | Reflux Temperature |
| T a.m.  T p.m.  R p.m. | 1 or 3  1 or 3  1 or 3 | 3  3  3 | T = Tbub  T < Tbub  T = Tbub | T = Tbub  T = Tbub  T < Tbub |

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1. McCabe, W. L, Smith, J. C., and P. Harriott. 2005. “Unit Operations of Chemical Engineering”,7th Edition, McGraw-Hill, Inc., New York, NY. Chapters 20 and 21.

2. Seader, J. D. and E. J. Henley. 2006. *Separation Process Principles*, 2nd edition, John Wiley & Sons, Inc., New York, NY. Chapter 7, pp 252-265 and 275-280.

**APPENDIX I**

**(FENSKE METHOD)**

For more information, see pages 687-688 in “Unit Operations of Chemical Engineering”,7th Ed.

**Fenske Equation**

Each equilibrium stage produces a liquid and a vapor that are in equilibrium with each other, thus they fall on the vapor-liquid equilibrium curve given by yi,n = Kixi,n. The liquid and vapor streams being fed to the stage are linked by material balances, and they fall on the operating line for the column, The minimum number of equilibrium plates required for a specified separation is found under total reflux conditions, where the reflux ratio is infinite and the operating line is y=x or the 45° line.

Material balance and vapor-liquid equilibrium equations can be written for each stage in a distillation column. The resulting set of equations can be simplified by assuming:

* Ideal solutions
* Constant relative volatility
* Constant liquid and vapor flow rates
* Total reflux

The solution to the simplified set of equations is the Fenske equation:



Where Nmin is the minimum number of equilibrium stages required for a separation. In this equation, *D* and B refer to the distillate and bottoms, *i* and *j* are components of interest in the system, *x* and *y* are mole fractions in the liquid and vapor phases, and αi,j is the relative volatility of component i with respect to component j. If the relative volatility varies from stage to stage, the value at the feed plate or the geometric mean on the values at the top and bottom of the column can be used as an approximation.

For a binary system, the Fenske equation simplifies to:



This is the minimum number of stages, so for a column equipped with either a partial reboiler or a partial condenser, one stage is already accounted for, and the minimum number of trays required is:



Similarly, for a column with both a partial reboiler and a partial condenser, the minimum number of trays required is:



**APPENDIX II**

**(ROTAMETER CALIBRATIONS)**

**Feed Rotameter:**



**Distillate Rotameter:**



**Reflux Rotameter:**



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**APPENDIX III**

**Column Start-up Procedures**

**Run Procedures**

**Shutdown Procedures**

**A. Column Start-Up Procedure** (See Figure 3):

1. Verify that the feed tank reservoir has been charged (through C-1) with 5 to 8 gallons of the isopropanol/water mixture.

2. Establish the flow of cooling water through the condenser.

* Open the cooling water supply valve to the cooling water tank in the closet. Verify that the tank contains water, and turn on the cooling water pump.
* Open the cooling water supply valve to the distillation system. Adjust the valve on the cooling-water rotameter to get a mid range reading. As the boil-up proceeds, adjust the rotameter until the top section of the condenser near the vapor inlet line is just warm to the touch.

3. Charge the boiler.

* Connect the flex-tubing feed line from the bulkhead to the boiler top through quick-disconnect coupling Q-1.
* Trace the line from the feed tank through the centrifugal feed pump to the boiler feed line. Open feed valve F-1a and bypass valve F-3. Close feed valve F-1b and rotameter valves F-2 and F-4.
* Turn on the main power switch and then the centrifugal feed pump switch. Verify that the indicator lights for these units are on.
* Switch the liquid level control toggle to the “auto” position. This pilot light will be on when the bottom solenoid drain valve is open.
* Monitor the liquid level as it rises in the boiler sight-glass. When the drain valve clicks open, turn off the centrifugal feed pump, and shut bypass valve F-3.
* Close feed valve F-1a, and open feed valve F-1b. Open the feed rotameter valves, F-2 and F-4, and turn on the feed pump at a setting of about 4.

4. Monitor the boiler level control.

* With a feed rotameter reading of ~120, the solenoid valve B-3 should maintain the appropriate boiler level by draining bottoms to the feed tank reservoir.
* The solenoid clicks as it operates, so when material flows at steady-state through the distillation column, one hears a steady clicking.

Note: **The clicking solenoid and the flashing valve-indicator light on the control panel show that the level in the boiler is being controlled. The level is falling if the drain valve stays constantly closed, and it is rising if the valve stays constantly open.**

5. Begin the heating cycle.

* Check the thermocouple and sample port tube fittings on each plate to insure that they are properly sealed.
* Turn the boiler power switch on; a pilot light should indicate heat input. If the light does not come on, press the reset button or check the fuse.

Note: If the liquid level ever drops below the electrical heating coils in the boiler, a thermal-overload switch set to 240°F interrupts the line power. This overload switch is located in the heater module mounted on the right hand side of the boiler. The reset is the red button in the center of the module. This device may be manually reset, but it can not be reset until the boiler temperature drops below the trigger value.

* Set the proportional power control switch for the boiler heater to turn full power until boiling begins, then throttle back to the desired value. Full power will be used for total reflux.
* Monitor the boiler temperature with the bimetallic thermometer on the front of the boiler and with thermocouple T-13.
* Open distillate valves R-2 and R-5 to prepare to send distillate back to the feed reservoir, and open reflux valve R-1 to prepare to send reflux back to the top of the column.
* The receiver drain valve R-3 initially should be opened for venting, but it must be closed as soon as condensate begins to be formed.
* The reflux pump may be turned on as soon as liquid covers the bottom of the overheads receiver. Once the level in the liquid level in the overheads receiver covers the tube supplying liquid to the distillate pump, the distillate pump may be turned on. Adjust the speed setting on the distillate pump to keep the level in the overheads receiver at the yellow line, and adjust the reflux rotameter to control the reflux ratio for the run.

Note: For the first week of the experiment, the students will be setting up a total reflux run. So warm up the fluid in the boiler, get the overheads receiver partially filled, and then turn off the power to the boiler, turn off the feed pump, and disconnect the feed line from the column. Use the distillate pump as needed to keep the overheads receiver from overfilling.

Note: For the second week of the experiments, the students will be making runs at different reflux ratios, so bring the system up and then run it at total reflux (no feed, no distillate, no bottoms) until the students arrive.

**Column Shut-Down Procedure** (See Figure 3):

1. Turn off the boiler power switch.

2. Turn off the feed and reflux preheaters and the feed and reflux pumps.

3. When the distillate receiver is empty, turn off the distillate pump.

4. When condensate no longer collects in the distillate receiver, open valve R-3 and drain the remaining liquid from the receiver and return the liquid to the feed reservoir. Leave valve R-3 open so the system can vent as it cools.

5. Monitor the temperature on the upper plate (Thermocouple 6). Turn coolant flow valve W-1 off when condensate no longer forms. Turn off the cooling water pump and close the cooling water supply line. Continue venting the system through distillate drain line valve R-3.

6. Wait for the entire system to cool.

* Drain the boiler through solenoid valve B-3 and drain line valve B-2 back into the feed reservoir. When draining, open vent C-1.
* Close valve R-3.
* Turn off the main power control switch.

**APPENDIX IV**

**(Refractometry Procedures)**

**Refractometry Procedures: Measuring the Refractive Index of a Liquid**

1. Establish the flow of cooling water through the refractometer.

* Turn on the water bath and the recirculation pump.
* Wait for the temperature of the refractometer to stabilize at 20 ºC.

2. Clean the glass surface. Be careful not to scratch the glass!

* Pivot the light down.
* Unlatch the sample cover and pivot it to reveal the sample plate.
* Clean the glass surface of the sample plate.
  + Place a couple of drops of DI water on the glass and wipe it dry with lens paper.
  + Place a couple of drops of acetone on the glass and wipe it dry with lens paper.
  + Place a couple of drops of sample on the glass and wipe it dry with lens paper.

3. Measure the refractive index of the liquid sample.

* Load the sample.
* Carefully place a couple of drops of sample on the glass.
* Pivot the cover into position and latch it.
* Adjust the light.
* Pivot the light up toward the refractometer.
* Turn the light on with the toggle on the left side of the refractometer.
* Adjust the direction of the light to maximize its intensity.
* Turn the light off to locate the cross hairs and scale inside the field of
* Adjust the line dividing light and dark.
* Toggle the light off to locate the cross-hairs and scale inside the field of view.
* Toggle the light on and align the line with the cross-hairs using the large knob on the right side of the refractometer.
* Eliminate color, get a sharp line using the small knob on the front of the refractometer.
* Read the refractive index.
* Toggle the light off, and read the RI off the scale inside the field of view.

4. Clean the glass surface. Be careful not to scratch the glass!

* Pivot the light down.
* Unlatch the sample cover and pivot it to reveal the sample plate.
* Clean the glass surface of the sample plate.
  + Place a couple of drops of DI water on the glass and wipe it dry with lens paper.
  + Place a couple of drops of acetone on the glass and wipe it dry with lens paper.

5. Shutting down the refractometer.

* + - Close and latch the sample cover.
    - Pivot the light into position, and turn it off.
    - Turn off the water bath and the recirculation pump.
    - Place the plastic cover over the refractometer.
    - Wash all sampling equipment and put it away.