

# Pycnometry and Continuous Distillation of Ethanol-Water mixtures

Joseph Zimmerman

**Abstract**—In this paper, two experiments were conducted on ethanol-water mixtures. A pycnometer and quartz-tubed densitometer were used to determine liquid densities across a variety of compositions of ethanol and water. Alcohol-gauging tables from the US Alcohol and Tobacco Tax and Trade Bureau (TTB) were used to correlate theoretical densities of various compositions of ethanol and water at various temperatures to apparent proofs at 60F and finally correct to true proof and mole fraction of ethanol. Densities, measured through the pycnometer and densitometer, were compared.

**Index Terms**—Article submission, IEEE, IEEEtran, journal, L<sup>A</sup>T<sub>E</sub>X, paper, template, typesetting.

## I. INTRODUCTION

**P**YCNOMETRY is a fundamental laboratory technique used to determine the density of solid or liquid substances by measuring their mass and volume and comparing them to a known volume. A pycnometer—a calibrated glass flask with a defined volume—is filled with the sample, and its mass is compared to the mass of the same flask filled with a reference fluid (water in our case). Digital densitometers can also be used to determine the density of a solution. Our digital densitometer measures density through a vibrating "U-Tube". The sample is introduced into a U-shaped borosilicate glass tube that is being excited to vibrate at its characteristic frequency electronically. The characteristic frequency changes depending on the density of the sample. Through determination of the characteristic

frequency the density of the sample can be calculated. In the first part of our experiment, we determined the densities of various compositions of ethanol-water through pycnometry and a digital densitometer. Alcohol-gauging tables from the US Alcohol and Tobacco Tax and Trade Bureau (TTB) were used to correlate theoretical densities of various compositions ranging from pure ethanol to pure water at various temperatures to apparent proofs at 60F and finally correct to extract true proof and mole fraction of ethanol.

This theoretical array of densities and corresponding mole fractions were then used in the second part of the lab, where we performed a continuous distillation of an ethanol-water mixture at two different reflux ratios, 4 and 5 in our case.

## II. THEORY

### A. Pycnometry

The pycnometer used in our experiment was a Kimble KiMax pycnometer. By measuring the mass of the empty pycnometer, the mass of the pycnometer filled with water (our reference fluid), the known density of water, and the mass of the pycnometer filled with the experimental solution, the density of the experimental solution can be determined by [1].

$$V = \frac{m_w - m_e}{\rho_{water}(t)} = \frac{m_{sample} - m_e}{\rho_{sample}} \quad (1)$$

where  $m_w$  is the mass of the pycnometer filled with water,  $m_e$  is the mass of the empty pycnometer,  $\rho_{water}(t)$  is the density of water at temperature T, and  $\rho_{sample}$  is the density of the sample at T. This equation can be arranged to solve for  $\rho_{sample}$ .

$$\rho_{sample} = \frac{m_{sample} - m_{empty}}{m_{water} - m_{sample}} \cdot \rho_{water}(T) \quad (2)$$

### B. Gauging alcohol with TTB tables

Table 6 from the TTB correlates specific gravities of ethanol-water mixtures at 60° F to proofs. In order to obtain proofs at other temperatures, one must convert the measured density ( $\rho_1$ ) at a given temperature (T1) to the hypothetical density ( $\rho_2$ ) that a glass hydrometer would indicate if calibrated at the standard 60°F reference temperature:

$$\rho_2 = \rho_1(1 + \alpha(T_1 - 60^\circ F)) \quad (3)$$

where  $\alpha$  is the coefficient of thermal expansion for the hydrometer material (typically  $25 \cdot \frac{10^{-6}}{^\circ C}$  for glass). At this corrected density, specific gravity can be calculated using the reference density of water at 60, °C 0.99904 g/cc. Then, Table 6 can be interpolated through a truncated Taylor series expansion to retrieve an apparent proof,  $C_2$ , implemented as equation 1 in python:

$$C_2 = f(\gamma_1, T1) = [f + (\gamma_1 - \gamma_R) \frac{\partial f}{\partial \gamma}] \quad (4)$$

where  $\gamma_1$  is the specific gravity of the sample corrected to 60°F. This apparent proof still has instrument and sample temperature effects, so it must be corrected to a true proof using TTB Table 1. The computed apparent proof  $C_2$  is rounded down to the nearest integer and used as a reference for interpolation of Table 1.

$$C_3 = C_2 + (C_2 - C_R) \frac{\partial f}{\partial C} \Big|_{C_R, T_R} + (T_1 - T_R) \frac{\partial C}{\partial T} \Big|_{C_R, T_R} \quad (5)$$

where  $C_3$  is the estimated true proof of the mixture corrected for temperature,  $T_1$ .  $C_R$  and  $T_R$  are reference proofs and temperatures from values corresponding to the rounded-down  $C_2$  in Table 1.

### C. Error Propagation

1) *Pycnometer Masses*: Uncertainty for each of the 10 mixtures in the pycnometer, the pure water in the pycnometer, and the empty pycnometer were calculated on a 95% Confidence Interval (N=3).

2) *Pycnometer Densities*: Uncertainties for the mixture densities determined with the pycnometer propagates from uncertainties in mass measurements. The standard formula for error propagation was applied to equation (2)

$$\delta d_f = \sqrt{\left(\frac{\partial d_f}{\partial m_f} \delta m_f\right)^2 + \left(\frac{\partial d_f}{\partial m_e} \delta m_e\right)^2 + \left(\frac{\partial d_f}{\partial m_w} \delta m_w\right)^2 + \left(\frac{\partial d_f}{\partial T} \delta T\right)^2} \quad (6)$$

where  $\delta d_f$  is the uncertainty associated with the computed density,  $\delta m_f$  is the uncertainty associated with the sample-filled pycnometer mass measurements,  $\delta m_e$  is the uncertainty associated with the empty pycnometer mass measurements, and  $\delta m_w$  is the uncertainty associated with the water-filled pycnometer mass measurements and the partial with respect to temperature is estimated with finite differences

### D. Distillation

1) *Vapor Liquid Equilibria*: The theoretical stages of our distillation column are assumed to be at vapor-liquid equilibrium (VLE). The VLE behavior of ethanol and water can be modeled using Antoine's equation for determining saturation pressures, and the Van Laar model for activity-coefficients. First, the activity coefficients,  $\gamma$ , are calculated

$$\gamma_1 = A_{12} \left( \frac{A_{21} X_2}{A_{12} X_1 + A_{21} X_2} \right)^2 \quad (7)$$

$$\gamma_2 = A_{21} \left( \frac{A_{12} X_1}{A_{12} X_1 + A_{21} X_2} \right)^2 \quad (8)$$

where  $A_{12}$  and  $A_{21}$  are Van Laar parameters for water and ethanol respectively.  $X_1$  is the mole fraction of ethanol in solution and  $X_2$  is the mole fraction of water. The Antoine Equation is used to determine saturation pressures of the pure components in the solutions and follows the form:

$$\log_{10} P^* = A - \frac{B}{T + C} \quad (9)$$

where  $P^*$  is the saturation pressure of the component and A, B, and C are tabulated constants. The VLE can then be modeled through the modified Raoult's Law:

$$\gamma_1 x P^{etOH*} = y P \quad (10)$$

$$\gamma_2 (1 - x) P^{H_2O*} = (1 - y) P \quad (11)$$

A solver like SciPy optimize's root function can be used to solve for saturation temperatures at a given pressure and a  $T_{xy}$  diagram can be constructed

2) *McCabe-Thiele diagram*: McCabe-Thiele analysis is based on the McCabe-Thiele assumption: that liquid is vaporized at the same rate vapor is condensed on a molar basis. With this assumption, two mole balances can be constructed: one for the operating (rectifying) line and one for the stripping line. These lines will be plotted against the  $T_{xy}$  equilibrium curve described earlier. The operating line passes through the point  $(x_p, x_p)$ , where  $x_p$  is the product ethanol mol fraction, and follows the equation:

$$y_i = \frac{O}{O+1} x_{i-1} + \frac{x_p}{O+1} \quad (12)$$

Where O is the reflux ratio of the column. The stripping line passes through the point  $(x_w, x_w)$ , where  $x_w$  is the waste ethanol mol fraction, and follows the equation:

$$y_i = \frac{O+F}{O+1} x_{i-1} + \frac{1-F}{O+1} x_w \quad (13)$$

Where F is the total molar flux per mole product. A feed line, often called 'q' or 'feed quality' line can then be drawn,

intersecting at the feed composition on the X=Y line, with a slope determined by the enthalpy of the feed stream.

$$q = \frac{H_F - H_L}{H_V - H_L} \quad (14)$$

where  $H_F$  is the enthalpy of the feed stream at feed conditions,  $H_L$  is the enthalpy of the feed stream at saturated liquid conditions, and  $H_V$  is the enthalpy of the feed stream at saturated vapor conditions. We assume that the feed stream is entirely saturated liquid at steady state and thus  $q = 1$ . Straight lines can then be traced from the product composition, horizontally to the bubble point, then vertically until reaching the rectifying line, then repeated until reaching the bubble point of the stripping section. Then, the vertical lines will be drawn until the stripping line, in a similar fashion. Once a horizontal line passes the waste stream composition, stop.

The overall column efficiency can then be calculated by

$$E_{Column} = \frac{N_{theoretical}}{9} \quad (15)$$

Where 9 comes from the 8 trays of the column, plus the reboiler stage.

Theoretical compositions of trays can be computed by solving for mole fraction values with our VLE data given steady state tray temperatures.

3) *Economic Analysis of Distillation*: We can de

### III. EXPERIMENTAL METHODS

#### A. Pycnometry

1) *Pycnometer Calibration*: The pycnometer was rinsed thoroughly with ethanol and dried with compressed air. The mass of the empty (stopped and capped) pycnometer was weighed 3 times with an analytical balance and recorded as  $M_e$ . The pycnometer was emptied, cleaned following the above procedure, and filled with deionized water (DIW). The mass of the water-filled pycnometer was weighed 3 times with an analytical balance and recorded as  $M_w$ . Then, 3 readings

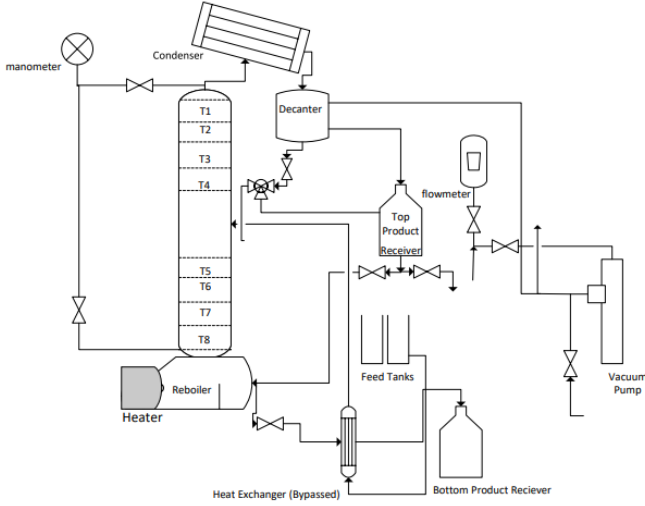


Fig. 1. Schematic of the experimental distillation configuration. T1-8 are trays, horizontal plates to facilitate vapor-liquid contact and mass transfer of ascending vapor or descending liquid streams. The feed pump delivers feed to the column at a constant speed. The heater-powered reboiler serves as an energy source to vaporize the feed and reflux streams. Electrical energy is converted to heat by the heater. The condenser serves as a heat exchanger to condense vapor rising from the top of the column by dropping the temperature of the vapor stream. It is supplied with cooling water as well to the jacket. The reflux valve is electronically controlled and controls the diversion of the decanted stream from the top product receiver back into the column at intervals based on the reflux ratio of the column. The manometer is used to measure the pressure differential between the top and bottom of the distillation column. It is only active when both adjacent valves are open.

of density and temperature were taken with the densitometer and recorded as  $\rho_w$

2) *Pycnometer Sample Measurements:* The pycnometer was emptied, rinsed thoroughly with ethanol and dried with compressed air. 10 ethanol-water mixtures ranging from pure ethanol to pure water were constructed. Various weights of ethanol and water were measured over 3 trials then combined in a beaker to form the samples we measured, cleaning the beaker and pycnometer before switching concentrations. The mass of the empty (stopped and capped) pycnometer was weighed 3 times with an analytical balance and recorded as  $M_e$ . Then, 3 readings of density and temperature were taken at every concentration with the densitometer and recorded as  $\rho_{d_N}$ .

### B. Continuous Distillation

The distillation system used in this lab was the Armfield UOP3. Figure 1 is a schematic for the experimental setup.

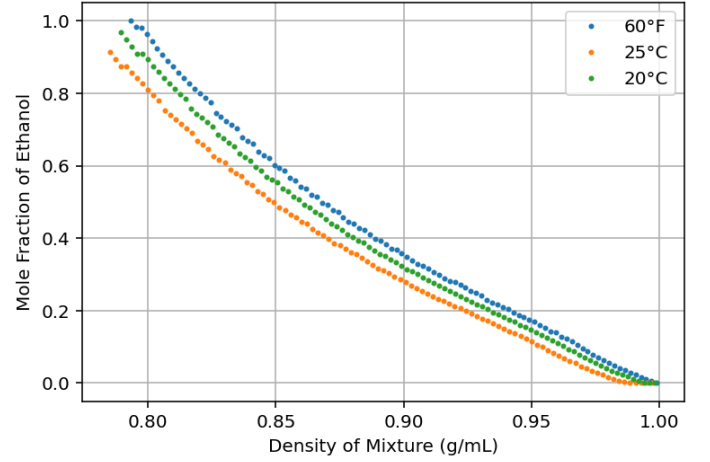


Fig. 2. Measured voltage readings from a PendoTec single-use pressure sensor recorded at various static pressures from a gas piston apparatus containing air. Static pressures were induced by adding weights of  $[84.248 \pm 0.007\text{g}; 164.817 \pm 0.007\text{g}; 239.434 \pm 0.002\text{g}; 328.00 \pm 0.01\text{g}$  and  $402.531 \pm 0.003\text{g}]$  to the apparatus and appear in the figure from left to right. Error bars were calculated based on a 95% confidence interval of recorded voltage readings in mV across three trials for each pressure ( $N=2$ ). Uncertainty

The reboiler power was set to 0.75kW, and the feed pump dial read '5.2', which can be corrected to a mL/s flowrate through a calibration equation. The column was initially ran in open reflux to reach steady state without producing waste streams. Steady-state operation was verified by performing a mass balance on the system and ensuring closure within 10%. Then, the reflux ratio was swapped to 4 (product flows to the top product receiver for 7 seconds, and back to the column for 28 seconds).

## IV. RESULTS

TABLE I  
THEORETICAL VS. EXPERIMENTAL MOLE FRACTIONS AT REFLUX 4

Tray	Theoretical	Experimental
2	0.09	0.11
4	0.12	0.13
6	0.50	0.44
8	0.68	0.65

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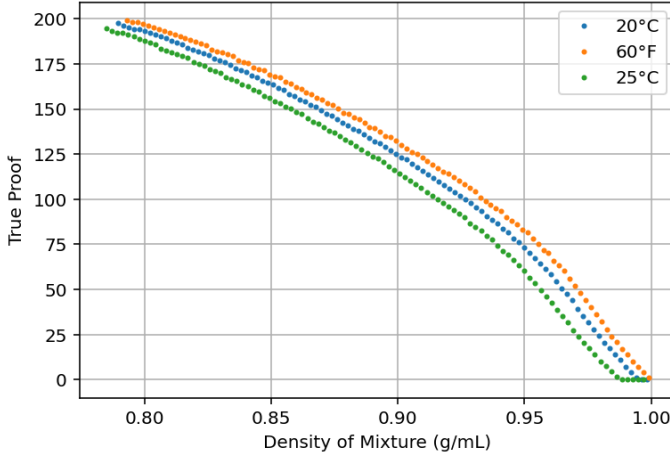


Fig. 3. Measured voltage readings from a PendoTec single-use pressure sensor recorded at various static pressures from a gas piston apparatus containing air. Static pressures were induced by adding weights of  $[84.248 \pm 0.007\text{g}; 164.817 \pm 0.007\text{g}; 239.434 \pm 0.002\text{g}; 328.00 \pm 0.01\text{g}$  and  $402.531 \pm 0.003\text{g}]$  to the apparatus and appear in the figure from left to right. Error bars were calculated based on a 95% confidence interval of recorded voltage readings in mV across three trials for each pressure ( $N=2$ ). Uncertainty

TABLE II  
THEORETICAL VS. EXPERIMENTAL MOLE FRACTIONS AT REFLUX 5

Tray	Theoretical	Experimental
2	0.08	0.09
4	0.12	0.12
6	0.50	0.45
8	0.75	0.66

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## V. DISCUSSION

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## VI. TECHNICAL ADVANCES

## VII. REFERENCES SECTION

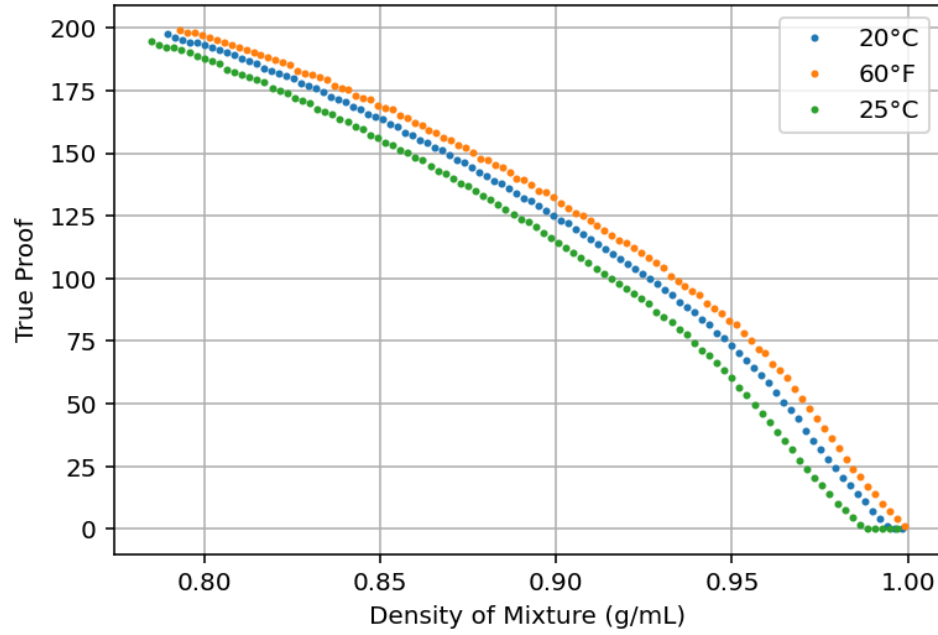
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## REFERENCES

- [1] *Mathematics Into Type*. American Mathematical Society. [Online]. Available: <https://www.ams.org/arc/styleguide/mit-2.pdf>
- [2] T. W. Chaundy, P. R. Barrett and C. Batey, *The Printing of Mathematics*. London, U.K., Oxford Univ. Press, 1954.
- [3] F. Mittelbach and M. Goossens, *The L<sup>A</sup>T<sub>E</sub>X Companion*, 2nd ed. Boston, MA, USA: Pearson, 2004.
- [4] G. Grätzer, *More Math Into L<sup>A</sup>T<sub>E</sub>X*, New York, NY, USA: Springer, 2007.
- [5] M. Letourneau and J. W. Sharp, *AMS-StyleGuide-online.pdf*, American Mathematical Society, Providence, RI, USA, [Online]. Available: <http://www.ams.org/arc/styleguide/index.html>
- [6] H. Sira-Ramirez, "On the sliding mode control of nonlinear systems," *Syst. Control Lett.*, vol. 19, pp. 303–312, 1992.
- [7] A. Levant, "Exact differentiation of signals with unbounded higher derivatives," in *Proc. 45th IEEE Conf. Decis. Control*, San Diego, CA, USA, 2006, pp. 5585–5590. DOI: 10.1109/CDC.2006.377165.
- [8] M. Fliess, C. Join, and H. Sira-Ramirez, "Non-linear estimation is easy," *Int. J. Model., Ident. Control*, vol. 4, no. 1, pp. 12–27, 2008.
- [9] R. Ortega, A. Astolfi, G. Bastin, and H. Rodriguez, "Stabilization of food-chain systems using a port-controlled Hamiltonian description," in *Proc. Amer. Control Conf.*, Chicago, IL, USA, 2000, pp. 2245–2249.



(a)

Fig. 4. Dae. Ad quatur autat ut porepel itemoles dolor autem fuga. Bus quia con nessunti as remo di quatus non perum que nimus. (a) Case I. (b) Case II.

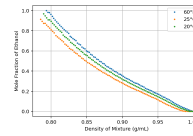
TABLE III  
 $\kappa$  VALUES FOR AIR, ARGON, AND CO<sub>2</sub>

Gas	$\kappa_{\text{Empty}}$	$\kappa_1$ Weight	$\kappa_2$ Weight	$\kappa_3$ Weight
Air	$1.37 \pm 4 \times 10^{-21}$	$0.95 \pm 3 \times 10^{-21}$	$1.10 \pm 3 \times 10^{-21}$	$1.20 \pm 3 \times 10^{-21}$
Argon	$1.74 \pm 3 \times 10^{-21}$	$1.61 \pm 4 \times 10^{-21}$	$1.53 \pm 2 \times 10^{-21}$	$1.64 \pm 3 \times 10^{-21}$
CO <sub>2</sub>	$1.28 \pm 1 \times 10^{-21}$	$1.36 \pm 4 \times 10^{-21}$	$1.32 \pm 2 \times 10^{-21}$	$1.28 \pm 2 \times 10^{-21}$

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