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Dehydration of ethanol with different salts in a packed distillation column

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ABSTRACT

This work aimed the evaluation of a saline extractive distillation for the ethanol production. A thermodynamic model was used to predict the influence of the salts in the liquid–vapor equilibrium of the system water–ethanol and inside the packed column. The experiments were done in a distillation unit, with an internal diameter of 5.9 cm and a packing section with 37 cm of height, packed with raschig rings with 0.73 cm of characteristic inner made of glass. All the bottom and top samples were analyzed by refractive index. Two synthetic charges with the same composition of ethanol that are produced in the refinery (0.02 and 0.25 mol.L⁻¹) were distilled under atmospheric pressure. Sodium chloride, calcium chloride, potassium acetate, calcium nitrate and a mixture of sodium and potassium acetates were added to the synthetic charges and the results were compared to the experiments already done without the presence of the salts, revealing the ethanol enrichment in the top product of the distillation unit, for all the systems analyzed. Another charge from the refinery, known as load of wine without yeast, was evaluated and the results indicated the same behavior, enriching the ethanol with the application of the saline extractive distillation.

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1. Introduction

Anhydrous ethanol is widely used in chemical industry as powerful solvent and as a raw material or intermediate in chemical synthesis of esters, organic and cyclic compounds chains, detergents, paints, cosmetics, aerosols, perfumes, medicine and food. Besides, ethanol can be used as fuel reducing environmental contamination and anhydrous ethanol addition octane index (Gil et al., 2008).

The separation of the components present in different mixtures is of great importance in a chemical industry, being the distillation the separation process mostly used nowadays. Some mixtures present characteristics that make the separation very difficult or prevent the total separation of the components. These mixtures are examples of systems that have azeotrope points like the mixture water–ethanol. For these mixtures, the total separation of the components needs

the addition of a third substance, which alters the liquid–vapor equilibrium behavior, in the distillation column. Normally, the added substance is a solvent. There are several liquid and solid separation agents that can be used in ethanol dehydration such as benzene, pentane, furfural, ethylene glycol, diethyl ether, toluene, glycerol, salts and ionic liquids.

Due to the toxicity properties of the organic solvents and because of the difficult separation after distillation, many researches have been done using different salts and ionic liquids.

In recent years, ionic liquids (ILs) have received considerable attention for their use in the chemical industry and are considered to be potential solvents for extractive distillation (Calvar et al., 2010; Geng et al., 2010). This interest is related to the new advantages that these compounds present, such as their negligible vapor pressure at normal temperature and pressure conditions, thermal stability, and their

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capability as solvents (Calvar et al., 2010). With the addition of an IL, the activity coefficients of the components to be separated change their values to a different extent. It is desirable that the changes in activity coefficients result in an increase of relative volatility (Geng et al., 2010). They are relatively new compounds, and the information about their physical and solvent properties is still scarce. Experimental phase equilibrium data are required for developing thermodynamic models and for understanding their thermodynamic behavior (Calvar et al., 2010).

Some salts also can modify the behavior of the liquid–vapor equilibrium of the mixtures. Differently from the solvents and similar to the ILs, the salts are not vaporized in the distillation process and, because of that, they decrease the energy consumed in the distillation, motivating their use in substitution of the solvents. Moreover, with the environmental constraints increasingly strict, the toxicity of the solvents has motivated the use of the salts.

So, another alternative process to produce anhydrous ethanol is the extractive distillation that uses soluble salts as separation agents. The salt, a non-volatile component, is introduced at the top or near the top tray of the distillation column, flows downward along the column, and is completely removed with the bottom product (Ligero and Ravagnani, 2003).

The same authors also cited that besides the lower toxicity of certain salts comparing with previously cited liquids used in the anhydrous ethanol production, one of the advantages of the salt extractive distillation is the production of a distillate completely free of energy savings due to the absence of the evaporation–condensation cycle of the volatile separation agent inside the column. Other advantages are equipments with lower dimensions as diameter of the column, recuperation capacity and recycle of the separation agent. Moreover, according to Gil et al. (2008), the saline extractive distillation is possible to solve several eventual problems of transport, dissolution, corrosion and obstruction found when only salt is used as separating agent. Moreover, Lei et al. (2002) highlighted that there are two factors that influence the extractive distillation, the separation step and the solvents. Assuming that the separation process is determined, the task is to select the basic solvent with high separation ability. When the basic solvent is found, this solvent should be further optimized to improve the separation ability of the solvent and to decrease the solvent ratio and liquid load of the extractive distillation tower.

Because of the advantages of the salts and the available liquid–vapor equilibrium data involving them and ethanol, the aim of this work is to study the operational conditions for the extractive distillation of ethanol, from synthetic charges and from original charges from an ethanol plant located at Rio de Janeiro (Brazil) using different salts as an entrainer.

2. Literature review

A salt dissolved in a solvent mixture is capable, through effects on the structure of the liquid phase, to change the composition of the vapor and liquid in equilibrium. When this occurs, the molecules or ions of the separate agent tend to form complex associations with the molecules of one of the components fed preferentially. This can change the relative volatility value, moving or eliminating azeotropes and thus facilitating the separation of the system to be distilled (Furter, 1972, 1992).

The number of industrial applications in a large scale of the saline extractive distillation has been low due to the solubility data restrictions and to the phenomena complexity (Furter, 1972; Furter and Cook, 1967). The first application is known as HIAG (*Holz Industrie Actien Gesellschaft*), licensed by DEGUSSA and based in two patents of Adolph Gorhan, in the period between 1932 and 1934. More than 100 plants, based on process and production capacity above 43 kt/year, were built between 1930 and 1950 in Europe (Furter, 1972, 1992; Restrepo and Arias, 2003).

The use of HIAG process required less capital and operating costs compared to conventional azeotropic distillation using benzene or extractive distillation using ethylene glycol. However, this process has never really been a success due to technical problems encountered in the dissolution and subsequent recrystallization of salt, and because of the need of special construction materials to avoid corrosion problems. The last plant closed in 1965 in Brazil (Furter, 1972, 1992; Barba et al., 1985). Moreover, at the time, energy conservation was not a priority that would encourage further research to solve these problems.

For the water–ethanol system, many salts are capable to break the azeotrope at atmospheric pressure and can be used in saline extractive distillation. Furter and Cook (1967) and Furter (1977) had done a comprehensive review on the effect of various salts in the distillation. According to Barba et al. (1985), calcium chloride (Nishi, 1975), cobalt II (Jaques and Galan, 1980), potassium and sodium (Pinto et al., 2000), sodium acetate (Merenda and Furter, 1971) and potassium acetate (Merenda and Furter, 1966), sodium iodide (Merenda and Furter, 1972) and potassium iodide (Merenda and Furter, 1972) and calcium nitrate (Miró et al., 1962) are among the salts more efficient and used in extractive distillation.

The correct choice of salt is not limited in their ability to break the azeotrope, but also on other factors such as toxicity, ease of handling, resulting from the system properties such as viscosity and melting temperature, availability and viability in the marketplace. In this study, five salts were used: potassium acetate, sodium acetate, sodium chloride, calcium chloride and calcium nitrate.

Cook and Furter (1968) studied the saline extractive distillation in a column of 12 plates on a pilot scale (10.16 cm of diameter and spacing of 10.80 cm between the plates). Salt, potassium acetate, was introduced into the top reflux of the column at various concentrations and the results proved the efficiency of saline extractive distillation for ethanol dehydration.

Barba et al. (1985) studied the reduction of energy consumption in extractive distillation for anhydrous ethanol production using calcium chloride. The operating conditions were tested in a pilot scale packed column with two or three packed connected sections with 5 cm of inner diameter and 60 cm in height. Through the salt effect, it was possible to produce anhydrous alcohol with an energy gain much larger than those obtained by traditional processes.

In quantitative terms, the study of Barba et al. (1985) is used in the literature as a basis for comparisons with other energy processes of dehydration of ethanol. Table 1 show the energy consumed values for the ethanol distillation processes using different separating agents, studied by different authors (Barba et al., 1985; Black, 1980).

Morschbacker and Uller (1985) studied the addition of the urea as entrainer in the separation of the system water–ethanol. The experimental tests were done in a pilot

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