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Feasibility Study of for Separation of Formic Acid – Water- Propionic Acid By Pressure-Swing Distillation

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ABSTRACT

The separation of the mixture formic acid - propionic acid - water into three high-purity products is difficult due to the presence of two binary and one ternary azeotropes that divide the ternary diagram into four distinct distillation regions. Fortunately, the compositions of these azeotropes change significantly with pressure. The pressure-swing distillation process was proposed for the separation of this ternary system. The process simulations were carried out using Aspen Plus 10 software. The effects of the number of theoretical stages (NT), feed stage (NF) and reflux ratio (R) were investigated to optimize the operating parameters of the pressure-swing distillation. The best operating process parameters were defined for systems containing 70% mol. in formic acid, 20% mol. in water and 10% mol. in propionic acid, It has been found that, the formic acid can be obtained in the distillate product in the first column operating at the pressure of 0.133 bar, then the water can be separated at pressure 1.013 bar in the distillate product in second one and propionic acid can be obtained in the bottom product of the third column operating at 1.013 bar. Formic acid is recovered a second time from the distillate product of the fourth column operating at 0.133 bar to increase its yield. The carboxylic acid obtained products in the four distillation columns have a purity of more than 99.9% mol. and the water product have a purity more than 97.0% mol. The residue stream from the fourth column is recycled to the first column.

Keywords: Pressure-swing distillation, Formic acid, propionic acid, Azeotrope ternary diagram.

1. Introduction

Under atmospheric pressure, formic acid and water forms a maximum-boiling binary azeotrope boiling at 380 K containing 57.5 % mol. in formic acid [1] and the propionic acid - water forms a minimum-boiling binary azeotrope boiling at 372.85 K containing 97.3 % mol. in propionic acid [2]. Formic acid - propionic acid - water mixture forms a tenary azeotrope boiling at 379.51 K containing 55.90 % mol. in formic acid, 39.50 % mol. in water and 4.60 % mol. in propionic acid [3].The study of the liquid-vapor equilibrium has shown that the formed azeotropes are pressure-sensitive [1-4].The thermodynamic behavior of liquid – vapor equilibrium of the ternary azeotropic mixture of formic acid – propionic acid - water was calculated at atmospheric pressure and low pressure using an NRTL model. The binary parameters was regressed in Aspen Plus V10 Simulis thermodynamic tool using experimental VLE by minimizing the deviation between the calculated and experimental VLE data. The activity coefficient can be calculated using the NRTL (Non-Random Two Liquids) model developed by Renon and Prausnitz [5].

The main equation of this model is formulated as follows for a mixture:

$$\gamma_i = exp\left[\frac{\sum_j x_j \tau_{ji} G_{ji}}{\sum_i x_k G_{ki}} + \sum_j \frac{x_j G_{ij}}{\sum_k x_k G_{kj}}\left(\tau_{ij} - \frac{\sum_l x_l \tau_{lj} G_{lj}}{\sum_k x_k G_{kj}}\right)\right]$$

With: $\tau_{ij} = a_{ij} + \left(\frac{b_{ij}}{T(K)}\right) \tau_{ij} = a_{ij} + \left(\frac{b_{ij}}{T(K)}\right)$ and $G_{ij} = exp\left(-c_{ij}\tau_{ij}\right)$

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Where: τ is the reduced temperature, R is the ideal gas constant, T is the temperature in Kelvin, x is the mole fraction of the component, α, b,c are the binary interaction parameters.

2. Results and Discussion

The regression of binary interaction parameters of the thermodynamic model from experimental results allowed the plotting of the following ternary diagram at two pressures, atmospheric pressure and low pressure of 0.133 bar, with indications of the formed azeotropes, and to accurately determine the distillation bondary..
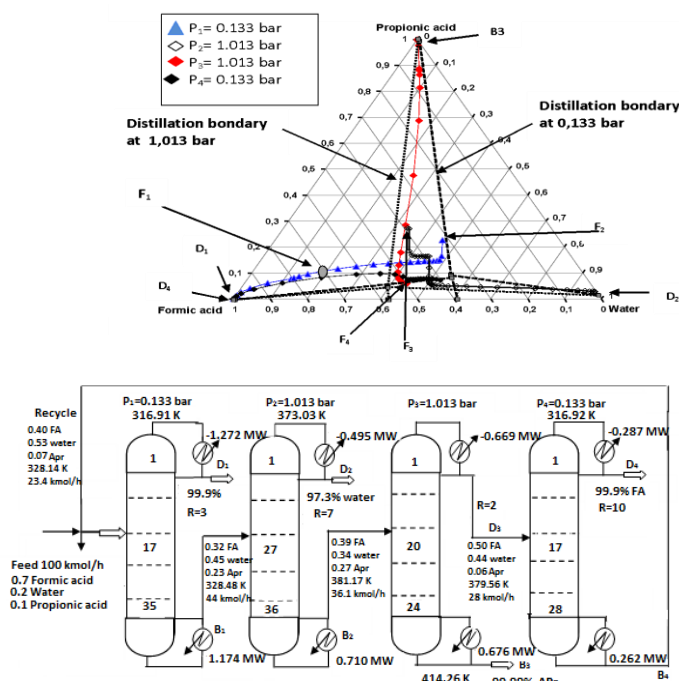
Figure. 1: shows the composition profil of pressure-swing distillation process for feed mixture containing 70 % mol. formic acid, 20 % mol. water and 10 % mol. acetic acid.

3. Conclusions

The design of the separation process for the ternary mixture consists of four consecutive columns operating at two pressures: low pressure (LPC) and pressure atmospheric (APC). The column LPC1 and LPC4 operating at pressure of 0.133 bar allow separating formic acid twice in the distillate with a high purity of 99.9%. The molar recovery ratios of formic acid in LPC1 and LPC4 columns are 80.0% and 32.85% respectively. The propionic acid can be obtained in the third column APC3 operating at atmos-pheric pressure with purity of 99.9 mol.% and molar recovery ratio in propionic acid of 81.0 %. The water can be obtained in the second column APC2 operating at atmospheric pressure with the recovery ratio of 39.5% in water at high purity of 97.25 mol. %. The stream obtained at the bottom of distillation column B4 from 23% of feed F1 is recycled to the first distillation column.

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