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Distillation of Ethanol–Water Solutions in the Presence of Potassium Acetate

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Abstract

Complete separation of ethanol–water mixtures through salt addition has been demonstrated in a continuously operated single sieve-plate-column including salt recycling. The effect of salt concentration as well as reflux ratio on the separation are outlined based on experimental data. The results clearly indicate that distillation in the presence of salts is an economical alternative to more conventional processes.

INTRODUCTION

A salt dissolved in a mixture of volatile components may affect the activity of the components through formation of associates or complexes (*1*). If this interaction is selective, the relative volatility of the volatile components may change drastically and thus facilitate separation of close boiling components or even azeotropic mixtures. A number of processes are described in the literature where salts proved successful as separating agents. The HIAG Process (*2–4*), for example, has been used from 1930 to 1950 to produce anhydrous ethanol from aqueous solutions by addition of alkali acetates. Quartaroli (*5*) separated solutions of organic acids and water using various salts. Similar experiments were carried out by Kyrides (*6*) as well as Samaddar and Nandi (*7*) with aqueous ethanol solutions. A distillation apparatus for separating phenol–water mixtures through addition of sodium

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chloride is described by Bogart and Brunjes (*8*). Ohe (*9*) cites the IHI Process where the salt is present only in the bottom of the still as a method for enriching isopropanol beyond its azeotropic point.

Except for the last case which is a simple evaporation, no quantitative data have been reported regarding the experimental results. Cook and Furter (*10*) describe the separation of ethanol–water mixtures in the presence of potassium acetate in a column with 12 bubble-trays. The salt was dissolved in the reflux and, after passing through the column, accumulated in the bottom. The measured concentration profiles along the column show oszillating ethanol fractions on the trays, indicating an unstationary operation of the still.

Because of both the lack of and partially contradicting experimental data, design of a distillation column taking advantage of the salt effect is difficult. Therefore, the study presented here was started with the objective to operate a distillation column with salt addition in the continuous mode, including recycling of the salt, and to study the effect of salt concentration, type of salt, and reflux ratio on the production of anhydrous ethanol from aqueous solutions (*11*).

EXPERIMENTAL

The flow sheet of the pilot unit allowing for a continuous operation and salt recycling is shown in Fig. 1. The pilot unit is a sieve tray column of 100 mm diameter with 16 trays at a spacing of 300 mm. The vapor is produced in the reboiler (2) and, after passing through the column, is totally condensed in the condenser (3). Depending on the operating conditions, the condensate is divided into three streams. One of them is returned to the bottom of the column via the flowmeter (10) whereas the other two pass Flowmeter 11 or 12 and the mixing vessel (4), and provide for the reflux to the top tray. This liquid flows down the column, passes Flowmeter 13, and is lifted by the gear pump into the evaporator (5). From this evaporator a concentrated salt solution is injected into the melting vessel (6) containing the molten salt at a temperature of ~305°C. The vapors produced are condensed in the respective condensers (7) and returned to the column via the appropriate flowmeters. The molten salt is metered into the mixing vessel (4) where it dissolves in the reflux liquid and, along with the reflux recycles, goes back to the column.

This particular method of recycling the salt was chosen because handling the salt in the solid state resulted in operating problems due to agglomeration and metering difficulties. In order to avoid catalytic decomposition of the salt, the equipment handling the molten salt was made of stainless steel.

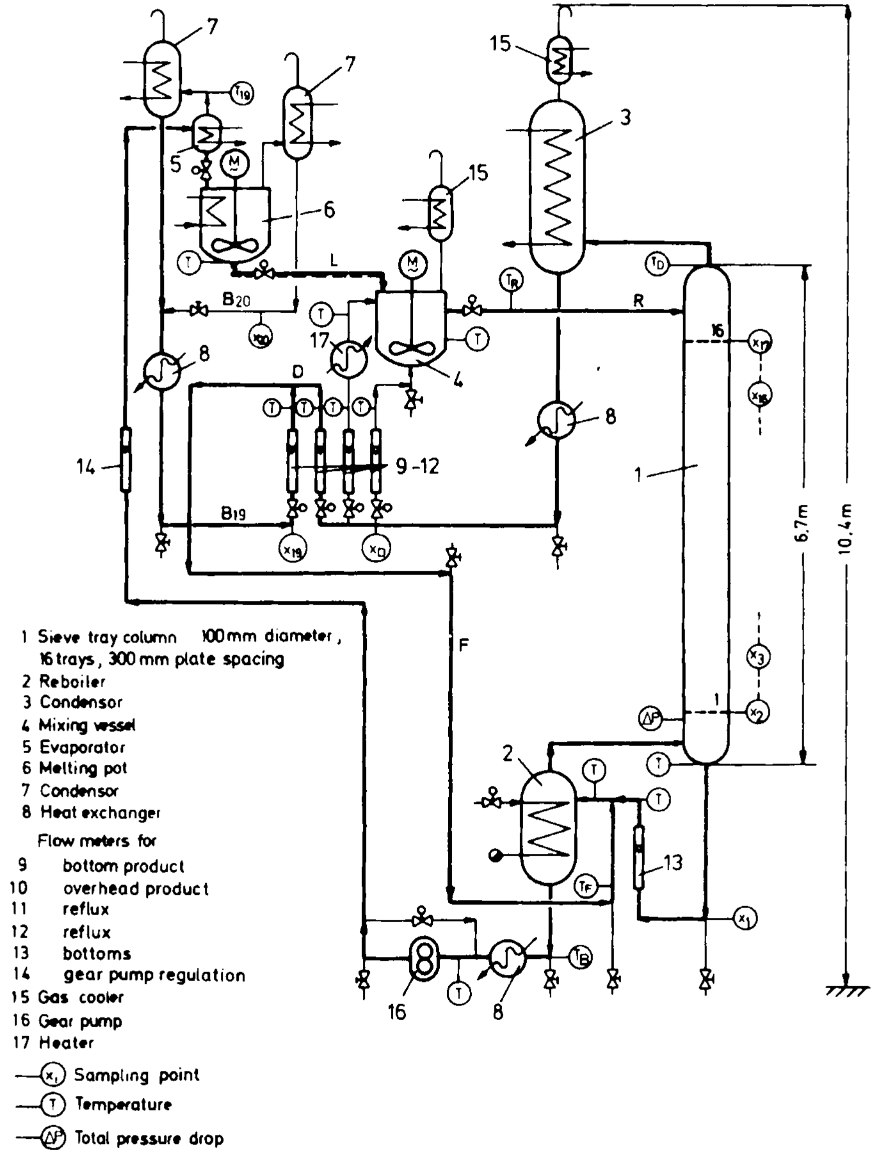

FIG. 1. Flow sheet of salt distillation pilot plant.

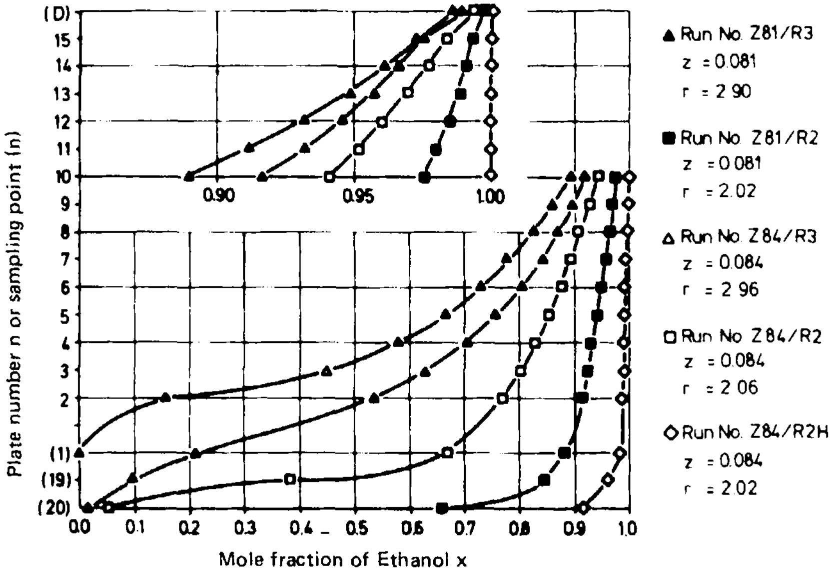

FIG. 2. Concentration profiles in the salt distillation pilot plant.

An aqueous solution of ethanol–water was used as the test mixture, and potassium acetate was provided for the salt effect.

ANALYTICAL TECHNIQUE

After steady-state conditions were obtained, 20 liquid samples of 4 mL were withdrawn from the column using a syringe. Due to the salt content, the analysis consisted of several steps. First the relative composition of the volatile components was determined by gas chromatography, i.e., injecting a liquid probe into an appropriate evaporator retaining the salt and transferring the volatile components by the carrier gas into the GC-column. From another probe the salt content was found by weighing the sample before and after evaporating the volatile components and melting the salt. The accuracy of the measured mole fractions is ±0.004.

RESULTS

Measured concentration profiles for ethanol as a function of reflux ratio and average salt content are shown in Fig. 2. The numbers in parenthesis

TABLE 1
Results of Salt Distillation Experiments

	Run no.				
	Z81/R3	Z81/R2	Z84/R3	Z84/R2	Z84/R2H
Mean salt concentration, z	0.081	0.081	0.084	0.084	0.084
Reflux ratio, r	2.90	2.02	2.96	2.06	2.02
Reflux temperature, T_R	339	347	338	345	337
Salt stream, L	0.0126	0.0126	0.0129	0.0125	0.0126
Feed, F:	0.250	0.276	0.261	0.171	0.294
x_F	0.229	0.879	0.175	0.618	0.973
T_F	307	306	306	302	307
Bottom:					
B_{19}	0.201	0.205	0.215	0.105	0.226
x_{19}	0.044	0.838	0.001	0.382	0.965
z_{19}	0.00006	0.00005	0.00005	0.00041	0.00002
T_{19}	365	356	380	369	356
Distillate, D:	0.049	0.071	0.046	0.066	0.068
x_D	0.987	0.998	0.990	0.994	1.000
z_D	0.00055	0.00006	0.00000	0.00004	0.00000
T_D	353	353	354	354	354

indicate the points of measurement, i.e., the melting pot (20), the evaporator (19), the still bottom (1), and the overhead product (D). The other numbers give the concentration of the liquid leaving the respective tray. As one would expect, the number of trays required for a given separation decreases both with increasing reflux ratio as well as with higher salt addition. A complete separation of ethanol/water is possible in a single column at a reflux ratio of about 2 and an average salt concentration of $z = 0.084$ as demonstrated by run Z84/R2H. The somewhat higher separation of the top tray with respect to ethanol as compared with the adjacent lower tray is due to the fact that because of the limited residence time of the salt in the mixing vessel (4), only part of the salt is dissolved in the refluxing liquid. The rest is carried in the form of a suspension to the top tray, resulting in a higher salt concentration on this tray as compared to the lower trays.

Table 1 summarizes the data of the runs given in Fig. 1 by the mass balances, the reflux ratios, and the temperatures. Since the top of the column did not contain a demister, entrainment of small liquid droplets and thus of minute quantities of salt in the overhead vapor product did take place in a number of runs.

Based on all experimental runs, Fig. 3 gives the number of practical plates required for separating ethanol/water mixtures from 60 to almost 100% ethanol as a function of salt concentration and reflux ratio. A maximum of

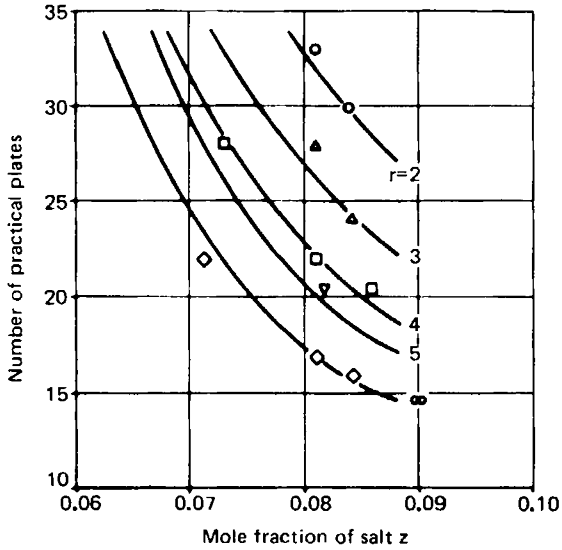

FIG. 3. Effect of potassium acetate and reflux ratio on the number of practical plates for a separation of ethanol from 60 to 100 mol%.

six additional practical plates are required to obtain a mixture with 60% ethanol from solutions with a low ethanol concentration. Anhydrous ethanol could not be produced with salt additions yielding less than 6% of potassium acetate in the refluxing liquid.

With respect to the tray efficiency, a decrease of the overall Murphree plate efficiency was observed with increasing salt concentration from 70% for the salt-free system to 60% for the salt solution. This may be explained by the changing hydrodynamic behavior of the froth on the trays as the droplet size distribution appeared to increase and the height of the froth decreased with rising salt content at a constant *F* factor. Evaluation of the overall Murphree plate efficiency is based on vapor–liquid equilibrium measurements. These data are available upon request and agree with the data given in Ref. *12*.

CONCLUSIONS

Anhydrous ethanol can be distilled from aqueous solutions in a single column by addition of potassium acetate. The feasibility of a continuous process, including recycling of the salt, has been demonstrated in a pilot-plant operation.

Acknowledgment

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SYMBOLS

B	flow rate of bottom product (mol/s)
D	flow rate of distillate (mol/s)
F	flow rate of feed (mol/s)
L	flow rate of salt (mol/s)
n	plate number
p	pressure drop (Pa)
R	flow rate of reflux (mol/s)
r	reflux ratio
T	temperature (°K)
x	moles of ethanol/total number of moles
z	moles of salt/total number of moles

Subscripts

1–20	sampling point (see Fig. 1)
B	bottom product
D	distillate
F	feed
R	reflux

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