

Methanol Recovery Optimization Via Distillation

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Methanol Recovery Optimization via Distillation for New
Biodiesel Venture for Brown industries, Inc.

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Final Report
Plant Monday

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We have neither given nor received unauthorized aid on this
report, nor have we concealed any violations of the Honor
Code.

Chris Lyon

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Abstract

[intro to distillation column, and fact that we're using it to distill the waste stream so methanol can be reused in the biodiesel production process.]

[Insert Super quick summary of major results]

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1. Overview

Brown Industries, Inc. is entering the biofuel market and is interested in designing and building a plant in Michigan to convert oil to biodiesel for commercial use. In this process, methanol will be recovered from waste streams and purified using distillation to be reused in the transesterification reaction and water purified enough to be reused in the POD extraction.

[talk about the 3 rotations to show we understand how our rotation fits in with the overall scope of the project] On September 7, 2012, you requested our team to conduct a feasibility study to determine whether building a packed column with “Pro-Pak” protruded metal packing (Scientific Development Co.) will be more economical than an equivalent tray column.

1.1 Objectives

Below are the objectives for the first rotation:

- Characterize methanol-water distillation process from pilot scale experiments
- Identify operational limits of column
- Develop a simulation model for the packed-bed distillation that incorporates economic analysis of the distillation process
- Investigate scale-up of the process unit to the corresponding industrial unit using ASPEN

In order to meet the above objectives, below are our goals for the first rotation:

- Determine a calibration curve for the Gas Chromatograph with methanol-water standards.¹
- Create a process flow diagram and determine mass-transfer parameters such as N_{og} and H_{og} for various runs. These parameters will be compared to the data from Scientific Development Co.¹
- Perform a “control run” at conditions which give methanol compositions in the distillate which are higher than 98 vol%. Assess the reproducibility of this run.
- Either validate the existing shortcut distillation modeling spreadsheet or develop a new model which can predict the performance of the pilot-scale column. Use experimental data to validate the accuracy of the model and to measure the characteristics of the packing.¹
- Correlate H_{og} vs. vapor velocity for the methanol-water system.¹

The purpose of this report is to describe how our team plans to meet these objectives, including the experimental design applied to accomplish the objectives, the results obtained, analysis performed, and recommendations for further improved investigation. We believe our

work on the distillation column provides a sound foundation for further G.G. Brown Industries, Inc. experimentation in rotations 2 and 3.

1.2 Summary of Key Results

The essential findings for each of the assignment objectives follow:

1.2.1 GC Calibration Curve

1.2.2 Mass-Transfer Parameters

1.2.3 Control Run

1.2.4 Validation Shortcut Distillation Spreadsheet

1.2.5 Correlation of Hog vs. Vapor Velocity

2. Background

Distillation is a method of separating mixtures based on differences in volatilities of components. Separation of components depends on the commercial uses of distillation columns currently range widely. Distillation columns are used for separating crude oil into fractions to be used for transport, power generation and heating. Columns are used to distilling water in order to remove impurities. Distillation columns can be used to separate air into pure oxygen and pure nitrogen.

To improve separations the use of trays can be supplemented by the use of packings. Packings are passive devices that are designed to increase the interfacial area for vapor-liquid contact. Packing can be strangely shaped pieces are supposed to impart good vapor-liquid contact when a particular type is placed together in numbers, without causing excessive pressure-drop across a packed section. This is important because a high pressure drop would mean that more energy is required to drive the vapor up the distillation column. Packing provides efficiency of separation in for the same column height of a tray column. Therefore, packed columns are usually shorter than trayed columns.

2.1 Distillation Column Apparatus

The TECHNOVATE Fractional Distillation Column can be operated in a constant recycle mode. This features allows the column to operate for a long time with a relative small amount of feed. In this operation, the distillate and bottom products are recombined and directed to the feed

tank. The apparatus includes a column, packed with 1/4-inch Pro-Pack stainless steel random packing. The column is 31 inches in height and has a 3 inch ID glass pipe section.

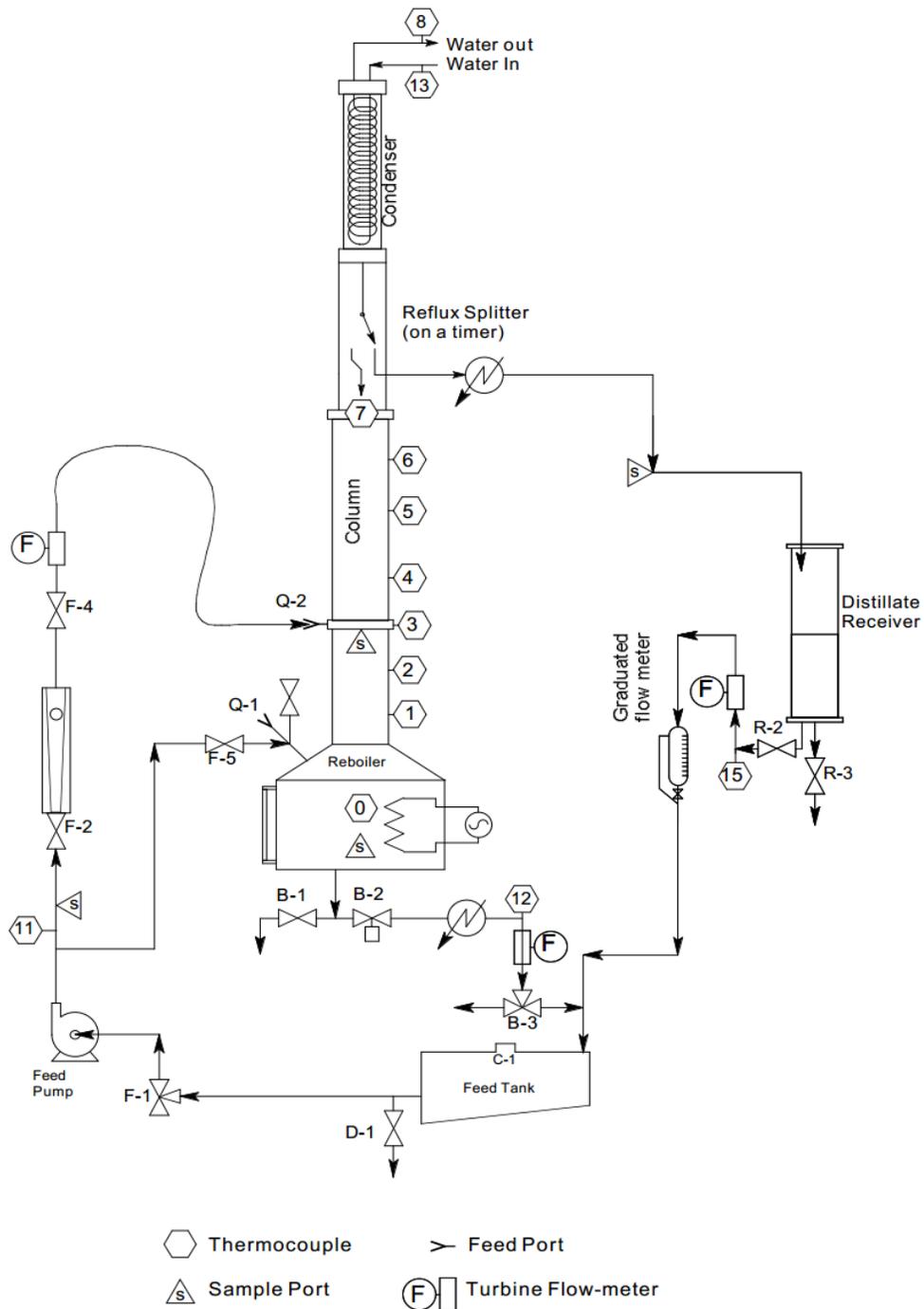
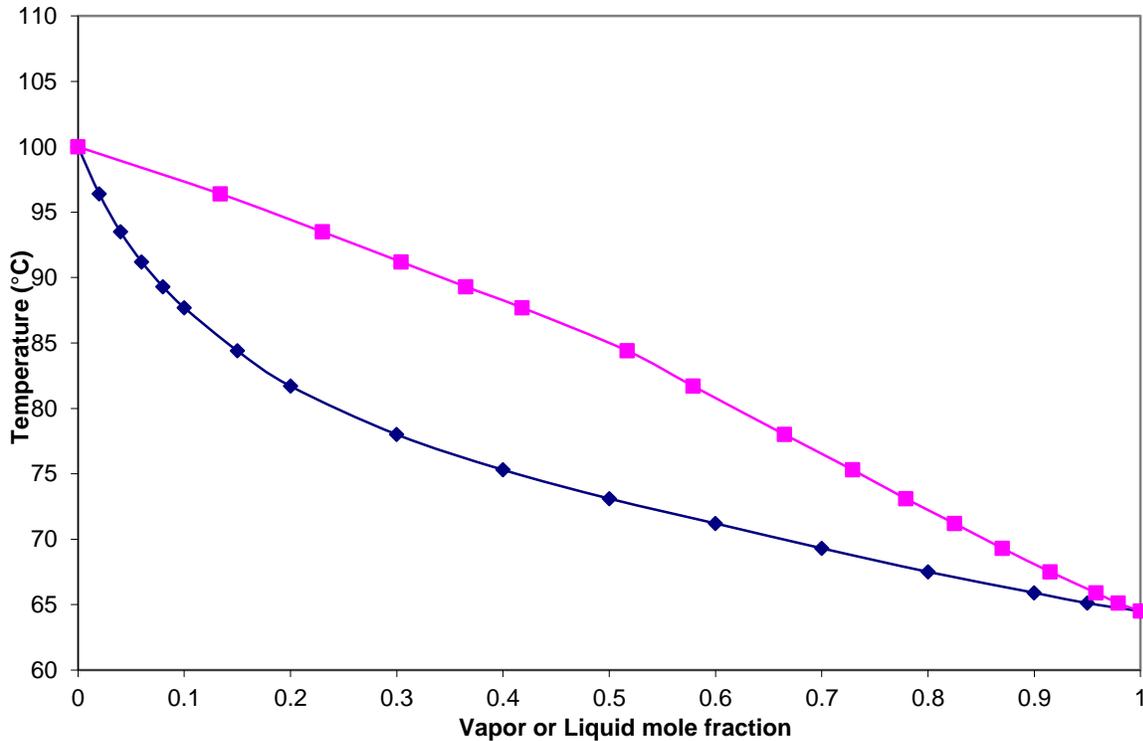


Figure 1: Piping and Instrumentation Diagram of the BI Packed Bed Distillation Column

2.2 Methanol and Water Separation

Distillation is possible for a methanol-water mixture because their vapor and liquid concentrations vary with temperature, as shown in a T-x-y diagram (Figure 2). Using this property of the methanol-water mixture, it is possible produce high purity methanol.



2.3 GC Correlation Curve

In order to determine the concentration of methanol in the distillate a Gas Chromatograph (GC) will be used. A GC will report the area under the curve for each component (methanol and water) which is proportional to the amount of each component in the sample. A calibration curve will be necessary to correlate the percentage of methanol in a sample to the area under the curve reported by the GC.

2.3 Mass-Transfer Parameters

$$Hog = \frac{V}{K_y' a S (1 - y_A)_{LM}}$$

Where:

$$(1 - x_A)_{LM} = \frac{(1 - x_A) - (1 - x_{A,i})}{\ln \frac{1 - x_A}{1 - x_{A,i}}}$$

and

$$N_{og} = \int_{y_{out}}^{y_{in}} \frac{(1 - y_A)_{LM} dy_A}{(1 - y_A)(y_A - y_{A,i})}$$

Where:

$$(1 - y_A)_{LM} = \frac{(1 - y_A) - (1 - y_{A,i})}{\ln \frac{1 - y_A}{1 - y_{A,i}}}$$

Where:

V = vapor flowrate
 Ky' = overall mass transfer coefficients
 a = interfacial area/ volume
 S = cross sectional area of packing
 X = liquid fraction
 Y = vapor fraction
 K = equilibrium constant

These Hog and Nog equations simplify to the following two equations with the assumption that the feed to the column is diluted in methanol, specifically that the feed used is less than 5% methanol:

$$H_{og} = \frac{V}{K_y' a S}$$

and

$$N_{og} = \frac{\ln \left[\frac{(A - 1)}{A} \times \frac{(y_{in} - K x_{in})}{y_{out} - K x_{in}} + \frac{1}{A} \right]}{\frac{A - 1}{A}}$$

Where: $A = \frac{L}{KV}$

$$L_t = H_{og} N_{og}$$

Where: L_t = Distillation tower height

2.4 Control Run

2.5 Shortcut Distillation Modeling Spreadsheet

2.6 Modeling Assumptions

Constant molar overflow is defined as the assumption that all liquid and vapor flows (on a molar basis) in the rectifying section are constant. As well, all liquid and vapor flows in the stripping section are constant but not necessarily the same as those in the rectifying section. This assumption is valid if the column is adiabatic, excluding the reboiler and condenser, as well as if the enthalpic contributions due to temperature changes are negligible relative to those due to phase change. Lastly, this assumption is valid if the heat of vaporization per mole is not concentration dependent. Enthalpy-concentration method differs from constant molar overflow assumption since it takes into account the thermal effects and the molar overflow

rates are not necessarily constant. The enthalpy–concentration method for a binary vapor–liquid mixture takes into account latent heats, heats of mixing, and sensible heats of the components of the mixture.

2.7 Correlation of Hog and Vapor Velocity

3. Materials and Methods

3.1 Equipment

The equipment consists of the following parts. Figure A-1 shows a schematic diagram of the exchange column:

- **Feed Tank Reservoir.** An 8-gallon stainless steel tank with a sloping bottom for proper drainage is provided to use the column in the recycle mode. This reservoir is fitted with a liquid-level sight-glass, a drainage valve, and a safety filler cap.²
- **Reboiler.** A cylindrical stainless steel tank with a capacity of approximately 3.8 - 4.0 gal at operating level. The boiler, covered with foam rubber insulating material, is encased top and sides with stainless steel sheet metal. The tank is fitted with a quick-disconnect coupling port for feed and a sight-glass for visual liquid level indication. The main heating element is a stainless steel sheathed bayonet-type 3-phase electric heater with a nominal power rating of 15 Kilowatts at 240 VAC (but operating at 208 VAC). Thermal-overload protection is provided by a manual-reset, pilot-lighted power switch located in an auxiliary heater and by a level switch that will not allow the heater to turn on until the liquid level is completely covering the heaters. The auxiliary heater power rating is 200 watts at 240 VAC (but operating at 208 VAC). The total maximum power generated by the reboiler heaters is approximately 11 kW at 208 VAC. The power to the two heating elements is controlled by an electronic switch which operates by cycling the heater on and off in 1 to 3 seconds intervals. The relative times the heaters are on or off determine the amount of power supplied to the reboiler. A flow switch located in the condenser water line assures that no power can be applied to the reboiler if the water flow to the condenser is shut-off. Liquid level control is obtained by means of a second level switch that actuates a solenoid-operated valve. This valve recycles excess liquid from the still boiler to the feed reservoir. The reboiler also has a drainage stopcock. A stainless steel flange-type fitting directly connects the distillation column to the boiler.²
- **Packed Column.** Consists of 2 packed bed sections each assembled from a 3- inch ID glass pipe section. Each section contains process fittings for feed, pressure and temperature measurement. A sample valve is available between the packed sections to sample the liquid leaving the rectifier (enriching) section. Fig. A-2 shows the layout of the sample port section at the middle of the column, indicating the liquid flow path

through the sample port and the position of the feed distributor. The packed column, when assembled, is approximately 31 inches in height, bolted to the top of the reboiler at the bottom and to the reflux splitter at the upper end. The packing sections are 12 and 18 inches long for bottom and top respectively, and they are filled with 1/4-inch Pro-Pack stainless steel random packing.²

- **Reflux Splitter.** Used to set the desired reflux ratio by switching the condensate flow from the reflux position to the distillate position a predetermined amount of time each. The default (power OFF) position for the reflux splitter is for total reflux. The timer to change the time allocated to each position is located on the rear of the apparatus. The green button to select the field to be changed, the red button changes the value of that field. The field values should be: TON distillate time; TOFF reflux time.²
- **Condenser.** Pyrex and stainless steel shell-and tube type heat exchanger, which contains the equivalent of 3.5 sq. ft. of spiral-tube heat exchange surface. The tube side coolant is water from the municipal water supply. Thermocouples are placed in the tube side to monitor the inlet and outlet temperatures of the cooling water. The top of the condenser is vented through a flame arrestor. The shell side condensate drains directly into a reflux splitter. The cooling water supply to the condenser is equipped with a flow-switch that will cut the power to the reboiler if there is a loss of water flow to the unit.²
- **Distillate Receiver.** A 3-inch OD by 12-inch long Pyrex glass tube that is flanged top and bottom with stainless steel caps. Condensate enters from the condenser through a 3/8-inch stainless steel tube into the top. There are two connections at the bottom of the receiver: a valve drain, and a valve connecting to the distillate flow flowmeter.²
- **Instrumentation and Control Panel.** A voltmeter and ammeter for power input indication, a boiler liquid level control switch for automatic operation, on/off electrical switches for main power, reboiler power, feed pump, reflux splitter, and a continuously variable control elements for the main boiler heater. The ammeter is calibrated with a 0-100% scale which corresponds approximately to 0-100% of the maximum power of the reboiler heater. This ammeter does not provide any information on the power used by the pumps, or the rest of the system, only on the power used in the reboiler. On the back side of the Distillation apparatus there is a 3-phase power meter, which is connected directly to the power supply to the reboiler heaters. This power meter has two digital indicators. The main power counter (non-resettable) located in top, records cumulative power in 100 watt-hour increments (0.1 kWh). The auxiliary power counter (user resettable) located below, records cumulative power in 1 watt-hour increments. These Power meters are more accurate than the ammeter in the front panel to estimate the power used by the reboiler.²
- **Thermocouples.** A total of 16 type K (chromel-alumel) thermocouples (TC) are installed at various locations throughout the distillation column system. These thermocouples are

connected to a computer for monitoring and data logging. Thermocouples 1, 2, 4, 5, and 6 are fixed to the exterior glass surface of the packed column wall and under the insulation. These 6 thermocouples are slow to respond to temperature changes and record temperatures that are slightly lower than the streams inside the column. All other thermocouples are inserted in the stream being measured. All temperature values are displayed and saved to file in degrees Celsius.² See Figure A-4 in appendix A for location of thermocouples.

- **Rotameters.** Mounted on the main panel, used to measure the feed and coolant flows. The feed rotameter is nominally rated at 700 cc/min for a liquid with a specific gravity of 1.0 at standard conditions. The scale reads from 10 to 100. Distillation Manual – 6 The floats inside the glass tubes are glass and tungsten carbide (carballoy) with a diameter of 0.25 inches and densities of 2.53 and 14.98 g/ml respectively. Flow rate data for a generalized calibration of this rotameter is available in the *Calibration of Distillation Column Rotameters* memo in the appendix to this section. The condenser cooling water rotameter has a nominal rating of 0 to 1.6 GPM. for water.²
- **Turbine Flow Meters.** There are three volumetric turbine flow meters to measure the feed, distillate and bottoms flows. Two of these flowmeters (Cole-Parmer models E-32250-00) and their associated instrumentation have a range of approximately 50 to 1600 ml/min for the feed and 50 to 800 ml/min for the distillate. The expected accuracy of these flow meters is ± 20 ml/min. The bottoms flow meter (Cole-Parmer model E-32250-30) has a range of approximately 500 to 20,000 ml/min, with an accuracy of ± 200 ml/min. These flow meters exhibit a non-linear behavior below the stated range. The signals from these flow meters are sent to a computer for monitoring and data logging. All units of flow in the monitor and data files are in ml/min. For more accurate readings of the distillate flow at very low flow rates a graduated cylinder with a stopcock at the bottom is provided at the outlet of the distillate flow meter (on the back side of the apparatus) so the flow can be measured manually with the collected volume and a timer.²
- **Piping and Valving.** All piping is either 1/4-inch or 3/8-inch stainless steel tubing. All tube connections are made with standard stainless steel tube type compression fittings. Process valves are stainless steel 1/4-inch or 3/8-inch needle or bar stock valves. Quick-disconnect couplings are used on the flexible hose feed line, packed column, and reboiler. These couplings, of the double ended, shut-off variety, are constructed of stainless steel with high temperature, solvent-resistant, synthetic gaskets and seals.²
- **Differential Pressure Gauge.** The high-pressure tap is connected to the vapor space above the reboiler (below the stripping section) and the low-pressure side is connected to the vapor space above the enriching section of the column. This gauge is useful to

predict flooding conditions in the packed column. Values of differential pressure displayed and stored are in inches of water column.²

- **Three-way Ball valves for switching service.** These valves are generally used either to switch a particular flow into 2 possible directions or to direct either one of 2 different flows into a desired destination. Fig, A-2 shows a schematic representation of these valves and how they operate. Valves F-1 and B-3 are used to select either the Production mode or the Feed-recycle mode of operation.²
- **Carle 100 Gas Chromatograph.** Located in room 3000 GG. Brown.³
- **PeakSimple1 Software.** Capable of data acquisition.³
- **2-mL sample vials.** For GC analysis of distillation column samples.³
- **1-mL capacity syringe.** Syringe has type 5 needle for sample collection from the still.³
- **1-microliter capacity syringe.** Syringe is set to deliver 0.2 microliter sample for sample injection into GC.³
- **LabVIEW.** Capable of data acquisition.³
- **Aspen software.** Capable of process flow diagrams.³

3.2 Materials

The following materials are necessary to perform the requested experimentation on the distillation column:

- **Methanol-water standards.** Various methanol in water compositions.
- **Cooling water.** Enough cooling water for condenser to operate for full laboratory time period.
- **Methanol-water feed solution.** Enough feed solution to run distillation column for full laboratory period.

3.3 Experimental Procedure

The follow sections will explain the procedures necessary to obtain the desired objectives.

3.3.1 Collection of Data

Use Personal Protection Equipment

Safety glasses, safety gloves and lab coats will be worn at all times.

Gas Chromatograph Operating Procedure

1. Make sure the GC was on for at least 1 hour prior to use.
2. Make sure that output pressure from the helium cylinder is 40psig.
3. Check that helium flows to the columns are set at 20 for both rotameters (this roughly 12ml/min).

4. Make sure that the GC control panel switches are in the following positions.
 - a. Min Powers On
 - b. Inlet delta T On
 - c. Column Temperature 90° C
 - d. Reaout: Right Column
 - e. Bridge Setting: Thermistor
 - f. Output: 1
5. . Make sure the Dell computer is attached to the GC and is turned on.
6. . The PeakSimple software must be turned on
 - a. Username: chelab; password; DataAnalyssis1
 - b. Double-click on icon named: Peak33-32bit-Shortcut.
 - c. From the file menu open the file named H20-MEOH.ASC
 - d. The software is now ready to use

Sample Injection to GC

1. Inject 0.2-microliters of the sample into Column B, located on the right of the GC by using a 1-microliter syringe.
2. Press the “Spacebar” on the computer key board immediately after injection.
3. When the run is finished, select from the Edit menu the “Smoothing” option. Then click the “Apply” button.
4. To see the results, select “Results” option under the “View” menu.
5. To print, click “Print” icon on toolbar.

3.3.2 Method for Data Analysis

Develop Calibration Curve Procedure

1. Test the seven standard methanol-water samples provided using the sample inject and Analysis section.
2. Mix additional trial methanol-water samples with large a percent of methanol to improve accuracy of the curve for samples with high concentrations of methanol.
3. Convert the given wt.% provided into mol %. See sample calculation #
4. Calculate the % of area under each peak from the results provide by the GC. See sample calculation #
5. In excel, make a scatter plot with mol. % on the y axis and % area of peak 1 on the x axis. On the same graph, plot mol. % on the y axis and and % area of peak 2 on the x axis.
6. Add a trendline and equation of the line to the plot.
7. Use trendline to calculate the mol.% methanol in any sample taken from

Determine mol% Methanol in Sample

1. Use GC Operating Procedure and Sample Injection and Analysis Procedure above to test sample on GC
2. Use equation of calibration curve, by plugging known % area into equation of line. See sample calculation.

3.3.2 Justification of Data Collection

4. Results and Analysis

We were able to analyze the packing by calculating the Hog of different runs and extracting the Ky of the packing. This was done by first numerically integrating to calculate Nog and using equation (XX) to determine the final value of Hog for each trial. An example of the numerical integration and calculation of Hog can be seen in Appendix XX.

$$N_{og} = \int_{y_2}^{y_1} \frac{dy}{y - y^*}$$

With this Hog analysis we were able to make a graph of Hog vs. vapor pressure for different run conditions and find a correlation, graph and correlation shown in Appendix XX. This correlation allowed us to use the spreadsheet provided to confirm our experimental values. [XX]

5. Discussion

6. Conclusions and Recommendations

7. References

[1] "ChE460 Distillation Assignment". Accessed September 6th, 2012. <https://ctools.umich.edu>

[2] "Tecnovate Pilot-Scale Distillation Column". Accessed September 6th, 2012. <https://ctools.umich.edu>

[3] "Standard Procedure of the Analysis of Methanol in Water Mixtures". Accessed September 6th, 2012. <https://ctools.umich.edu>

[4] "Distillation an introduction" Accessed September 12, 2012. <http://lorien.ncl.ac.uk/ming/distil/distilint.htm>

8. Nomenclature Table

List of Appendices

- Appendix A: Distillation Equipment
- Appendix B: Example Calculations
- Appendix C: Extra Figures
- Appendix D: Error Analysis Example Calculations
- Appendix E: Raw Experimental Data
- Appendix **XX**: Sample Numerical Integration
- Appendix **XX**: Hog vs. Vapor Pressure

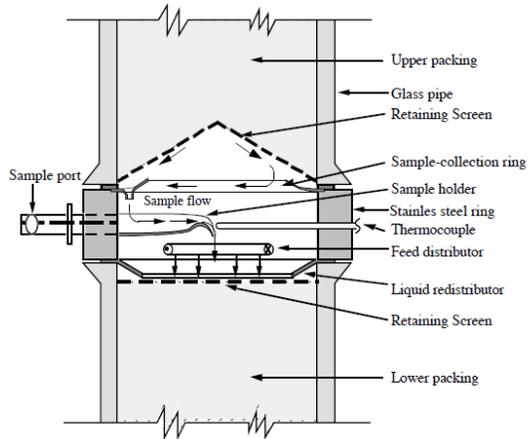


Figure A-2. Feed and sample port layout at the center of the column. Figure adapted from “Technovative Pilot-Scale Distillation Column” by Brown Industries

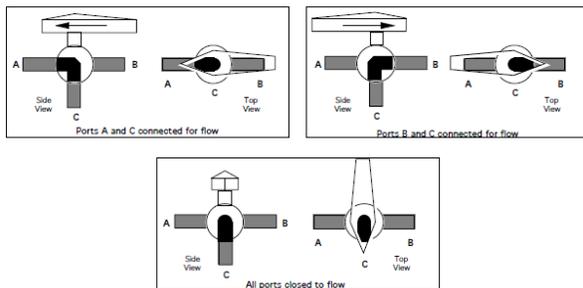


Figure A-3. 3 way valve for switching directions of liquid streams. Figure adapted from “Technovative Pilot-Scale Distillation Column” by Brown Industries

TC No.	Location
0	Reboiler
1	Column wall (external) 4.0 inches above lower packing support.
2	Column wall (external) 8.0 inches above lower packing support.
3	Column interior, between lower and upper packing sections, above the feed inlet.
4	Column wall (external) 4.5 inches above upper packing support.
5	Column wall (external) 9.0 inches above upper packing support.
6	Column wall (external) 13.5 inches above upper packing support.
7	Column interior, above upper packing section, inside the reflux splitter. It measures the vapor temperature leaving the column.
8	Cooling water temperature leaving condenser
9	Not used.
10	Not used.
11	Liquid temperature at the feed flow meter.
12	Liquid temperature at the bottoms flow meter.
13	Cooling water temperature entering condenser
14	Not used.
15	Liquid temperature at distillate flow meter.

Figure A-4. Location of thermocouples. Figure adapted from “Technovative Pilot-Scale Distillation Column” by Brown Industries

Appendix B: Example Calculations

Create Calibration Curve Procedure

- Convert the given wt. % provided into mol %.

$$\begin{aligned} \text{mol. \%}_{\text{MeOH}} &= \frac{\text{wt. \%}_{\text{MeOH}}}{M_{\text{W}_{\text{MeOH}}}} \times (X_{\text{MeOH}}M_{\text{W}_{\text{MeOH}}} + X_{\text{H}_2\text{O}}M_{\text{W}_{\text{H}_2\text{O}}}) \\ &= \frac{49.88 \text{ wt. \%}}{32.04 \frac{\text{g}}{\text{mol}}} \times (0.4988 \times 32.04 \frac{\text{g}}{\text{mol}} + 0.52012 \times 18.02 \frac{\text{g}}{\text{mol}}) = 39.18 \end{aligned}$$

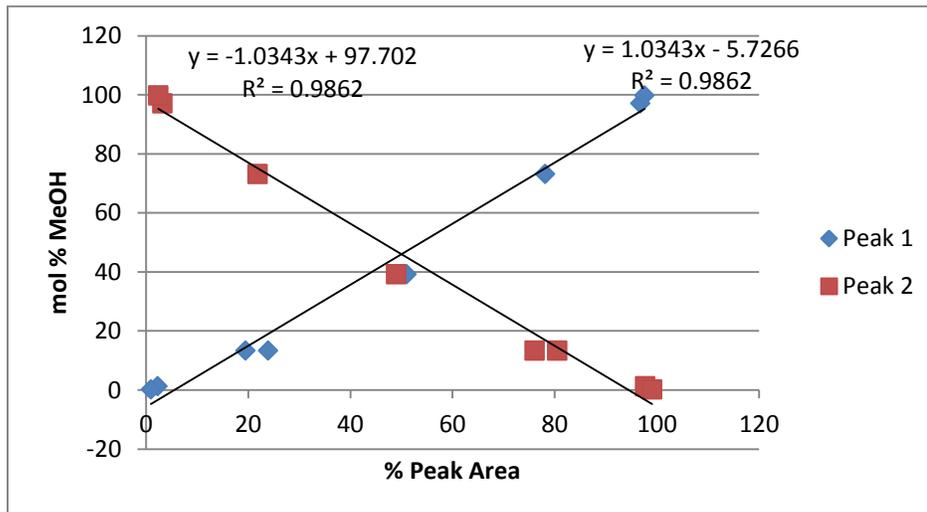
Similar calculation can be done to find mol. % H₂O

- Calculate the % of area under each peak from the results provide by the GC.

$$\begin{aligned} \% \text{ Area Peak 1} &= \frac{\text{Area Peak 1}}{\text{Area Peak 1} + \text{Area Peak 2}} \times 100 \\ &= \frac{24.3351}{24.3351 + 401.9275} \times 100 = 5.71 \end{aligned}$$

Similar calculation can be done to find the % Area of Peak 2

- In excel, make a scatter plot with mol. % on the y axis and % area of peak 1 on the x axis.
- On the same graph, plot mol. % on the y axis and the % area of peak 2 on the x axis. Add a trendline and equation of the line to the plot.

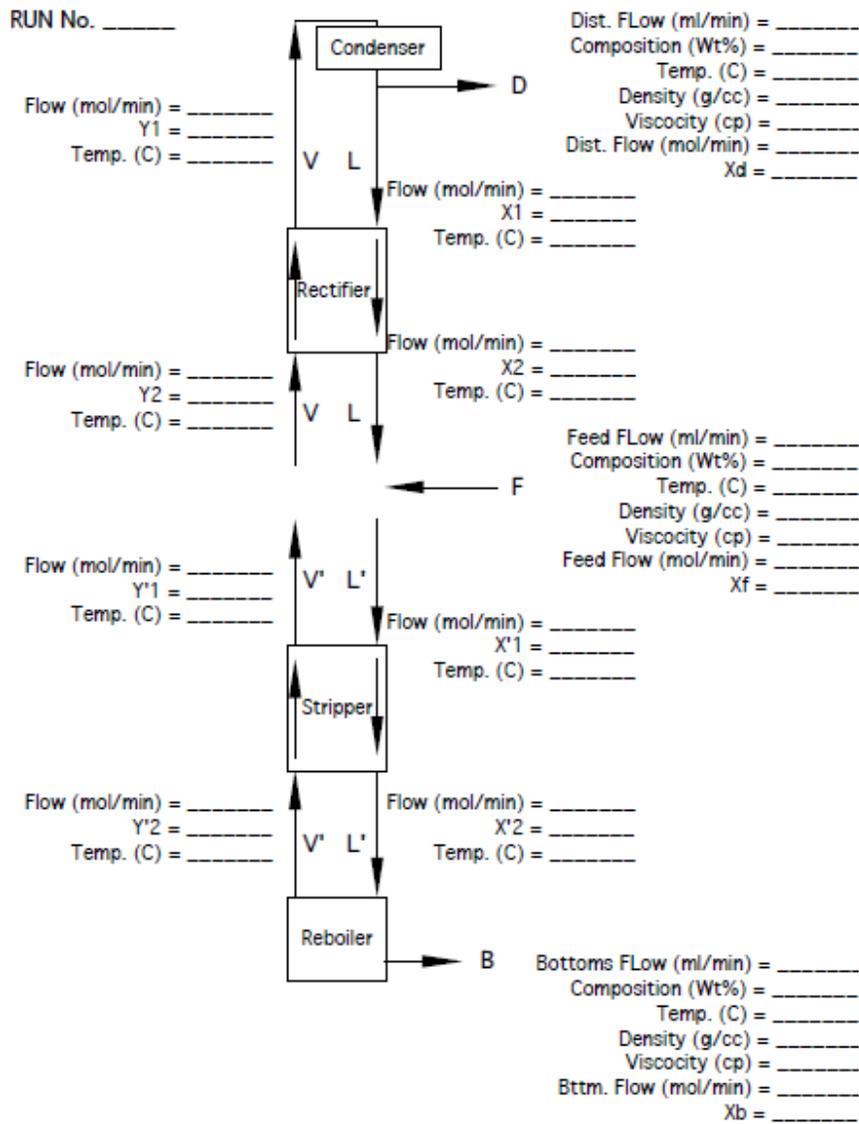


- Use trendline to calculate the mol.% methanol in any sample taken from the column

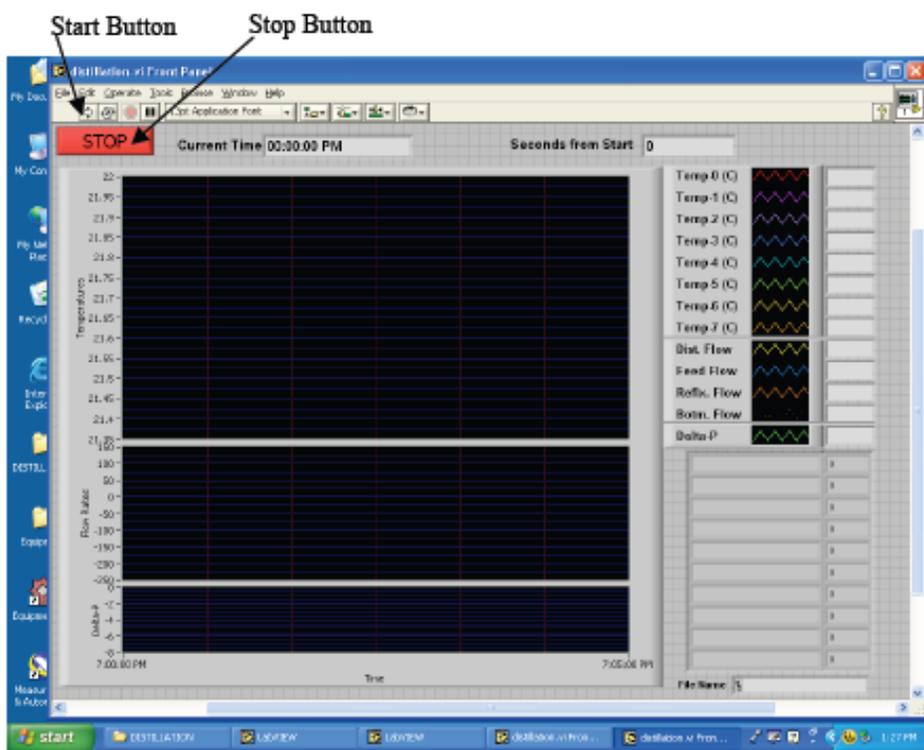
$$\text{mol. \%}_{\text{MeOH}} = 1.0343 \times \% \text{ Peak 1 Area} - 5.7266$$

When % area of Peak 1 is 5.7089:

$$\text{mol. \%}_{\text{MeOH}} = 1.0343 \times 5.7089 - 5.7266 = 0.18\%$$



Figure#. Process Flow Diagram. Figure adapted from “Technovative Pilot-Scale Distillation Column” by Brown Industries



Figure#. LabVIEW software interface. Figure adapted from “Technovative Pilot-Scale Distillation Column” by Brown Industries

Appendix **XX**: Sample Numerical Integration