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, LaTeX, paper, template, typesetting.

I. INTRODUCTION

PYCNOMETRY 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].

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

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 ρ_{sample} is the density of the sample at T. This equation can be arranged to solve for ρ_{sample}.

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

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 (ρ_1) at a given temperature (T1) to the hypothetical density (ρ_2) that a glass hydrometer would indicate if calibrated at the standard $60°F$ reference temperature:

$$\rho_2 = \rho_1(1 + \alpha(T_1 - 60°F)) \qquad (3)$$

where α is the coefficient of thermal expansion for the hydrometer material (typically $25 \cdot \frac{10^{-6}}{°C}$ 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:

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

where γ_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.

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

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 was calculated on a 95% Confidence Interval (N=3).

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

$$\delta d_f = \sqrt{\begin{array}{c}\left(\frac{\partial d_f}{\partial m_f}\delta m_f\right)^2 + \left(\frac{\partial d_f}{\partial m_e}\delta m_e\right)^2 \\ + \left(\frac{\partial d_f}{\partial m_w}\delta m_w\right)^2 + \left(\frac{\partial d_f}{\partial T}\delta T\right)^2\end{array}} \tag{6}$$

where δd_f is the uncertainty associated with the computed density, δm_f is the uncertainty associated with the sample-filled pycnometer mass measurements, δm_e is the uncertainty associated with the empty pycnometer mass measurements, and δm_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, γ, are calculated

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

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

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:

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

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:

$$\gamma_1 x P^{etOH*} = yP \tag{10}$$

$$\gamma_2(1 - x)P^{H2O*} = (1 - y)P \tag{11}$$

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:

$$y_i = \frac{O}{O+1}x_{i-1} + \frac{x_p}{O+1} \tag{12}$$

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:

$$y_i = \frac{O+F}{O+1}x_{i-1} + \frac{1-F}{O+1}x_W \tag{13}$$

Where F is the total molar flux per mole product.

III. EXPERIMENTAL METHODS

A. Calibration

The pressure sensor was calibrated using air as a fluid by taking multiple voltage measurements of static pressure with 6 combinations of weights (with one of them being the unweighted plunger) added to the piston. Voltage readouts were recorded for each weight. Voltage was then plotted over pressure, then the pressure sensor calibration was calculated in units of [mV/psi/9V] and compared to the manufacturer's stated value. The data acquisition system (DAS) was configured and tested to ensure proper operation.

B. Ruchardt Experiment

The Ruchardt experiment was first conducted with air as the internal fluid across 4 different initial pressures. The piston height was set to 60mm every trial to ensure than the volume remained constant between trials, although our apparatus had considerable leakage.
With the DAS running, oscillations were induced by pressing and abruptly releasing the piston. Oscillations containing 5 peaks or more were considered acceptable. Three acceptable trials were recorded for every weight value.

The experiment was then repeated, using Argon and CO2 instead of air. Before conducting the experiment, the air in the apparatus was purged twice with the respective gas. Three trials were conducted for each of the four weights tested, accepting oscillations with five peaks or more.

IV. RESULTS

A. Calibration

The calibration value was determined from the slope of the linear regression of recorded voltages, in mV, against varied pressures, in psi. This value was divided by 9V to match PendoTec specifications to be $0.270756 \pm 0.0000001 \frac{mV}{psi \cdot 9V}$. This value was used to determine the pressure in the apparatus from voltage readings in the following Ruchardt experiments

TABLE I
GAS PROPERTIES

| Gas	Condition	P_0 (Pa)	C (Pa)	κ (s^{-1})	ω (rad s^{-1})	ϕ (rad)
Air	Empty	102171.80 ± 7.20	4518.24 ± 886.00	37.53 ± 2.97	217.85 ± 2.87	-9.62 ± 3.02
	1 Weight	103076.35 ± 2.59	2061.26 ± 545.07	14.59 ± 1.03	118.06 ± 0.64	-10.88 ± 7.99
	2 Weight	103389.06 ± 1.81	4264.83 ± 513.42	10.45 ± 0.76	90.98 ± 0.63	-8.53 ± 6.94
	3 Weight	104821.81 ± 12.52	-1212.16 ± 513.84	10.03 ± 0.56	79.06 ± 0.73	-15.93 ± 9.20
Argon	Empty	102269.40 ± 4.39	-1487.97 ± 3403.32	16.59 ± 4.37	207.72 ± 0.38	-12.77 ± 6.63
	1 Weight	103093.24 ± 3.53	23.81 ± 945.56	15.69 ± 0.08	120.07 ± 0.51	-15.62 ± 4.69
	2 Weight	104000.11 ± 21.84	1201.48 ± 2621.70	17.28 ± 1.22	80.95 ± 0.35	-31.05 ± 8.21
	3 Weight	104882.66 ± 36.64	349.51 ± 7984.72	14.13 ± 0.50	77.39 ± 0.91	-15.90 ± 11.16
CO_2	Empty	102304.81 ± 15.52	882.70 ± 1867.09	32.71 ± 5.98	178.53 ± 1.66	-22.61 ± 15.44
	1 Weight	102216.12 ± 3.98	890.54 ± 3907.62	14.78 ± 3.93	106.12 ± 2.15	-22.41 ± 23.91
	2 Weight	103976.97 ± 3.03	-1087.62 ± 2016.17	9.09 ± 1.17	83.14 ± 0.42	-25.64 ± 13.47
	3 Weight	104000.26 ± 14.20	-6199.73 ± 518.83	6.59 ± 1.27	68.67 ± 0.14	-13.64 ± 11.07
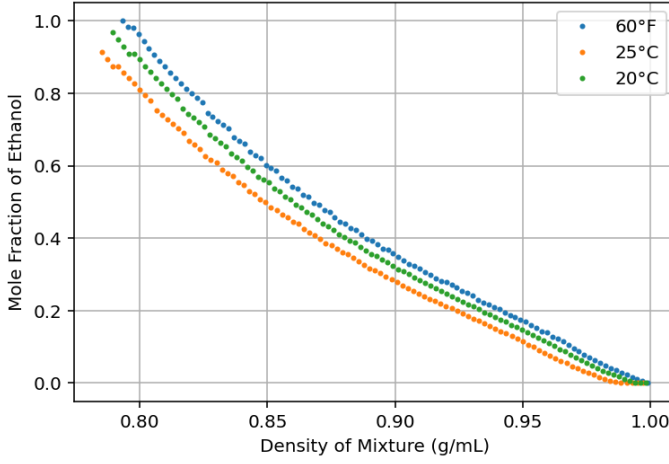
Fig. 1. Measured voltage readings from a PendoTec single-use pressure sensor recorded at various static pressures from a gas piston apparatus containing air. Static pressures were induced by adding weights of [84.248 ± 0.007g; 164.817 ± 0.007g; 239.434 ± 0.002g; 328.00 ± 0.01g and 402.531 ± 0.003g.] 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
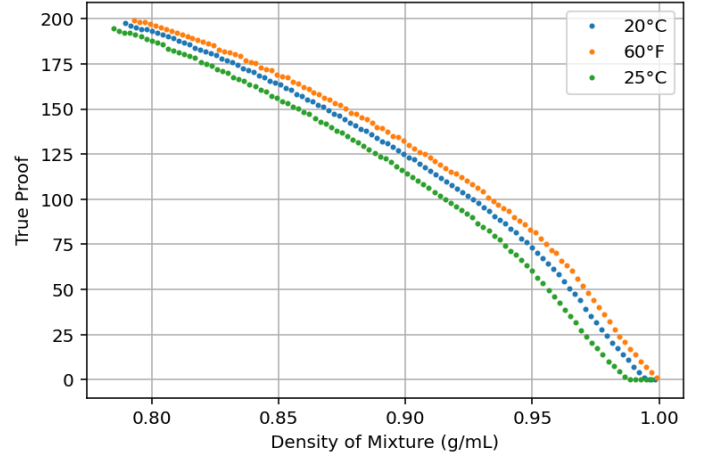

Fig. 2. Measured voltage readings from a PendoTec single-use pressure sensor recorded at various static pressures from a gas piston apparatus containing air. Static pressures were induced by adding weights of [84.248 ± 0.007g; 164.817 ± 0.007g; 239.434 ± 0.002g; 328.00 ± 0.01g and 402.531 ± 0.003g.] 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

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V. DISCUSSION

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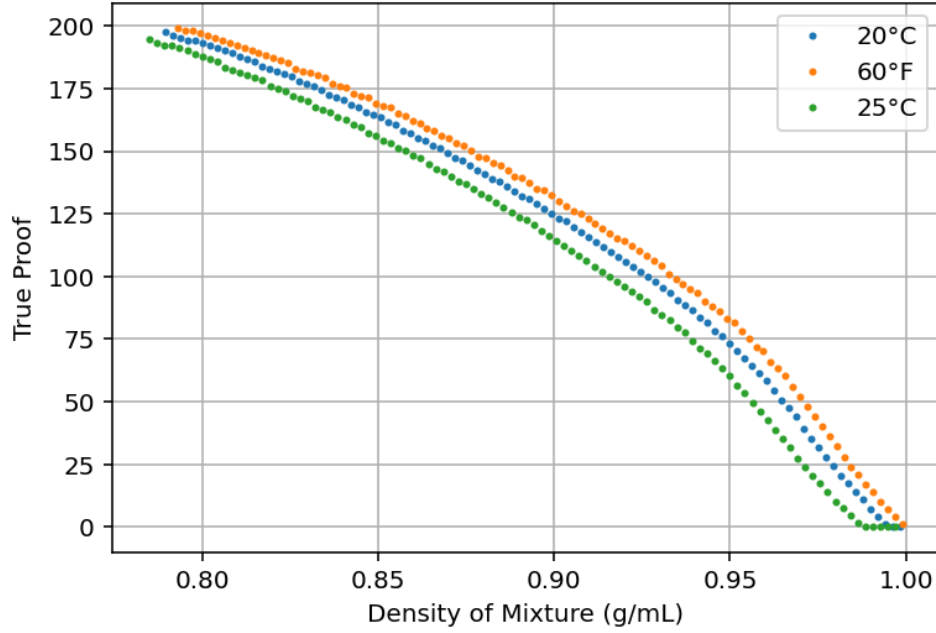
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TABLE II
κ VALUES FOR AIR, ARGON, AND CO_2

| Gas	κ_{Empty}	$\kappa_{1 \text{ Weight}}$	$\kappa_{2 \text{ Weight}}$	$\kappa_{3 \text{ Weight}}$
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_2	$1.28 \pm 1 \times 10^{-21}$	$1.36 \pm 4 \times 10^{-21}$	$1.32 \pm 2 \times 10^{-21}$	$1.28 \pm 2 \times 10^{-21}$

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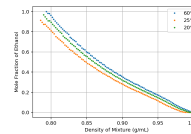
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