Separation of an Azeotropic Mixture by Reverse Extractive Distillation

J. Hunek
Technical University of Budapest
H-1521 Budapest, Hungary

S. Gal, F. Posel
P. Glavič
Department of Chemical Engineering
University of Maribor
YU-62000 Maribor, Yugoslavia

In a methanol synthesis plant the by-product contains water and C1-C5 alcohols in decreasing amount with the number of carbon atoms in the molecule. All but the methanol form azeotropic mixtures with water at normal pressure. This means that none of the higher alcohols can be produced in a satisfactory quality if the separation is carried out batchwise. At the first guess one would say the same applies to a continuous process; it is only true however, if the separation train is going to be built up in the usual way, i.e., the second column separates the methanol as a top product and all of the higher alcohols and water as the bottom product. We have found another solution where the separation of water was possible at normal pressure, see Figure 1.

The column, D1, is an existing unit in a methanol synthesis plant. Its task in the process is to distillate out all alcohols from the waste stream. It has 30 Glitsch-ballast valve trays, operating at 2 bar pressure and separating approximately 3 t/h process water from a nearly azeotropic mixture of about 60 kg/h. The ethanol flow rate itself can reach over 100 kg/d, which cannot be negligible. This material is serving as a fuel at present.

The aim of this study has been to analyze the possibility of the separation of higher alcohols in the by-product with satisfactory purity. To make any economic feasibility study, a model of the separation has to be set up. The present contribution deals only with this side of the problem, regardless of economy.

Methods Applied

We decided to use rigorous simulation in our work. The column calculation procedure was that of Naphtali and Sandholm (1971) except that the following simplifications were made:

- Murphree stage efficiencies were equated to unity; overall column performance of $\eta = 0.7$ was considered when necessary (Glitsch Co., 1959; Hoppe et al., 1967).
- The vapor phase was assumed to be ideal.
- Constant molal overflow was imposed.

To describe phase equilibrium in multicomponent mixtures, the most successful methods currently used for the prediction of activity coefficients in the liquid phase are group contribution methods. The best known of those proposed so far is the UNIFAC model, Fredenslund et al. (1977). It has already been used successfully in many areas (Gmehling, 1987; Weidlich and Gmehling, 1987). We chose it because of the reliable results produced for VLE as well as for its wide area of application (Gani et al., 1987; Gmehling, 1987).

The program, UNIDIST, for multicomponent distillation (Magnussen, 1982), was used for the simulation where the above described methods are built in. The original version of UNIDIST has been extended to ten components. Computations were carried out using a VAX-8800 computer. The most important simulation results were checked experimentally, in industrial-, pilot plant-, or laboratory scale.

Results

To check the model, simulation of the existing D1 column was carried out for typical operating conditions in steady state. Pressure, reflux ratio, and total product streams were chosen, based on averages of a four hour period. Feed composition and total feed were calculated from the material balance, based on analysis of the top product at the second hour. The bottom product was practically pure water. Overall column efficiency ($\eta = 0.7$) resulted in $N = 0.7 * 30 + 2 = 23$ theoretical trays. When the

---

Correspondence concerning this paper should be addressed to J. Hunek.
Research for this work was performed at the University of Maribor.

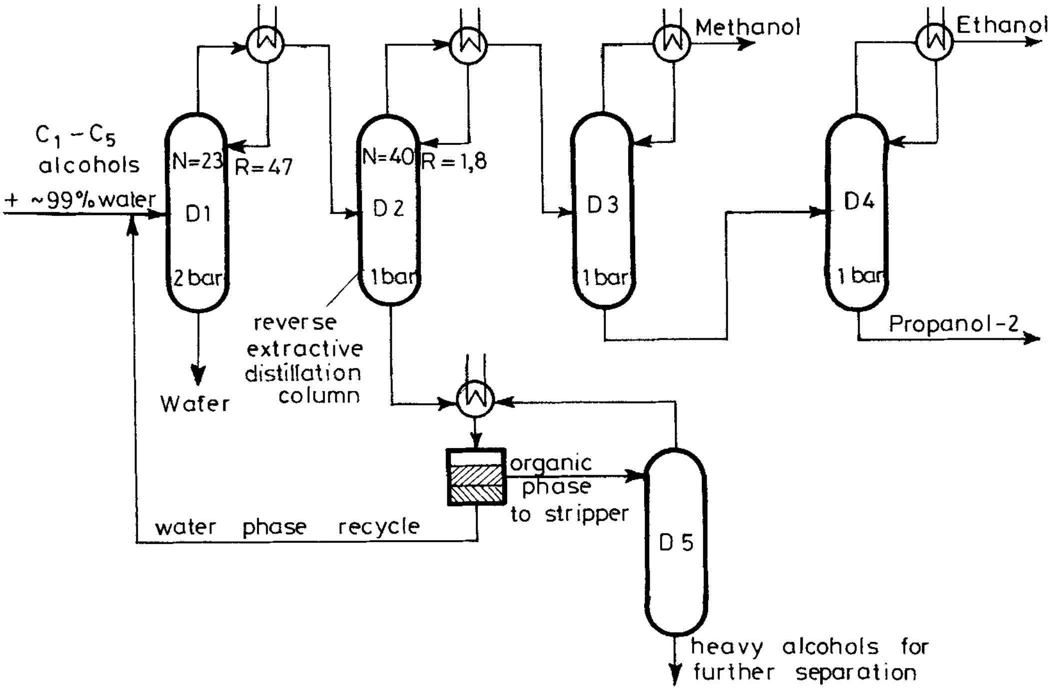

Figure 1. Separation of multicomponent water alcohol mixtures by reverse extractive distillation.

computed content of the products was compared to the measured one, we obtained very good agreement, Table 1.

If the top product of D1 is to undergo further separation, the least possible water content is preferable. This value was determined by simulation as $w(H_2O) = 7.0\%$. This simulation was carried out in the following way: for the chosen feed and operating conditions a series of model runs were made by gradually decreasing the flow rate of distillate from the measured one (1.378 kmol/h) until methanol resulted in the bottom product (Figure 2). At the same time, a shallow minimum in the top temperature signals the minimum water content of the distillate (optimum composition, Table 1). This gives the optimum operating conditions for column D1.

The further separation of this distillate was studied next. By lowering the pressure to 1 bar, the equilibrium conditions change so that, in the presence of the considerable quantity of methanol, no water-containing azeotrop is formed. This observation has led us to solution of the separation problem. The methanol content of the mixture can be utilized as an extractive agent separating the azeotropes in a process somewhat similar to extractive distillation (i.e., it changes the activity coefficients in the liquid phase). However, in a sense, this case is just the opposite of what is described as extractive distillation because the "separation agent" has higher volatility than water and so its move through the column is in the reverse direction. Thus, we may better name it "reverse extractive distillation" to emphasize the difference. In our case, the feed contains the agent too, because it comes from the technology itself.

Table 1. Waste Composition

Component, i	x_i Meas. %*	x_i Comp. %*	x_i Opt. %*
Water	17.0	17.0	12.3
Methanol	76.0	76.1	80.4
Ethanol	4.47	4.50	4.75
Propanol-2	0.43	0.44	0.46
Propanol-1	0.87	0.87	0.92
Butanol-2	0.74	0.73	0.77
Iso-Butanol	0.24	0.22	0.23
Butanol-1	0.04	0.04	0.04
Pentanol-2	0.15	0.15	0.15
2-Methyl-1-Butanol	0.01	0.01	0.01

*Mole amount fraction

Simulations have been made for a following D2 column at 1 bar pressure to determine its optimum operating conditions. It was found that the "reverse extractive distillation" separates ethanol and propanol-2 from the water and other alcohols. The result was unexpected. We checked its reliability with pilot-plant experiments by continuous rectification of an artificial ternary mixture of water-methanol-ethanol of nearly the same feed composition (Gal et al., 1987). The water content of the distillate was below $w(H_2O) = 0.1\%$. From calculations on the basis of published ternary VLE data (e.g., Wankat, 1981) this could, however, be foreseen.

According to the simulation results, the amount fraction of the methanol ethanol and propanol-2 in the bottom product is less than 0.05% of their content in the feed. The bottom product of D2 contains the water, propanol-1, and all the heteroazeotrope-forming alcohols (C4, C5). This product splits into two immiscible liquid layers by cooling. From the organic layer, water can be stripped out in the usual method, resulting in a water-free mixture of the higher alcohols which can now be separated batchwise or in a further continuous-separation train. The flowsheet of the whole process has been shown in Figure 1. The water phase can be recycled from the settler to the feed of D1. An undesirable buildup of the light components at the top of D5 can be avoided by a recycle stream from there to the feed of D1.

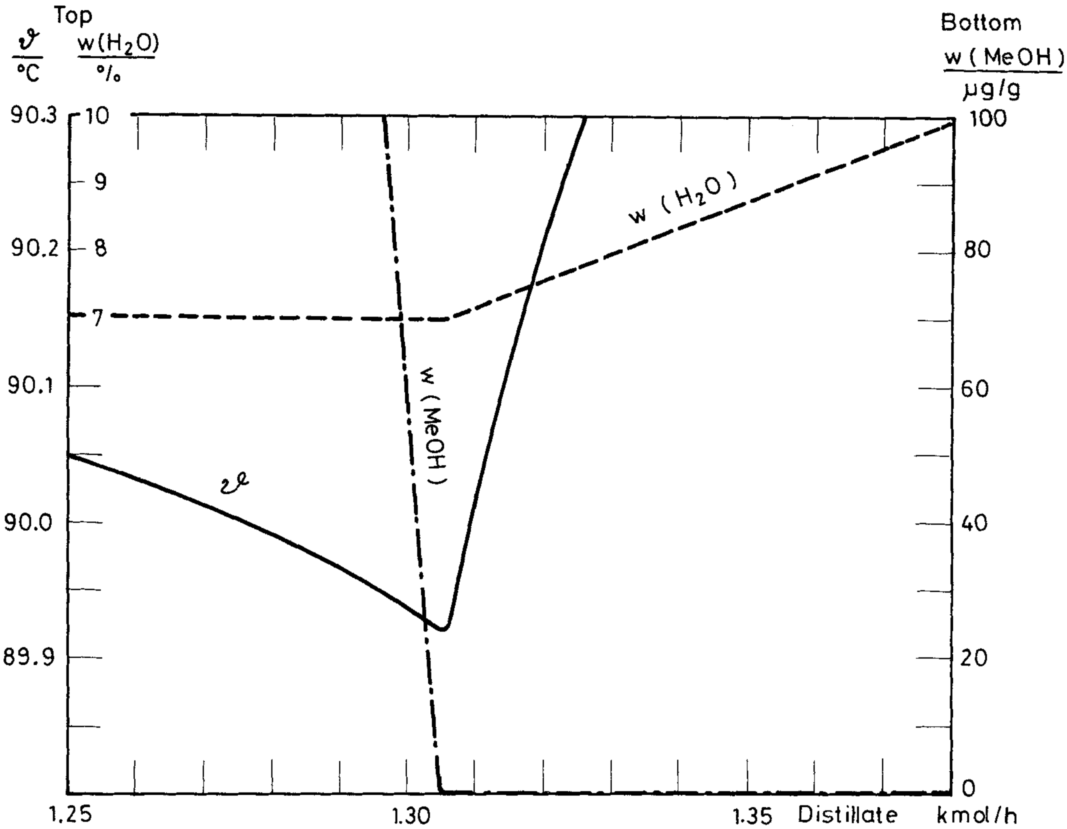

Figure 2. Simulation of the D1 column.

Since UNIFAC does not describe LLE as well as VLE, the phase splitting of the bottom product of D2 after cooling, was also checked experimentally. These laboratory tests confirmed the formation of two layers. Another verification was made with a different method where experimental binary VLE data (Gmehling and Onken, 1977) were used as input. There was some deviation in the results (at most, 20%) but the formation of the two layers, which is the basic condition of the possibility of the separation, was again confirmed.

Conclusion

The most important conclusion of our work is that, at the separation of a mixture of water and alcohols, methanol can be utilized as an extractive or, more precisely, as a "reverse extractive" agent, and the separation becomes possible at atmospheric pressure if the flowsheet shown in Figure 1 is applied. Generally speaking, the new term, "reverse extractive distillation," has been introduced to emphasize some differences within the field of extractive distillation. It can be utilized for the same purpose as extractive distillation (i.e., it must lower the activity coefficient of the less volatile azeotrope-forming component at low concentrations) with one main difference: the component termed, "the separating agent," moves in the reverse direction (upwards) in the column.

Acknowledgment

The authors wish to express their great appreciation to Dr. S. Kemény (Technical University of Budapest, Hungary) for his useful advice in reviewing this paper, and to Dr. J. Gmehling (University of Dortmund, Federal Republic of Germany) for the valuable information he gave about the UNIFAC method.

Notation

n = number of theoretical trays
w = composition in mass fraction

Greek letters

η = overall column efficiency
θ = temperature

Literature Cited

Fredenslund, A., J. Gmehling, and P. Rasmussen, *Vapor-Liquid Equilibria Using UNIFAC*, Elsevier, Amsterdam (1977).

Gal, S., S. Pečnik, and F. Posel, "The Study of Economical and Technological Possibilities of Use and Separation of Alcohols-Water Mixture as a Byproduct of Methanol Synthesis," Graduation Thesis. Faculty of Technical Sciences, Maribor, (1987).

Gani, R., M. Castier, and A. Fredenslund, "A Policy for the Unification of UNIFAC Based Models," CHISA Congress, Praha, (Aug.–Sept., 1987).

Glitsch Co., Prospectus of Glitsch Firm, Fractionating Research Inc. Report, No. 160, (Sept., 1959).

Gmehling, J., and U. Onken, "Vapor-Liquid Equilibrium Data Collection," DECHEMA *Chem. Data Ser.*, Vol. **1**, DECHEMA, Frankfurt, (1977).

Gmehling, J., "From UNIFAC to Modified UNIFAC," 3rd CODATA Symp., Budapest (Sept. 6–8, 1987).

Hoppe, K., and M. Mittelstrass, *Grundlagen der Dimensionierung von Kolonnenboden*, Theodor Steinkopf, Dresden, 223 (1967).

Magnussen, T., "Multicomponent Distillation Using UNIFAC," *Phase Equilibria and Separation Processes,* Inst. for Kemitehnik, Denmarks Tekniske Hojskole, Lyngby (1982).

Naphtali, L. M., and D. P. Sandholm, "Multicomponent Calculations by Linearization," *AIChE J.* **17,** 148 (1971).

Tiegs, D., and J. Gmehling, "A Modified UNIFAC Model," CHISA Congress, Praha (Aug.–Sept., 1987).

Wankat, P. C., "Graphical Multicomponent Distillation," *AIChE Modular Inst.,* Ser. B, Vol. **2,** 13 (1981).

Weidlich, U., and J. Gmehling, "A Modified UNIFAC Model," *Ind. Eng. Chem. Res.,* **26,** 1372 (1987).

Manuscript received Nov. 28, 1988, and revision received Mar. 17, 1989.

Errata

In the paper entitled "Analytic Solution for Adsorber Breakthrough Curves with Didisperse Sorbents (Zeolites)" by P. L. Cen and R. T. Yang (**32,** Oct., 1986, p. 1635), ψ should be replaced by ψ^{-1} in Eqs. 17a, b; β should be replaced by δ in Eqs. 18–20 and 26; M_2 should be multiplied by 10 in Figures 1–5.