Salt Effect on the Composition of Alcohols Obtained From Wine By Extractive Distillation

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The effect of $CaCl_2$, $CoCl_2$, $CuCl_2$, and NaCl on the composition of alcohols obtained by extractive distillation has been studied using wine as raw material. Salts were introduced into distillation column dissolved in the reflux stream in a concentration range of 0% to 17% weight. $CaCl_2$, $CoCl_2$, and $CuCl_2$ could break the ethanol-water azeotrope, and hence hyperazeotropic ethanol was achieved. NaCl could not break the azeotrope, but it increased the energetic efficiency of the alcohol separation. A possible catalytic effect has also been found for $CuCl_2$ to detect an increased concentration of ethyl acetate in distillate and a corresponding acetaldehyde concentration decrease.

KEY WORDS: extractive distillation, salt effect, alcohol, composition, anhydrous ethanol

In the countries with a wine surplus, part of the surplus is distilled to produce ethyl alcohol, which can be used in raising the alcohol content of wine, or in anhydrous form, to be used as fuel for vehicles, *etc.* All of this requires highly versatile installations with large energy costs.

Therefore, there is a need for new operating methods which allow greater separation with lower energy consuption in the distillation plants. These methods include the addition of electrolytes into distillation towers, dissolved in the reflux stream, which alter the composition of the vapor-liquid equilibria, thus obtaining greater separation among the components (2,3). In some azeotropic systems, the equilibrium can be broken, leading to greater separation with corresponding energy savings (1).

However, as the salt effect occurs on all volatile components of raw material fed into the distillation column, produced distillate compositions are different from those produced in absence of salts. This is a very important factor in the alcoholic beverage industry, in which rigorous control of the components accompanying the ethanol is required. This means that in some cases, the concentration of some of them must be reduced or even eliminated.

The aim of the present work was to study the effect of $CaCl_2$, $CoCl_2$, $CuCl_2$, and NaCl on the composition of distilled alcohols using wine as raw material.

The reason for using these salts lies in the manifested enhancement of the volatility of the main volatile components of wine (6) normally present in distilled alcohols, such as ethanol, acetaldehyde, methyl and ethyl acetates, methanol, *n*-propanol, *i*-butanol, *n*-butanol, and *i*-amyl alcohols. Among these salts, the former three can break the ethanol-water azeotrope (4,5,7).

Materials and Methods

Figure 1 shows a schematic representation of the glass-packed distillation column used. The column was made by connecting three sections 50 cm long, having an i.d. of 4 cm, and packing with Raschig rings. Each section was equivalent to about five theoretical stages.

In each run, wine was introduced between the first and second sections starting from the bottom. The reflux at a constant salt concentration was realized as shown in Figure 1 by introducing two streams into a mixer at a constant flow rate. The first of these two streams was made up of condensed over-head vapor and the second of condensed over-head vapor saturated with salt. The reflux was set up, in each run, by regulating

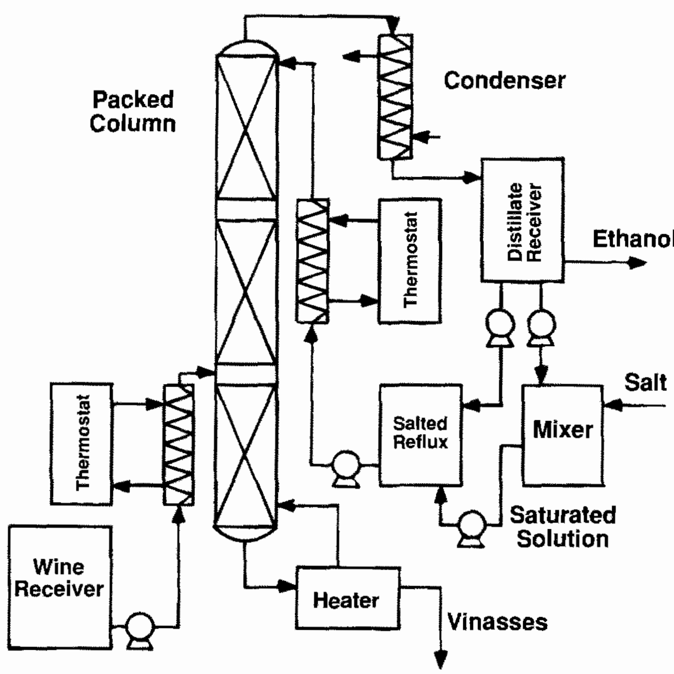

Fig. 1. Schematic representation of the plant used for the experimental runs of extractive distillation with salts.

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the metering pumps so that the set-up mixing ratio should give the desired salt concentration in the reflux.

Salt concentration in the reflux was periodically controlled by taking small samples for analysis. The weight percentage of salt was determined by weighting the initial solution and the solid obtained after complete drying.

In each run, when unit steady-state behavior was assured, samples were taken from the distillate stream, and then analyzed. Two different analyses were made on samples. First, ethanol concentration was determined by measuring the density of the liquid at 20°C using the pycnometric method. Then, the composition of the rest of volatile components were determined by gas chromatography.

Gas chromatographic analysis was made using a Perkin-Elmer gas chromatograph model 881. The chromatographic peaks were quantified with a Hewlett-Packard integrator model 3390A. A 2-m long and 1.8-mm i.d. stainless steel chromatographic column was used. The stationary phase was composed of Carbowax 1500 supported on Chromosorb 80-100 mesh. Analytical conditions were: dual flame ionization detector; injector temperature, 200°C; detector temperature, 150°C; oven temperature, 90°C; carrier gas, nitrogen; flow rate, 30 mL/min; and 2-pentanol as internal standard.

The raw material used was sherry-type wine, whose characteristics and composition are shown in Table 1.

The salts used were analytical grade $CaCl_2$, $CoCl_2$, $CuCl_2$, and NaCl. Both $CaCl_2$ and $CoCl_2$ were chosen for their known solvation capacity (5,7). $CuCl_2$ was studied because many industrial distillation towers are made of copper, which is attacked and dissolved during the operation resulting in the presence of this salt, though in small proportions, during the distillation process. In addition, the solvation effect of $CuCl_2$ is well known (4), so that along with the possibility of its acting as a catalyst during the process (8), it was an attractive subject of study. Finally, NaCl was used because its low cost makes it desirable from an industrial viewpoint, especially in southern Spain.

Results and Discussion

Effect of the salts on ethanol recovery: In Table 2, the results obtained are reported for each of the ten experimental runs for similar reflux ratios and increasing salted reflux.

Table 1. Composition of wine used as raw material for the extractive distillation with salts.

Component	Concentration (mmol/L)
Acetaldehyde	7.74
Methyl acetate	0.03
Ethyl acetate	0.59
Methanol	1.72
Ethanol	2.80×10^3
n-Propanol	1.48
i-Butanol	0.78
n-Butanol	-
i-Amyl alcohols	2.54

Table 2. Experimental results for the extractive distillation with salts using wine as raw material.

Salt Added	Internal reflux ratio	Reflux Salt (wt%)	Salt to distillate ratio (wt%)	Ethanol in distillate (wt%)
-	0.83	-	-	92.3
NaCl	0.86	0.24	1.5	93.5
	0.84	0.7	3.6	93.8
	0.85	8.7	35.1	93.9
$CaCl_2$	0.80	4.3	15.2	97.9
	0.85	8.8	35.3	98.2
	0.83	13.9	44.1	98.6
	0.85	16.9	53.5	99.7
$CoCl_2$	0.85	8.6	34.8	98.4
$CuCl_2$	0.84	8.4	32.5	98.0

Table 2 shows that the use of NaCl did not lead to hyperazeotropic ethanol, since this salt can not break the ethanol-water azeotrope (7). However, concerning conventional distillation, an important increase in separation efficiency was achieved. The higher the salt concentration in the salted reflux, the more efficient the separation process is, but this effect was more remarkable at concentration values lower than 1% weight. This means that the addition of a small amount of NaCl (*ca* 50 g/L distilled alcohol) into a distillation column produces an ethanol concentration increase in distillate of about 1.5% weight; if the ethanol concentration is maintained in distillate, this represents an important energy savings.

$CaCl_2$ could break the ethanol-water azeotrope, hence hyperazeotropic ethanol was obtained in the full range of salt concentrations studied here. It is worthy pointing out that 17% weight. $CaCl_2$ concentration (or higher) produced anhydrous ethanol, which means that it is not necessary to work at saturated reflux (*ca*. 50% wt. $CaCl_2$) to attain the maximum separation efficiency from this salt.

In Table 2, the effects of $CaCl_2$, $CoCl_2$, and $CuCl_2$ produced at the same concentration (about 8.5% wt.) in the salted reflux can be compared. Both $CoCl_2$ and $CuCl_2$ could break the azeotrope, and ethanol concentrations reached in distillate are similar to those obtained by $CaCl_2$. Accordingly, these salts seem to be almost equivalents. However, $CaCl_2$ is more conveniently used because of its lower cost. In addition, it does not produce catalytic effects suvh as the ones produces by $CuCl_2$.

Salt effects on distillate composition: The levels of volatile component concentration found in distillates for five experimental runs are shown in Figure 2: one with no salts, and the others adding the four salts studied here in the reflux stream at similar concentration (about 8.5% wt. salted reflux). Reflux ratio 0.85 was used for each case.

As can be seen in Figure 2, the volatile concentra-

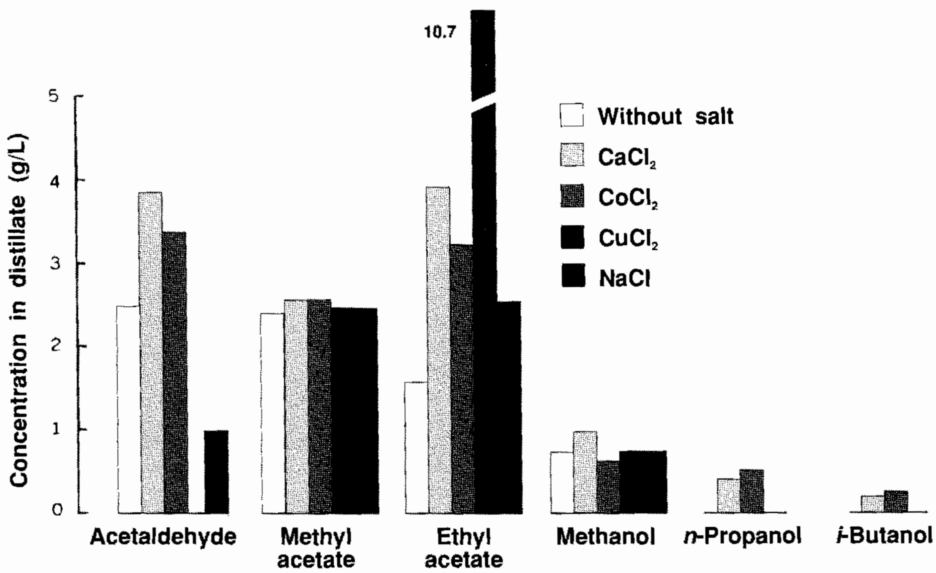

Fig. 2. Concentration of volatile compounds in the distillates obtained by extractive distillation using salts at similar concentration (8.5% wt. salted reflux).

tion was increased in the distillate as both $CaCl_2$ and $CoCl_2$ were added into the distillation column due to the fact that as the salts are dissolved in aqueous medium, they split into ionic species which undergo solvation, resulting in the restructuring of water (9). The practical effect is the removal of water from the environment; consequently, the effective concentration of the other components present in the liquid phase increase, and their concentration alters in the vapor phase in equilibrium. It is clear that the presence of the salts in liquid causes the volatile components to move towards the vapor enriching it.

It is worth noticing the catalytic action of $CuCl_2$, which caused a fall in the presence of acetaldehyde in the vapor phase with a corresponding ethyl acetate rise. This effect was established by the authors in a previous work (6) by using an equilibrium still. Here, as a multistage equilibrium column was used, a much more dramatic effect was observed and acetaldehyde was completely removed from distillate as can be seen in Figure 2.

NaCl produced a similar catalytic effect to that of $CuCl_2$, but moderate. Thus, acetaldehyde content diminished in distillate (and ethyl acetate increased). Concerning the other volatile components, both $CuCl_2$ and NaCl produced moderate increasing effects, so that the profiles of the salted and conventional distillates were almost identical.

As the presence of the salts in the reflux stream caused a removal of water from the environment, the solubility of some compounds also increased; consequently, they were held more firmly in the liquid phase. This effect can be higher than the salting-out effect as it occurs in the case of *i*-amyl alcohols. This is why, when salts were added into the reflux, *i*-amyl alcohols were not found in the distillate.

Conclusions

$CaCl_2$, $CoCl_2$, and $CuCl_2$ broke the ethanol-water azeotrope, and hence hyperazeotropic ethanol was achieved. This means that anhydrous alcohol can be easily obtained from its fermentation broths by using extractive distillation with any of these salts.

NaCl could not break the ethanol-water azeotrope, but increased the efficiency of the ethanol separation. This effect also occurs when using the former three salts, but at very low concentrations. This denotes that from the energy-saving viewpoint, extractive distillation is more profitable than conventional distillation.

The presence of salts bring about their disturbances on the distillate composition concerning volatile compounds. Both $CaCl_2$ and $CoCl_2$ increased the concentration of these components, but $CuCl_2$ changed completely the distillate profile, removing acetaldehyde. NaCl only produced little changes in distillate composition.

As it has been pointed out above, when wine or alcoholic beverage industries are the destination of the alcohol production, fitting recycling streams or purges on the distillation tower is necessary to readjust the disturbed distillate profile and recover a profile like the original.

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