

Bioethanol Dehydration by Extractive Distillation with Propylene Glycol Entrainer

A preliminary case study

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The purpose of the paper is to evaluate the selection criteria of entrainers for bioethanol dehydration by extractive distillation process. The entrainer candidate is propylene glycol (1,2 propanediol). This entrainer provide slightly lower selectivity and capacity compared to well known entrainers such as ethylene glycol or glycerol. The minimum number of theoretical stages and minimum reflux ratio for extractive distillation column were estimated based on pseudo-binary equilibrium curves on entrainer-free base, also. Despite of some unfavorable characteristics, the propylene glycol is safety and environmentally friendly, compared to the ethylene glycol, which is considerably toxic moreover, propylene glycol is a renewable product derived from bio-glycerol.

Keywords: bioethanol, extractive distillation, propylene glycol

In chemical engineering processes the environmental issue is a current preoccupation. Chemical engineers must design the processes in order to minimize utilization of non-renewable resources and to ensure a minimal environmental impact. Applying the concept of green engineering led to total or partial substitution of fossil fuel with renewable and environmentally friendly raw materials based on biomass for obtaining clean-burning fuel for automotives engines [1, 2]. High purity bio ethanol is one of the most valuable products from a biorefinery and it is used as fuel for internal combustion engines or such as intermediate for the chemical synthesis of ethers, mainly for ethyl *tert*-butyl ether and *tert*-amyl ethyl ether synthesis. The production of anhydrous ethanol from diluted ethanol-water mixtures produced by the fermentation process is a classic example of extractive distillation [3-5]. Several liquid solvents are used to produce anhydrous ethanol. These include ethylene glycol, tetraethylene glycol, diethyl ether, gasoline, glycerol or ethylene glycol-glycerol mixture [6-10]. Ethylene glycol is environmentally dangerous and harmful for health, therefore, there is a high probability that its use to be prohibited in the next future [11]. So, a new entrainer for bio ethanol dehydration by extractive distillation must be proposed. Taking into account the commercial availability, low toxicity and biodegradability of propylene glycol this compound can be a potential solvent to substitute the most widely used ethylene-glycol [12]. In an integrated biorefinery with modern oil refinery it is an important benefit the utilization of glycerin-derived propylene glycol to an extractive distillation process for recovery of high purity bioethanol from fermentation broth.

The purpose of this paper is to evaluate the selection criteria of solvents for bioethanol dehydration by extractive distillation process. The entrainer candidates need to fulfill some constraints [13-15]: high selectivity and capacity, they should not form any new azeotropes with ethanol or water, should not cause any immiscible regions, be non-volatile, have high boiling point in order to facilitate an easy separation from water (in regeneration column), should also be safety and environmentally friendly, have

acceptable price and availability. All these criteria were investigated for propylene glycol (PG) and the results were compared with ethylene glycol (EG) and glycerol (GLY) solvents.

Experimental part

Methodology

The ethanol-water mixture has a non-ideal behaviour and it forms a minimum-boiling azeotrope at 88.7 mol% ethanol and 78.14°C (at 101.3 kPa). Separation of azeotropic mixtures by classical distillation is not feasible. One of the common alternatives is extractive distillation. An additional component, the so-called entrainer, is introduced into the original mixture to facilitate its separation.

The ease of separation of the key components *i* and *j* from a mixture (with ideal vapour phase) is given by the relative volatility, defined by [16]:

$$\alpha_{ij} = \frac{y_i / x_i}{y_j / x_j} = \frac{\gamma_i \cdot P_i^0}{\gamma_j \cdot P_j^0} \quad (1)$$

where *x* is the molar fraction in the liquid phase, *y* is the molar fraction in the vapor phase, γ is the activity coefficient, and P^0 is the pure component vapour pressure.

The entrainer is introduced to change the relative volatility as long away from one as possible. Since the ratio of P_i^0 / P_j^0 is constant for given temperature changes, the only way that the relative volatility is affected by entrainer is the change of the ratio γ_i / γ_j . This ratio, in the presence of the entrainer (*E*), is called selectivity, S_{ij} :

$$S_{ij} = \left(\frac{\gamma_i}{\gamma_j} \right)_E \quad (2)$$

In the ethanol-water azeotropic mixture the key components are *i*-ethanol and *j*-water. The entrainers selectivity are the ability to more increase the ethanol activity coefficient toward water activity coefficient. In this case, the ethanol would appear in the overhead product of the extractive distillation column.

Another measure to assess the suitability of the entrainer is the capacity, which are determined by:

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$$C_{j,E} = \frac{1}{\gamma_j} \quad (3)$$

A larger capacity denote the stronger of the interactions between component water and the entrainer, these means that water-entrainer mixture appear in the bottom product of extractive distillation column.

Prior to design any distillation column, is proper to evaluate two separation criterions, namely minimum number of theoretical stage (noted as N_{min}) and minimum molar reflux ratio (noted as R_{min}). The Fenske equation has used for calculating the N_{min} :

$$N_{min} = \frac{\ln\left(\frac{x_d}{1-x_d}\right) - \ln\left(\frac{x_b}{1-x_b}\right)}{\ln \alpha} \quad (4)$$

where N_{min} is the minimum number of the theoretical stages at reflux total (of which the reboiler is one), x_d and x_b are the molar fractions of ethanol in distillate product and bottom product of the extractive distillation column, respectively. The relative volatility α of the ethanol-water azeotropic mixture fed to the extractive distillation column is calculated with eq. (1).

The minimum reflux ratio will require an infinite number of trays to attain the specified separation of x_d and x_b . The following equation is used for R_{min} calculation:

$$R_{min} = \frac{x_d - y_f}{y_f - x_f} \quad (5)$$

where x_f and y_f are the ethanol molar fractions in liquid phase and vapor phase, in equilibrium, on the theoretical feed stage.

Results and discussions

In order to evaluate the effect of entrainers on the ethanol and water activity coefficients, the activity coefficients plots versus ethanol or water molar fraction were performed in the presence of the PG, EG and GLY, in turn. All plots were generated at 101.3 kPa with help of PRO/II simulation tool. The activity coefficients were calculated by using NRTL model supplied with UNIFAC model. From these plots, all the γ_i and γ_j values were provided at the i, j components concentrations in azeotropic point. The

selectivities of entrainers were calculated according to eq. (2), and the capacities of entrainers capacities were calculated according to eq. (3). The activity coefficients of ethanol (γ_i) and water (γ_j) in the presence of PG, EG or GLY, the selectivities (S_{ij}) and its capacities ($C_{j,E}$) of entrainers are presented in table 1.

As can be observed in table 1, the propylene glycol entrainer candidate developed slightly lower selectivity and capacity compared to ethylene glycol and far less than glycerol. The PG entrainer abilities suggest an increase in the minimum number of theoretical stages and in the minimum reflux ratio for the extractive distillation column compared to the ethylene glycol or glycerol. To support this preliminary observation, the N_{min} and R_{min} were calculated, based on some value provided from the ethanol-water pseudo-binary equilibrium curves on entrainer-free base. Pseudo-binary plots were obtained by equilibrium calculations taking into account a fixed mole percent of the entrainers. Therefore, the pseudo-binary equilibrium curves on entrainer-free base, at 101.3 kPa, were performed for the ethanol-water-propylene glycol (PG concentration in molar basis: 50; 70; 90%), for the ethanol-water-ethylene glycol (EG concentration in molar basis: 10; 30; 50; 70%) and for the ethanol-water-glycerol (GLY concentration in molar basis: 30; 50; 70%) systems (figs. 1-3).

Pseudo-binary equilibrium curves show the influence of the entrainers on the relative volatility of ethanol-water azeotropic mixture. From figures 1-3 it can be seen that the azeotropic point disappears, for entrainer concentrations above 30% mol. The entrainers that increase the relative volatility of the key components follow the next order: glycerol, ethylene glycol and propylene glycol. This behaviour indicates that when PG is used as entrainer, a higher feed ratio of PG would be needed to break the ethanol-water azeotrope.

Fenske minimum trays for extractive distillation column were estimated based on the pseudo-binary equilibrium curves on entrainer-free base (50% mol. entrainer), as well the minimum reflux ratio. Firstly, the relative volatilities for the ethanol-water azeotropic mixture in the presence of the selected entrainers must be calculated according eq. (1). The ratio of P_i^o / P_j^o is constant, at 2.29 value, for the azeotropic temperature. The pure components vapour pressures were performed by Antoine equation handling with PRO/II simulator. Next, the minimum number of theoretical stages were calculated with eq. (4), based on

| Entrainer | γ_i | γ_j | S_{ij} | $C_{j,E}$ |
|-----------|------------|------------|----------|-----------|
| PG | 1.01039 | 1.0497 | 0.966 | 0.953 |
| EG | 1.04943 | 0.8715 | 1.204 | 1.147 |
| GLY | 1.02316 | 0.12018 | 8.513 | 8.321 |

Table 1
SELECTIVITIES AND CAPACITIES FOR SELECTED ENTRAINERS

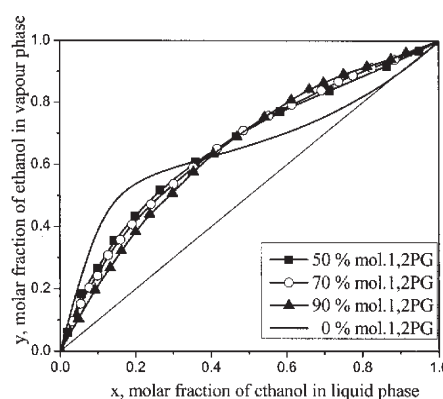


Fig.e 1. Pseudo-binary equilibrium curves for ethanol-water-PG (101.3 kPa).

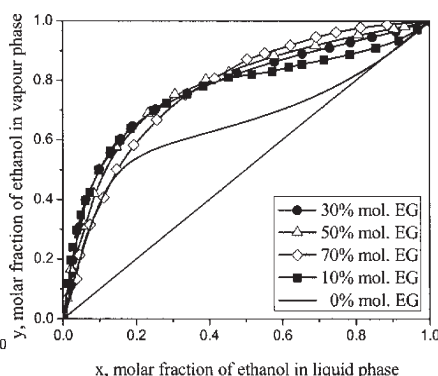


Fig. 2. Pseudo-binary equilibrium curves for ethanol-water-EG (101.3 kPa).

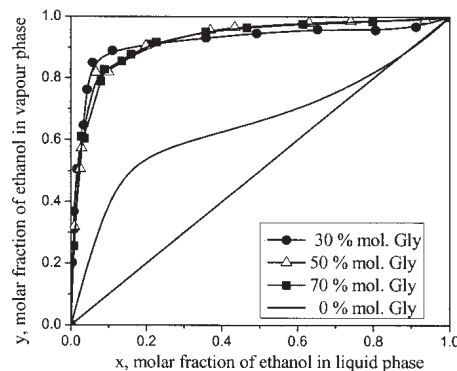


Fig. 3. Pseudo-binary equilibrium curves for ethanol-water-GLY (101.3 kPa)

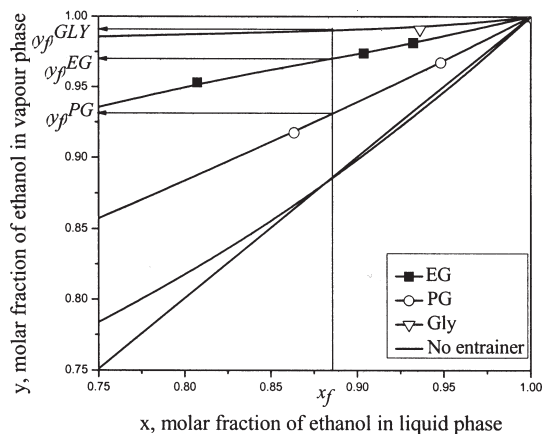


Fig. 4. Ethanol concentration in vapour phase y_f from pseudo-binary equilibrium curves of the ethanol-water-entrainers

assumptions: 99.5% mol ethanol concentration in distillate product ($x_d = 0.995$ molar fraction) and 0.1% mol ethanol concentration in bottom product ($x_b = 0.001$ molar fraction). The azeotropic ethanol-water mixture has fed as saturated liquid at 78.14°C and $x_{az} = x_f = 0.887$ ethanol molar fraction. The minimum reflux ratios were calculated with eq. (5). In eq. (5), y_f were obtained from pseudo-binary equilibrium curves on entrainer-free base (fig. 4). The results of these calculations are presented in table 2.

According to data from table 2, the propylene glycol entrainer candidate requires highly minimum number of theoretical stages and highly minimum reflux ratio for the extractive distillation column than in the ethylene glycol or glycerol cases.

An entrainer candidate for extractive distillation must have some other characteristics. Based on our evaluation, propylene glycol does not form any azeotropes with ethanol or water and does not cause any immiscible regions. The entrainers boiling points should be 80°C higher than the corresponding for the water, in order to be easily separated by this, in the regeneration column. All investigated entrainers respect this criterion. The propylene glycol vapour pressure is slightly higher than that of ethylene glycol, but without significant entrainer losses in anhydrous ethanol. The glycerol and propylene glycol are safe and environmentally friendly, compared to the ethylene glycol, which is considerably toxic. The cheapest entrainer would be ethylene glycol, followed by glycerol and propylene glycol [17].

Conclusions

Propylene glycol seems to be a reliable entrainer to separate ethanol and water by extractive distillation process and it is a good candidate to replace the ethylene glycol. The most important advantage derived by utilization of propylene glycol such as entrainer is represented by the renewability of the product derived from bio-glycerol [18-20]. That is the main reason why many chemical companies re-route to produce environmentally PG, reducing thus their dependence on the petroleum-derived propylene oxide [21].

Of course, several further investigations are needed to demonstrate the viability of the propylene glycol for

Table 2
MINIMUM THEORETICAL TRAYS AND THE MINIMUM REFLUX RATIOS FOR EXTRACTIVE DISTILLATION COLUMN WITH SELECTED ENTRAINERS

| Entrainer | α_{ij} | y_f | N_{min} | R_{min} |
|-----------|---------------|-------|-----------|-----------|
| PG | 2.212 | 0.930 | 15.36 | 1.512 |
| EG | 2.758 | 0.970 | 12.37 | 0.301 |
| GLY | 19.466 | 0.990 | 4.11 | 0.049 |

extractive distillation process – by process simulation – and in the near future we will establish the operating conditions at plant level for this ethanol-water separation process.

References

1. GWEHENBERGER, G., NARODOSLAWSKY, M., Process Safety and Environmental Protection, **86**, 2008, p.321
2. BENNETT, S., PEARSON, P., Chemical Engineering Research and Design, **87**, 2009, p.1120
3. KNAAP, J.P., DOHERTY, M.F., AIChE Journal, **36** (7), 1990, p.969
4. FEITOSA DE FIGUEIR DO, M., GUEDES, B. P., MONTEIRO DE ARAÚJO, J.M., VASCONCELOS, L.G.S., BRITO, R.P., Chemical Engineering Research and Design, **89**, 2011, p.341
5. GARCÍA-HERREROS P., GOMEZ, J.M., Industrial & Engineering Chemistry Research, **50**, 2011, p.3977
6. KUMAR, S., SINGH, N., PRASAD, R., Renewable and Sustainable Energy Reviews, **14**, 2010, p.1830
7. MEIRELLES, A., WEISS, S., HERFURTH, H., Journal of Chemical Technology and Biotechnology, **53** (2), 1992, p.181
8. RAVAGNANI, M.A.S.S., REIS, M.H.M., MACIEL FILHO, R., WOLF-MACIEL, M.R., Process Safety and Environmental Protection, **88**, 2010, p.67
9. DIAS, M.O.S., JUNQUEIRA, T.L., FILHO, R.M., MACIEL, M.R.W., ROSSELL, C.E.V., Anhydrous bioethanol production using bioglycerol-simulation of extractive distillation processes, 19th European Symposium on Computer Aided Process Engineering – ESCAPE19, J. Jeowski and J. Thullie (Editors), p.519
10. ROUSSEAU R.W. (Ed.), Handbook of separation process technology, John Wiley & Sons, New York, 1987
11. LETHA, P.M., GREGERSEN M., Forensic Science International, **155**, 2005, p.179
12. *** Product Safety Assessment (PSA): propylene glycol, in, <http://www.dow.com/propyleneglycol/about/index.htm>.
13. VAN WINKLE, M., Distillation, Mc Graw Hill, USA, 1972, p. 675
14. SEADER, J.D., HENLEY, E.J., Separation Process Principles, John Wiley & Sons, New York, 1998
15. LANGSTON, P., HILAL, N., SHINGFIELD, S., WEBB, S., Chemical Engineering and Processing, **44**, 2005, p.345
16. LEI, Z., LI, C., CHEN, B., Separation & Purification Reviews, **32** (2), 2003, p.121
17. GÓMEZ, P.A., GIL, I.D., Latin American Applied Research, **39**, 2009, p.275
18. DASARI, M.A., KIATSIMKUL, P-P., SUTTERLIN, W.R., SUPPES, G.J., Applied Catalysis A: General, **281**, 2005, p.225
19. DUȘESCU, C., BOLOCAN, I., Rev. Chim. (Bucharest), **63**, no. 3, 2012, p.305
20. DUȘESCU, C., BOLOCAN, I., Rev. Chim. (Bucharest), **63**, no. 7, 2012, p.732
21. SHELLEY, S., (Contributing Editor), A Renewable Route to Propylene Glycol, www.aiche.org/cep August 2007, CEP, p. 6.

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