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The Effects Of Different Salts/Acids On The Vapor-Liquid Equilibrium Of The Binary System Of Water/Ethanol

Tim Petrik[2], Kris A. Berglund[1,3]

Department of Food Science and Human Nutrition[1] and Department of Chemical Engineering & Materials Science[2],
Michigan State University, East Lansing, Michigan 48824 USA
Division of Chemical Engineering[3], Luleå University of Technology, SE-971 87 Luleå SWEDEN

Abstract

In an effort to reduce the operating and investment costs of the production of high proof spirits such as vodka, an improved distillation process was revisited. The improvement involves the introduction of non-volatile salts or acids to the mixture of volatile components that are to be distilled. A series of experiments involving a number of different organic components is described to evaluate the change in relative volatility in an model ethanol/water mixture caused by the addition of the salt/acid. Finally, focusing on the compound that showed the highest increase in relative volatility (potassium acetate), trials to study the effect of potassium acetate on the vapor phase concentration of other volatiles such as low boilers and fusel alcohols are described. It could be concluded that the addition of potassium acetate also causes a reduced accumulation of acetaldehyde and methanol in the condensate.

Introduction

The azeotrope of ethanol and water results in a minimum boiling composition (96.4 % alcohol by volume (ABV)) at a constant temperature of 78.1℃. The azeotropic point must be viewed as a theoretical composition of water/ethanol since it can only be achieved by an infinite number of consecutive distillations. Since the production of vodka and other high proof spirits calls for a content of ethanol very close to the azeotrope (95% ABV), a typical distillation process either involves a high number of theoretical stages (increased capital cost) or a high reflux (increased energy demand) coupled with a low product throughput. In practice, either option represents a significant financial hurdle for small scale distilleries or startup ventures.

The purpose of this paper is to present the results of a series of experiments involving the

Materials and methods

Experimental set-up

The experimental setup is depicted in Figure 1. The liquid fraction is contained in a three-neck flask (2) and can be heated up by the surrounding heat transfer oil (1). A digital

technique of adding non-volatile salts or acids to the distillation mixture in an attempt to break or modify the azeotropic composition favorably. Ideally, this will lead to reduced overall capital/operating cost (Furter 1967). Theoretical models of vapor-liquid equilibriums of mixtures containing electrolytes such as salts and acids are believed to be a complex function of interactions and self-interactions between all systems components. As a general rule, Johnson (1957) showed that a salt will increase the chemical potential of the solvent component in which it is less soluble and vice versa. This rule was used as a guideline with respect to the choice of salts and acids in the present work; however, other electrolytes have also been included in the experiments.

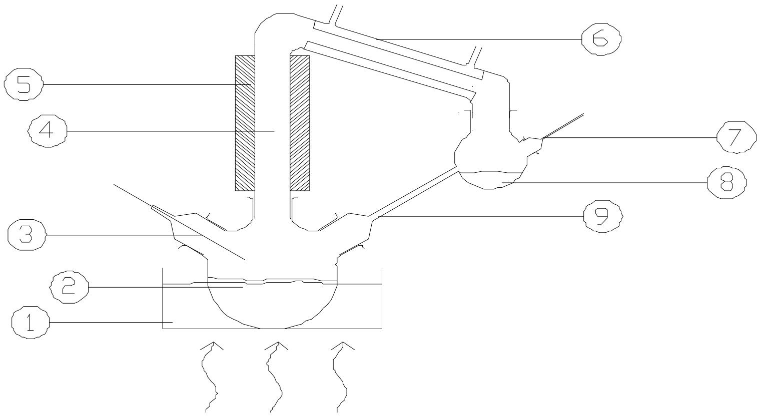

Figure 1: Experimental setup

the condenser (6). The generated condensate accumulates in the reflux flask (8) where it can be sampled. The opening (7) is very small in diameter to minimize the loss of volatile components and maintains atmospheric pressure within the apparatus. The reflux can drain back into the bottom fraction through connection (9). Since the experimental setup does not provide for pressure control other than through opening (7) and has a strong tendency of generating reflux in the neck (4), experiments focused solely on whether a given salt/acid could break the azeotrope. Therefore, the initial composition of the liquid phase was chosen to be very close to this point. If a given salt/acid has the capacity of increasing the vapor fraction of ethanol beyond the azeotropic point, the condensed vapor phase would consist of more than 95.5 mass% ethanol.

Analytical assays

The analysis of bottom (liquid phase) and head fraction (condensed vapor phase) with respect to water content were done by using a Coulometric Karl Fischer titration device (Aqua Counter AQ-2100).

Gas chromatography was used to quantify volatile components. The analyses were conducted using a Shimadzu GC-2010 gas chromatograph with flame ionization detection and a 30 m long capillary column (Stabilwax-DA) with an inner diameter of 0.18 mm. For the first 8 minutes of each chromatographic run, the column was temperated at 40 degree Celsius followed by a 15 K/min ramp-up to 160 degree Celsius. The samples (0.2 µl) were injected in their undiluted form to obtain sizable peaks using a Shimadzu auto sampler (AOC-20i). Samples containing salt were not analyzed in the GC due to the potentially damaging effects of salt on the chromatographic column and liner. These samples were only analyzed for their water content by Coulometric Karl Fischer titration.

Results

Table 1 illustrates the raw data derived by Coulometric titration. Apparently only two of the examined salts/acids seem to be capable of breaking the azeotropic point at 95.5 mass% ethanol: sodium acetate and potassium acetate.

In an effort to further evaluate the potential of each salt/acid, relative volatilities were calculated by converting the absolute concentrations of ethanol (index 1) and water (index 2) in the vapor (y) and liquid (x) phase into relative volatilities as follows:

$$\alpha_{1,2} = \frac{y_1/x_1}{y_2/x_2}$$

where

$$x_1 + x_2 = 1$$

and

$$y_1 + y_2 = 1$$

The only statistically significant increases in relative volatility of ethanol were caused by potassium acetate or sodium acetate. The following experiments will therefore focus on these two salts exclusively.

Table 1: Change in composition of an ethanol/water mixture (95/5 Mass%, respectively) with and without the addition of various salts and acids; amount salt/acid added to the mixture in [Mole%]: 0; 0.4; 3.8; 15.3; 4.8; 11.8; 14.5; 14.8; 2.8; 10.1 from top to bottom

salt/acid	Ethanol [Mass%]		Relative volatility
	Bottom	Head	
none	95.03	95.24	1.05
Disodium Succinate	94.94	95.09	1.03
Sodium Acetate	95.20	96.04	1.22
Succinic Acid	95.25	95.44	1.04
L-Glutamic Acid	94.95	95.17	1.05
Citric Acid anhydrous	95.89	95.49	0.91
L-(+) Tartaric Acid	95.04	95.44	1.09
DL-Malic Acid	95.41	95.72	1.08
Citric Acid Trissodium salt	94.90	95.05	1.03
Potassium Acetate	95.99	97.52	1.65

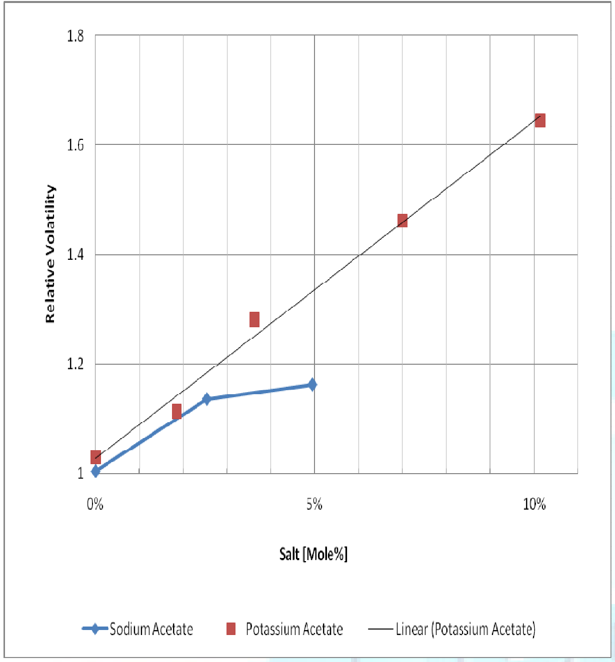

Figure 2: Relative volatility of an ethanol/water mixture (95/5 Mass%) with different amount of salts added

Effects of Salt on Fusel Oils and Low Boilers

Ethanol represents the major fraction of alcohols produced by yeast in a fermentation process. However, prior to and during fermentation a number of side-products and intermediates are produced, as well (Tanner 1998). These components are to some degree desired to give the distilled spirit its distinctive flavor. On the other hand, an excess of these alcohols, esters, and aldehydes can cause off-flavors or can be potentially harmful to the consumer (e.g. methanol). Therefore, a set of experiments was conducted to measure the effect of potassium acetate on these substances in the condensate. For that purpose, the pot still was filled with a representative mixture of ethanol and water as well as fusel oils and low boilers. After 30 min of operation, steady state was assumed and the condensed vapor phase as well as the pot still mixture was sampled. Then, potassium acetate (7.8 mole %) was added to the mixture and both phases were sampled in the same way. Figure 2 lists the difference in concentration in the condensed vapor phase of each examined component with or without potassium acetate added to the mixture. In order to test for statistical significance, a paired, two-tailed t-test was calculated for each set of data and compared to the critical t-value necessary to reject the null hypothesis with 95% confidence. As Figure 2 indicates, the only three concentrations affected by the addition of potassium acetate to the mixture are those of acetaldehyde, methanol and water. The observed result causes an average reduction in head-concentration for acetaldehyde and methanol of [%] 26.6 and

12.2, respectively (data not shown). The very high t-value for the examined data on water in the condensed vapor phase further proves the statistical significance of the effect of potassium acetate on the liquid-vapor equilibrium of ethanol/water.

Conclusions. Potassium acetate alters the vapor-liquid equilibrium (VLE) of ethanol/water to the point that a commercial distillation of high proof spirit could be conducted more cost effectively. Even small amounts of salt (about 10 mole%) added to the ethanol/water mixture at the azeotropic point are capable of increasing the relative volatility of ethanol by approximately 65%.The

Experiment number	**Difference in concentration in condensed vapor phase, $C_{no\ PA} - C_{with\ PA}$ [g/l]**						
	Acetaldehyde	**Acetone**	**Ethylacetate**	**Methanol**	**Iso-Amylalc.**	**1-Butanol**	**H2O**
1	3.3	2.4	0.3	0.50	-0.01	-0.01	18.3
2	3.2	-1.6	0.1	0.20	0.02	0.01	17.1
3	8.2	3.0	1.1	1.20	-0.09	-0.14	14.8
4	3.0	-0.4	-0.7	0.60	0.00	-0.01	20.8
5	13.7	3.3	0.7	1.30	-0.03	0.00	14.5
mean	**6.3**	**1.3**	**0.3**	**0.76**	**-0.022**	**-0.030**	**17.2**
STD	**4.69**	**2.20**	**0.68**	**0.47**	**0.042**	**0.062**	**2.6**
paired t-test, 2-tailed	**3.00**	**1.36**	**0.99**	**3.60**	**1.169**	**1.081**	**14.7**
critical t-value for 95% confidence, df=4	**2.13**	**2.13**	**2.13**	**2.13**	**2.13**	**2.13**	**2.13**
P-value	**0.04**	**0.24**	**0.37**	**0.02**	**0.300**	**0.340**	**10^{-4}**

Table 2: Effects of Potassium Acetate (PA) on low boilers, fusel oils and water evaluated by statistical analysis.

increase in relative volatility seems to be proportional to the amount of potassium acetate added. At the same time, the addition of potassium acetate also causes a reduction in concentration of the low boilers acetaldehyde and methanol in the condensate, which could allow for an earlier switch from head-cuts to the desired heart-fraction of the distillate. The relative volatility of other examined compounds do not seem to be effected.

Future research will focus on practical ways to introduce potassium acetate into a commercial distillation column. Additionally, different methods of salt recovery will be examined.

References

1 Furter WF, Cook RA (1967). Salt effect in distillation: A literature review. *Int. J. of Heat Mass Transfer*. 10: 23-36.

2 Johnson, AI, Furter WF (1957). Salt effect in vapor-liquid equilibrium. *Can. J. Technology*. 34: 413-424.

3 Tanner H, Brunner, Hans R (1998) *Obstbrennerei heute*. Heller Chemie.