BEHAVIOR OF VARIOUS IMPURITIES IN SIMPLE DISTILLATION OF AQUEOUS SOLUTION OF ETHANOL

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Equilibrium ratios of 29 impurities in aqueous solution of ethanol are expressed as functions of the concentration of ethanol. The constants of these functions have been determined by use of the vapor-liquid equilibrium data in the literature.

A mathematical model of a pot-still is presented, in which open-steam heating, partial condensation and the passing of live steam are taken into consideration.

The simultaneous differential equations are solved numerically and the distillation curves of the impurities are obtained. It is shown that the curves have characteristic shapes according to the type of minor component and are affected mostly by the concentration of ethanol in the charge.

The calculated distillation curves are compared with the observed ones, which were obtained from papers on the production of distilled spirit.

Introduction

A pot-still is commonly used for simple distillation in the production of distilled spirit. In such distillation the behavior of impurities is more important than that of ethanol, because the characteristic taste or bouquet is decided by the proportion of impurities.

The vapor-liquid equilibria of aqueous solutions of ethanol containing a minute amount of 1-butanol or furfural were measured, and the simple distillation of these solutions was discussed by one of the authors and his coworkers2~4).

In the present paper, the equilibrium ratios of various impurities in an aqueous solution of ethanol are obtained from the vapor-liquid equilibrium data in the literature. They are expressed as functions of the concentration of ethanol.

Distillation curves of the various impurities were calculated on an approximate mathematical model. The calculated results were compared with the observed values in the literature7,8).

1. Equilibrium Ratio of Impurity

The vapor-liquid equilibrium of a water-ethanol system containing a minor component was measured by Williams10), Sundholm9), Heitz11) and Ikari2~4). From these data, those of 29 impurities, which are shown in Table 1, were taken up.

The equilibrium ratio of a minor component was plotted on semilogarithmic graph paper against the mole fraction of ethanol in the water-ethanol system, and a smoothed curve was drawn. The curve is expressed as the following equation:

$$\log K_m = A_m (1 - x_2) + B_m x_2 + x_2 (1 - x_2)$$

where $A_m$ is the value of $\log K_m$ in water and $B_m$ is that in ethanol. The constants, from $A$ to $G$, of each impurity are shown in Table 1.

2. Basic equations

2.1 Model and assumptions

A schematic model of a pot-still is shown in Fig. 1. In a time interval, $dW$ moles of steam is blown through the still. A part of the steam ($dW'$) condenses and the remainder ($dS$) passes through. The partial condensation of a vapor mixture ($dV'$) occurs, and $dL''$ moles of liquid returns to the still.

The following assumptions have been introduced to make the problem tractable.
The vapor-liquid equilibrium of the water-ethanol system. The equilibrium ratio of a minor component is a function of the concentration of ethanol, but is independent of the concentration of the minor component.

Even if various impurities coexist, the equilibrium ratio of a minor component is not affected by the impurities.

The vapor-liquid equilibrium of the water-ethanol system at 1 atm is represented by the following equation, as in the previous papers.

\[ y_x dV' = x'_x dL' + y'_x dV'' \]  

for the vapor section of the still.

\[ dV' = dV + dS \]  

for the liquid section of the still.

\[ dL = dL'' + dW - dV \]  

(5)  
\[ d(x_L) = x'_x dL'' - y_x dV' \]  

(6)  
\[ dW = dW'' + dS \]  

(7)

The ratio of partial condensation, \( \beta \), is defined by Eq. (8). (0 \( \leq \beta \leq 1 \))

\[ \beta \equiv dL'/dV' \]  

(8)

The ratio of uncondensed steam, \( \delta \), is defined by Eq. (9). (0 \( \leq \delta \leq 1 \))

\[ \delta \equiv dS/dW \]  

(9)

A parameter, \( \alpha \), is defined by Eq. (10), representing the method for heating the still.

\[ \alpha \equiv dW'/dV \]  

(10)

When closed-steam heating is used, \( \alpha = 0 \). When \( \alpha \) is smaller than unity, it means that superheating steam is blown through the still or open-steam heating and closed-steam heating are used simultaneously. When steam at normal boiling point is introduced into the still, \( \alpha \) is nearly equal to unity. If \( \alpha \) is larger

\[
\begin{array}{ccccccccc}
\text{Group No.} & \text{No.} & \text{Minor component} & A & B & C & D & E & F & G \\
1 & 1 & \text{Formic acid} & -0.3665 & -0.8447 & -0.94867 & 2.2671 & -8.2371 & 11.805 & 5.4854 \\
2 & 2 & \text{Acetic acid} & -0.1612 & -0.9431 & -4.2669 & 10.986 & -18.330 & 15.798 & -5.3647 \\
3 & 3 & \text{Propionic acid} & -0.0915 & -1.2366 & -2.1204 & -6.75767 & 30.624 & -41.209 & 18.463 \\
4 & 4 & n-\text{Butyric acid} & 0.2824 & -1.4962 & -6.3921 & 11.337 & -10.161 & 2.6598 & 0.88562 \\
5 & 5 & \text{Isobutyric acid} & 0.2175 & -1.4034 & -1.3165 & -20.366 & 78.253 & -102.59 & 45.463 \\
6 & 6 & n-\text{Valeric acid} & 0.2856 & -2.3768 & -5.6556 & 6.9076 & -0.31487 & -4.9661 & 2.5095 \\
7 & 7 & \text{Acetaldehyde} & 1.7924 & 0.7520 & -4.2166 & 16.374 & -38.950 & 42.991 & -17.286 \\
8 & 8 & \text{Propionaldehyde} & 1.7634 & 0.4346 & -1.7375 & -1.8182 & 10.589 & -14.850 & 6.7373 \\
9 & 9 & \text{Acrolein} & 1.5563 & 0.6021 & -2.5980 & 1.1493 & -5.4102 & -9.3586 & 4.8084 \\
10 & 10 & n-\text{Butyraldehyde} & 2.0792 & 0.2765 & -3.3200 & 4.1050 & -8.3651 & 11.370 & -5.4149 \\
12 & 12 & n-\text{Valeraldehyde} & 2.2788 & -0.0458 & -8.7586 & 32.483 & -78.050 & 89.110 & -37.183 \\
13 & 13 & \text{Aetal} & 1.5798 & 0.7348 & -1.5866 & 3.1436 & -7.1565 & 8.9346 & -3.9711 \\
14 & 14 & n-\text{Propyl alcohol} & 1.1931 & -0.2518 & -4.1378 & 0.63768 & 15.538 & -25.794 & 12.434 \\
15 & 15 & \text{Isopropyl alcohol} & 1.3118 & -0.0605 & -4.2119 & 4.0304 & 6.1326 & -15.520 & 8.3888 \\
16 & 16 & \text{Allyl alcohol} & 1.0607 & -0.3143 & -7.3838 & 35.856 & -94.000 & 110.42 & -46.739 \\
17 & 17 & n-\text{Butyl alcohol} & 1.4048 & -0.6108 & -6.7722 & 15.473 & -24.054 & 20.820 & -7.3688 \\
18 & 18 & \text{Isobutyl alcohol} & 1.4914 & -0.4318 & -6.2533 & 14.345 & -22.371 & 18.825 & -6.3868 \\
19 & 19 & \text{t-Butyl alcohol} & 1.4771 & -0.1192 & -3.6749 & 2.8230 & 3.8001 & -8.8681 & 4.4434 \\
20 & 20 & n-\text{Amyl alcohol} & 1.4771 & -0.9281 & -8.4051 & 22.160 & -36.377 & 30.875 & -10.278 \\
21 & 21 & \text{Isomyl alcohol} & 1.5441 & -0.8356 & -7.7054 & 14.247 & -11.415 & -0.40047 & 3.4196 \\
22 & 22 & \text{Isopropyl acetate} & 2.2227 & 0.2552 & -5.8636 & 6.9604 & -2.5821 & -3.2930 & 2.9080 \\
23 & 23 & \text{Isobutyl formate} & 1.8692 & 0.1987 & -5.1009 & 11.26 & -8.784 & -2.9856 & 4.7137 \\
24 & 24 & \text{Ethyl isobutyrate} & 2.6021 & -0.0458 & -10.450 & 29.784 & -45.822 & 32.634 & -8.2281 \\
25 & 25 & \text{Ethyl isomylate} & 2.5052 & 0.0 & -14.854 & 66.002 & -152.04 & 162.23 & -64.094 \\
26 & 26 & \text{Ethyl isovalerate} & 2.4771 & -0.3010 & -12.213 & 56.361 & -138.63 & 151.61 & -59.788 \\
27 & 27 & \text{Furfural} & 0.8739 & -0.6478 & -6.1601 & 8.8821 & -2.3593 & -6.7646 & 3.8696 \\
28 & 28 & \text{Diacetyl} & 1.3243 & 0.4314 & -1.5266 & -0.087272 & -5.5697 & 12.579 & -6.7795 \\
29 & 29 & \text{Acetoin} & 0.5798 & -0.8477 & -10.453 & 15.753 & 13.988 & -49.918 & 29.066 \\
\end{array}
\]
than unity, it designates the presence of heat loss from the still.

By using the above equations, the relations between the concentration at each section of the still can be obtained as follows.

\[ y'_s = y''_s + y'_s(1-\beta) \]  
\[ y'_s = \frac{1-\beta}{1-\delta+\alpha\delta}y_2 \]  
\[ \text{The ratio of moles of distillate to that of the charge is represented by } z, \text{ defined as } \]
\[ z = \frac{V''}{L_0} \]  
\[ \text{From the above equations, the following equation is obtained.} \]
\[ dV'' = \frac{(1-\beta)(1-\delta+\alpha\delta)}{C} dL \]  
\[ C = \beta(1-\delta+\alpha\delta)+\alpha(1-\delta) \]  

After integrating Eq. (14), substitution of \( V'' \) in Eq. (13) results in
\[ z = \frac{1-\beta(1-\delta+\alpha\delta)}{C} \left( \frac{L}{L_0} - 1 \right) \]  

From Eqs. (2), (4), (6), (15) and (16), the following equation can be obtained.

\[ \frac{dx_m}{dz} = -\frac{Cy'_m + y'_m(1-\beta)(1-\delta+\alpha\delta)}{Cz + (1-\beta)(1-\delta+\alpha\delta)} \]  

where
\[ C = \beta(1-\delta+\alpha\delta)+\alpha(1-\delta) \]

If the value of \( x_s \) is obtained, \( y_s \) is calculated from the relation of the vapor-liquid equilibrium of the water-ethanol system. The value of \( y'_s \) is obtained from Eq. (12). By solving Eq. (11), the values of \( x'_s \) and \( y'_s \) can be obtained.

2.2.2 Concentration of a minor component

The equilibrium ratios of a minor component, \( m \), at the still and the partial condensation section are denoted respectively by \( K_m \) and \( K'_m \), which are the function of the concentration of ethanol at each part, \( x_2 \) and \( x'_2 \).

\[ y'_m = K_m x_m \]  
\[ y''_m = K'_m x'_m \]  

The material balances of a minor component at each section yield the following equations:

\[ y'_m dV'' = x'_m dL'' + y''_m dV'' \]  

for the partial condensation section

\[ y'_m dV'' = x'_m dL'' + y''_m dV'' \]  

for the vapor section of the still

\[ y'_m dV'' = y'' dV \]  

for the liquid section of the still

\[ d(x_m L) = x''_m dL'' - y'' dV \]  

From the above equations, the following equation can be derived.

\[ \frac{y'_m}{x_m} = \frac{K_m K'_m (1-\beta)}{(1-\delta+\alpha\delta)[\beta + K'_m (1-\beta)]} \times \frac{x_m}{x_m} \]  

From Eqs. (20), (21), (15), (22) and (16), the following equation can be obtained.

\[ \frac{d(x_m/x_m)}{dz} = \left[ 1 + \frac{K_m K'_m (1-\beta)(1-\beta)}{C[\beta + K'_m (1-\beta)]} \right] \times \frac{C(x_m/x_m)}{Cz + (1-\beta)(1-\delta+\alpha\delta)} \]  

3. Numerical results

3.1 Calculation procedure

When a system consists of water, ethanol and \( M \) impurities, the \( (M+1) \) simultaneous differential equations, comprising Eq. (17) and Eq. (22) \((m=1 \text{ to } M)\), is solved numerically by the Runge-Kutta-Gill method.

The calculation was performed by a FACOM 230-60 in Kyushu University. The Subroutine of Runge-Kutta-Gill method (SRKG2S) was used in the program.

3.2 Discussion

A representative calculation was performed, in which the mole fraction of ethanol in the charge \((x_20)\) is 0.0891 and \(\alpha=\beta=\delta=0\). The calculated results of the impurities shown in Table 1 are presented in the five figures as follows:

1 acid
2 aldehyde and acetal
3 alcohol
4 ester
5 others

The number in the figures refers to the compound, which has the same number in Table 1.

It can be seen from these figures that the distillation curves of the compounds in each group, except the last group, represent similar characteristic shapes.

As the influence of \( \alpha, \beta \) and \( \delta \) on the distillation curve of a minor component was discussed in detail in the previous papers\(^3,4\), only an illustration is presented here.

For simplicity, a representative compound is selected from each group, as follows.

1 acid No. 2 Acetic acid
2 aldehyde and acetal No. 7 Acetaldehyde
3 alcohol No. 18 n-Butyl alcohol
4 ester No. 25 Ethyl isobutyrate
5 others No. 13 Furfural

Comparison between the two cases in which the ethanol concentration in the charge is the same \((x_20=0.0891)\) but the parameters, \(\alpha, \beta \) and \(\delta\) are different is shown in Fig. 7. This figure suggests that the influence of \(\alpha, \beta \) and \(\delta\) on the distillation curve of a minor component is not so large as that of the ethanol concentration in the charge, which is described below.

The comparison between the two cases in which the parameters are the same \((\alpha=\beta=\delta=0)\) but the ethanol concentration in the charge is different is
shown in Fig. 8. It can be seen that the shape of the distillation curve of a minor component changes appreciably with the ethanol concentration in the charge.

4. Comparison with observed distillation curves

4.1 Distillation of raw whisky

The distillation curves in the second distillation of
The abscissa, which was expressed as the fraction number, was converted into the ratio of the weight of distillate to that of charge.

In the original paper, the concentrations of ethanol and total acid in the charge were reported, but the concentrations of the other impurities could not be found. These values \(x_{20}\) were assumed so as to match the calculated curves to the observed ones at the beginning of distillation. The calculations were performed at \(x_{20}=0.0985\) and \(\alpha=\delta=0\). The value of \(\beta\) was chosen as 0.2 after some trials.

The comparison between the observed and calculated distillation curves is shown in Fig. 9. With the exception of the case of acid, the shape of the calculated curves is similar to that of the observed ones.

4. 2 Distillation of mash

The distillation curves in the distillation of mash were shown in the paper described by Sugama\(^7\) on the production of shōchū (local spirit in South Kyushu). The concentrations were converted to mole fraction, but the abscissa remained as it was.

As the concentrations in the charge could not be found in the paper, \(x_{20}\) was estimated at 0.0443 and the values of \(x_{n0}\) were assumed so that the shape of the calculated curves resembled that of the observed ones. Because open steam was introduced into the still, \(\alpha\) was taken as 1 and \(\beta\) was estimated at 0.2. The value of \(\delta\) was chosen as 0.1 after some trials.

The comparison between the observed and calculated distillation curves is shown in Fig. 10. Because the abscissas of the two figures in Fig. 10 are different, the length of a unit is adjusted so that the curves of ethanol come into agreement with each other. It can be seen that the shape of the calculated curves of impurities is similar to that of the observed ones.

The calculated curve of furfural is not plotted because furfural does not exist in mash but is produced during distillation, as is discussed elsewhere\(^5,6\).

5. Conclusion

To make clear the behavior of impurities during the distillation of raw materials of distilled spirit, a method for calculating the distillation curves was developed.

It has become possible to predict the behavior of 29 impurities, which are contained in aqueous solution of ethanol, under various conditions.

The calculated distillation curves are in rough agreement with the observed ones. The differences between the calculated and the observed curves need further clarification.
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Nomenclature

\[ A \sim G = \text{constants in the equation of equilibrium ratio} \]  
\[ C = \text{defined by Eq. (15)} \]  
\[ K = \text{equilibrium ratio at still} \]  
\[ K'' = \text{equilibrium ratio at partial condensation section} \]  
\[ L = \text{quantity of liquid in still} \]  
\[ L'' = \text{quantity of liquid in partial condensation section} \]  
\[ S = \text{quantity of steam passed through the liquid in still} \]  
\[ V = \text{quantity of vapor issuing from the liquid in still} \]  
\[ V'' = \text{quantity of vapor in still} \]  
\[ V''' = \text{quantity of vapor in partial condensation section} \]  
\[ W = \text{quantity of steam blown into still} \]  
\[ W'' = \text{quantity of steam condensed at still} \]  
\[ x = \text{mole fraction in liquid in still} \]  
\[ x'' = \text{mole fraction in liquid in partial condensation section} \]  
\[ y = \text{mole fraction in vapor issuing from the liquid in still} \]  
\[ y' = \text{mole fraction in vapor in still} \]  
\[ y'' = \text{mole fraction in vapor in partial condensation section} \]

\[ z = \text{defined by Eq. (13)} \]  
\[ \alpha = \text{parameter defined by Eq. (10)} \]  
\[ \beta = \text{parameter defined by Eq. (8)} \]  
\[ \delta = \text{parameter defined by Eq. (9)} \]  
\[ \text{Subscripts} \]
\[ 0 = \text{initial} \]  
\[ 2 = \text{ethanol} \]  
\[ i = \text{ethanol or minor component} \]  
\[ m = \text{minor component} \]

Literature Cited