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GLYCERIN AS ENTRAINER IN ETHANOL EXTRACTIVE DISTILLATION

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Elimination of azeotrope for ethanol-water system has been reported by using salts such as $CaCl_2$, KNO_3 and some solvents like ethyleneglycol and propyleneglycol, but there are not studies about using glycerin as entrainer. In this work, vapor liquid equilibrium has been established for ethanol-water-glycerin system at 75 kPa and compared against Wilson, NRTL and UNIQUAC models calculations. Additionally, ethanol extractive distillation with glycerin as entrainer was simulated using Aspen Plus® in order to establish the main operating parameters to obtain anhydrous ethanol. The results show that glycerin is a very interesting entrainer from technical and economical point of view.

Introduction. Ethanol is one of the most used and important biofuels that contributes reducing environmental effects of fossil fuels. Extractive distillation is a partial vaporization process, in the presence of a non-volatile and high boiling point separating mass agent that it is usually called entrainer or separating agent, which is added to the azeotropic mixture to alter the relative volatility of the key component without additional azeotrope formation. The most common solvents used in extractive distillation are glycols (Meirelles et al., 1992), gasoline and for the case of saline extractive distillation, acetate and inorganic salts such as: $CaCl_2$, KNO_3, K_2CO_3 (Ligero and Ravagnani, 2003; Llano and Aguilar, 2003).
The aim of this work is to study VLE for ethanol-water-glycerin system and establish industrial operating conditions for the extractive distillation of ethanol using glycerin as entrainer and therefore generating a new application for residual glycerin obtained in biodiesel process.

Methods. Solutions were prepared with ethanol (MERCK, 99.8%) and glycerin (EM SCIENCE, 99.5%) analytical grade. Equilibrium cell was a modification of the still described by Othmer. Temperature measurements were made by a RTD PT-100 sensor (± 0.2ºC precision) connected to a PID Autonics TZN4S controller. Assays were isobarically carried out at 750 mbar (563 mmHg) measured with a GPB 1300 barometer with a precision of ±0.5% FS. Compounds (ethanol, water and glycerin) were analyzed by gas chromatography, using an Internal Standard, (GC-2010, Shimadzu, USA) equipped with a Carbowax 20M column (50 m, 0.32 mm i.d., 0.3 μm) capillary column and thermal conductivity detector (TCD).

Extractive distillation simulation was developed in Aspen Plus® using Wilson, NRTL and UNIQUAC models in order to establish the better VLE adjustment.

Results and discussion.

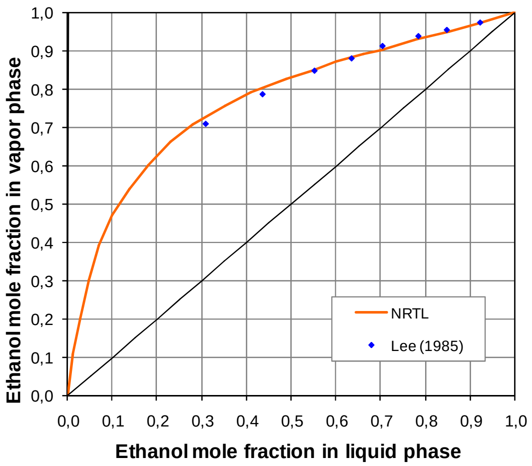

Fig. 1. Pseudobinary vapor liquid equilibrium for ethanol-water-glycerin system.

Conclusions. Obtained results presented thermodynamic consistency, and NRTL model fits properly the experimental vapor-liquid equilibrium data for the mixture studied. Thereby, the simulation results show that is possible obtaining anhydrous ethanol using a glycerine to ethanol azeotropic ratio of 0.6 and with low reflux ratios (R=0.5) in a 20 theoretical stages column.

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