Applicability of the Perturbed Hard Chain Equation of State for Simulation of Distillation Processes in the Oleochemical Industry. Part II: Purification of Glycerol

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Abstract

Glycerol is a major by-product in the oleochemical industry with extensive end-use markets. Synthetic and natural glycerine fractions are currently purified using steam distillation at subatmospheric pressures. Due to the increasing interest of the pharmaceutical industry in ultrapure glycerol, supercritical fluid extraction followed by appropriate fractionation steps are also employed. It would therefore be convenient to utilize a single thermodynamic model that is capable of predicting all thermodynamic properties needed, and that also covers the whole pressure range which is currently applied in both industries. Different equations of state and activity coefficient models were scanned, and the perturbed hard chain equation of state (PHC-EOS) provided better results than those obtained using activity coefficient models. Pure component parameters were computed using vapor pressure data for glycerol. The fitted parameters were incorporated in the PHC-EOS and resulted in good reproduction of binary vapor–liquid equilibria. Calculations of multicomponent mixtures were performed using these binary parameters. A flow-sheeting program was utilized to simulate a steam distillation process consisting of two integrated columns, operated at subatmospheric pressures, for the purification of different glycerine feedstocks. The simulated flow rate, concentration, and temperature profiles were compared with some operating data obtained from a major oleochemical plant. Analysis of this comparison revealed that the PHC-EOS is very well suited for simulating different distillation processes for the purification of crude glycerine feedstocks.

INTRODUCTION

The main objective of this work was to select a single thermodynamic model that is capable of predicting all thermodynamic properties needed for fatty acids and glycerol to simulate purification processes utilized in the oleochemical industry. The model should also cover the whole pressure range which is currently applied in this industry. The results obtained for

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fatty acids were presented in Part I of this work (*1*), while those concerning the purificiation of glycerol are presented in this paper.

Glycerol, the simplest trihydric alcohol, may be synthesized from petrochemical feedstocks (synthetic glycerol) or obtained as a by-product of various processes within the oleochemical industry (natural glycerol). Propylene is used as feedstock to produce synthetic glycerine mainly by chlorination to allyl chloride. The process by which natural glycerine is obtained is typically either the hydrolysis of fats and oils, or their alkaline saponification to produce soap. Transesterification of fats and oils by methanol to produce fatty acid methyl esters, and the direct processing of fats and oils and ethanolamine to produce fatty alkanolamides, also result in a crude glycerine by-product which is subsequently refined.

World natural glycerine production is expected to increase from 510 kton in 1988 to 664 kton by the year 2000 (*2*). Historically, natural glycerine production is a factor of the demand for soap, fatty acids, and detergent alcohols. However, the projected increasing demand for methyl esters and certain types of low-caloric fat substitutes will have a large impact on the production level of natural glycerine. Glycerine is consumed in several end-use markets where the pharmaceutical and cosmetic industry is by far the most important group, followed by the tobacco, food, and plastics industries.

In this investigation, particular attention has been devoted to simulate low pressure distillation processes utilized for the purification of glycerine mixtures containing water. Equations of state and activity coefficient models were compared to select a reliable thermodynamic model which can be used in simulating these processes.

PROCESSING OF NATURAL GLYCEROL

Sweetwater, containing 10–18 wt% glycerol together with varying amounts of dissolved inorganic salts and color and fat impurities, is obtained as a by-product during the hydrolysis of fats and oils to split the triglycerides into mixed fatty acids and glycerine. The sweetwater should be processed promptly after fat splitting to avoid degradation and loss of glycerol by fermentation. The spent lyes resulting from current soapmaking processes generally contain 10–15 wt% glycerol and 10–20 wt% inorganic salts. These dilute aqueous solutions are first treated to neutralize entrained fatty acids or precipitate some organic impurities, and then concentrated to about 88 wt% glycerol in a multiple-effect evaporation unit.

Refining of this crude glycerine stream to meet the rigid specifications required by the food, pharmaceutical, and cosmetic industries is usually accomplished by distillation. Before entering the distillation plant, part of the remaining water content is evaporated in a vacuum drier/degasser to
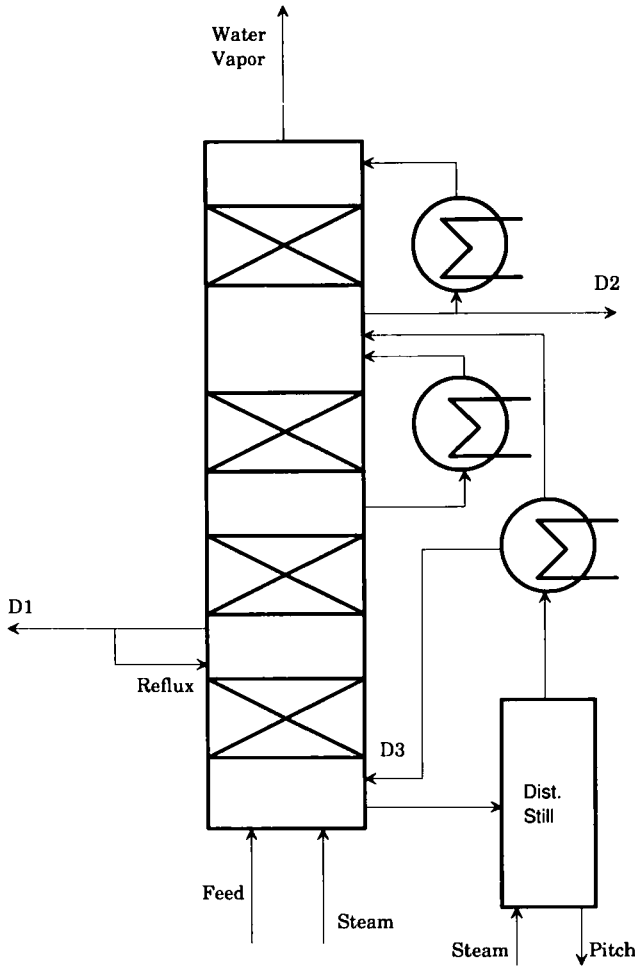
FIG. 1. Flow sheet of a distillation process for purification of crude glycerine feedstocks.

a residual water concentration of approximately 5 wt%. Figure 1 shows a simplified flow sheet for a distillation unit commonly used for refining different crude glycerine streams. The unit consists of a main distillation column integrated with two distillation stills. In modern glycerol distillation plants, the main column is divided into four sections, packed with an efficient packing material. The crude feed is generally fractionated into three streams; two distillate streams D1 and D2, and a bottom waste stream usually known as pitch. The main distillate stream D1 has a purity exceeding

99.5 wt% glycerol whereas the by-product stream D2 contains about 90 wt% glycerol. The overhead stream D3, leaving the distillation still, is usually redistilled in the main column.

Preheated and degassed, the crude glycerine feed stream is pumped to the first two stages of the reboiler unit of the distillation column. The reboiler is divided, on the liquid side, into four chambers connected in series. From the last chamber, the enriched bottom stream flows by gravity into one of the distillation stills. An adequate amount of high pressure saturated steam is supplied to the reboiler to evaporate the quantity of glycerol required to produce the distillate streams D1, D2, and the reflux. The vapor stream leaving the four chambers of the reboiler flows through the stripping section of the column to strip off the low-boiling components using about 20% of D1 as reflux. This reflux stream, together with the high-boiling components, are allowed to flow back to the reboiler to be redistilled. The glycerol/water vapors now enter the rectifying section where rectified liquid glycerine leaves as the main product, with a purity exceeding 99.5 wt% and a temeprature of approximately 150°C. This stream is first cooled to about 80°C and then pumped to a bleaching unit for final processing using active carbon adsorption at 74–79°C.

In the first condensation section, arranged on top of the rectifying section of the column and operating as a partial condenser, a considerable amount of the glycerine stream is withdrawn from the column, cooled and circulated back on top of the first condensation section, and used to condense most of the glycerol vapors in that section. Related to the pressure maintained above this section, the circulating glycerol stream is considerably super-heated in order to flash off some of the glycerol together with the remaining water content. The generated glycerol-water vapors will escape to the final condensation section, where 5–10% of D1 will be condensed, using another loop of circulating glycerine stream having the same quality as distillate D2. Compared to D1, the by-product stream D2 has a lower quality and consists of 90 wt% glycerol. It is usually sold as such to some end-use markets within the chemical industry. The water vapor, together with non-condensable gases, leaving the final condensation section at 40°C, are sucked to the vacuum system for condensation and evacuation, respectively.

The undistillable components which are concentrated in the fourth stage of the reboiler of the distillation column will flow, together with approx-imately 10% of the originally available glycerol quantity, to one of the distillation stills designed for batchwise mode of operation. This type of still is considered to function as a single-effect evaporator due to the lack of reflux stream. The overhead vapors enter a partial condenser where most of the glycerol is condensed. The condensate, constituting the third

distillate stream D3, is, however, of inferior quality, since it contains a considerable amount of the high-boiling components entering with the feed, and is therefore fed back to the distillation column for redistillation. The overhead cut obtained toward the end of the batch distillation cycle, where the bottom temperature approaches 185°C, is however, mixed with the second glycerine loop, utilized as a cooling stream in the final condensation section of the column. The residue, usually called pitch, containing the remaining part of the high-boiling components together with inorganic salts, is withdrawn from the still at about 185°C. The flow rate of the pitch stream is about 21–22% of the main distillate stream D1.

Distillation of glycerol under atmospheric pressure is not practicable, since glycerol decomposes to some extent at 204°C. A combination of vacuum and steam distillation is therfore used. Injection of direct steam, usually superheated, has two main objectives: to ensure sufficient agitation of the viscous mixture circulating in the heating surfaces of the reboiler units and to reduce the partial pressure of glycerol vapors especially in the lower parts of the columns. For instance, at 60 mbar, glycerol boils at 204°C with no direct steam present. Keeping the total pressure constant at 60 mbar, injection of direct steam would reduce the partial pressure of glycerol vapors from 60 to 20 mbar. The boiling temperature of glycerol can thus be suppressed from 204 to 175°C. In practice, the distillation unit shown in Fig. 1 is operated at a pressure range of 5–13 mbar. This would reduce the amount of direct steam required to about 8–10% of the glycerine feed stream, allow the use of relatively low pressure steam, and permit the main distillation column to be operated at a temperature of 157–163°C, thus resulting in minimum decomposition of glycerol.

SIMULATION RESULTS AND DISCUSSION

The thermodynamic framework was outlined in Part I of this work (1). Different equations of state and dual models were scanned, and the perturbed hard chain equation of state, PHC-EOS, was selected to predict vapor pressures and phase equilibrium data for fatty acids at low pressures. Since it is convenient to utilize a single thermodynamic model that is capable of predicting all thermodynamic properties needed in this type of industry, the PHC-EOS was also selected to simulate distillation processes used for glycerol refining.

The physical properties of glycerol are listed in Table 1. Vapor pressure data for glycerol (3) were used to fit Antoine constants, and the results of parameter fitting are displayed in Table 2 together with the valid temperature range and the average relative deviation, σ_{pav}. As indicated, two temperature ranges were chosen to increase the accuracy of parameter fitting, resulting in σ_{pav} values of 1.42 and 1.94%, respectively.

TABLE 1
Physical Properties of Glycerol

Property	Value	Units
Chemical formula	$C_3H_8O_3$	—
Molecular weight	92.092	kg/kmol
Normal melting point	291.2	K
Normal boiling point	563.2	K
Critical temperature	725.0	K
Critical pressure	66.5	kPa
Critical volume	255.0	cm^3/mol

The pure component parameters T^*, v^*, and the Prigogine factor c were also fitted using the vapor pressure data. The weighted least-squares method and an appropriate objective function were applied in these computations. The upper part of Table 3 shows the computed pure component parameters together with the valid temperature range and pressure deviations. The PHC-EOS prediction of vapor pressure is illustrated in Fig. 2, where the average relative deviation, σ_{pav}, is plotted against temperature. These results reflect the performance of the PHC-EOS for vapor pressure predictions. As can be seen, this equation provided results which are as good as those obtained in fitting Antoine constants, and in some cases better.

The binary interaction parameter to be used in the PHC-EOS, k_{ij}, was fitted to vapor–liquid equilibrium (VLE) data for binary water–glycerol mixtures. In this work, the k_{ij}, characterizing the physical interactions between two different molecules, were considered to be temperature-independent. The results of these computations are displayed in the lower part of Table 3, where the binary interaction parameter (k_{ij}), pressure, and average relative deviation of liquid and vapor phase composition are given.

There are a number of experimental VLE data published for the binary system water–glycerol that covers both the subatmospheric and atmospheric pressure range, extending from 13 mbar to 1.013 bar. The activity coefficients for the different dual models were, however, not computed in Gmehling et al. (4), probably due to the unusual steep behavior of this

TABLE 2
Fitted Antoine Constants for Glycerol

Temperature range (K)	A	B	C	σ_{pav}
291–390	290.0000	−73,528.18	−0.265510	1.42
390–563	61.7502	−17,492.27	−0.0340761	1.94

TABLE 3
Pure Component Parameters and Binary Interaction
Parameter for Glycerol

| Parameter	Value	Units
Temperature range, T	291–563	K
Characteristic temperature, T^*	443.4515	K
Characteristic volume, $100v$	4.1543	dm^3/mol
Prigogine constant, c	3.7342	—
Average relative deviation, $(\sigma_p)_{av}$	1.51	%
Maximum relative deviation, $(\sigma_p)_{max}$	2.50	%
Pressure, P	13.0	mbar
Binary interaction parameter, k_{ij}	-0.0817	—
Average relative deviation, $(\sigma_x)_{av}$	0.18	%
Average relative deviation, $(\sigma_y)_{av}$	0.45	%
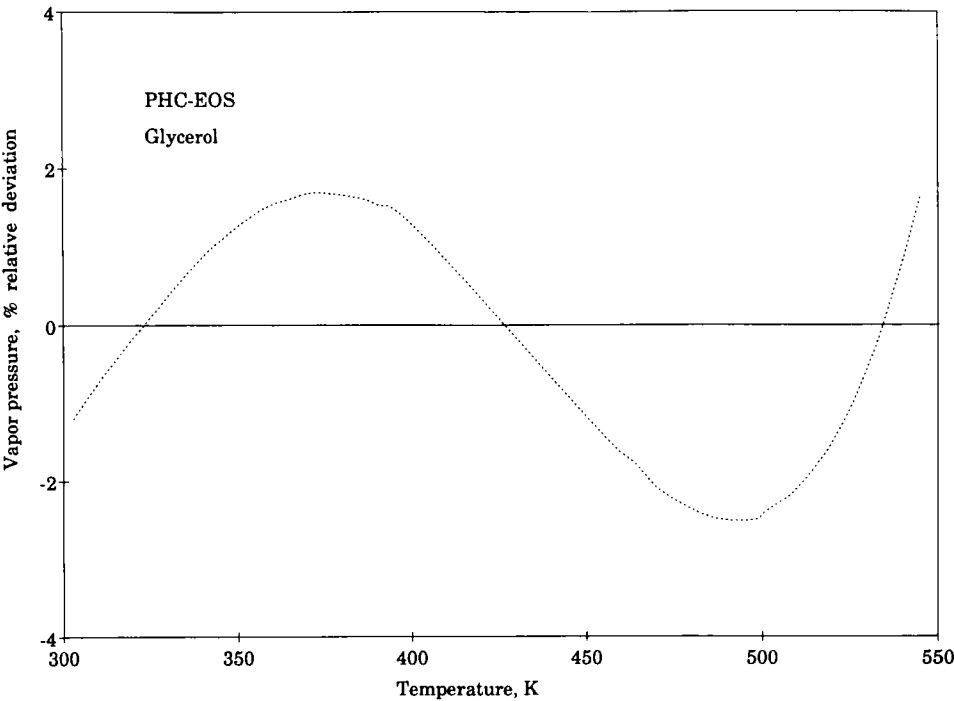
FIG. 2. Relative deviation of the PHC-EOS vapor pressure prediction for glycerol.

system. Water concentration in the vapor phase exceeds 99 wt% at a liquid phase concentration of 2.0 wt% water. Experimental VLE data at 13 mbar (5) were thus used to fit the activity coefficients of six different dual models utilizing the computer package EQUIL (6). Different objective functions were minimized in these simulations, and the Wilson model (7) gave the best results. An objective function, based on both pressure and vapor phase concentration, was minimized to 0.2788 and resulted in an average deviation in vapor phase concentration and temperature of 2.53 mol% water and 3.43°C, respectively. The computed values of Wilson activity coefficients were $\Lambda_{12} = 3.5145$ and $\Lambda_{21} = 2.3587$.

The performance of the PHC-EOS in predicting VLE was compared to that obtained using the Wilson model. The results are depicted in Figs. 3 and 4 for the water–glycerol binary system at 13 mbar. Figure 3 covers the entire concentration range of the equilibrium curve, whereas the lower part, up to 3.0 wt% water in the liquid phase, is enlarged in Fig. 4 for better comparison between the PHC-EOS and Wilson model. As can be seen, these results clearly indicate that the PHC-EOS reproduces binary VLE at very low pressures with a higher degree of precision compared to
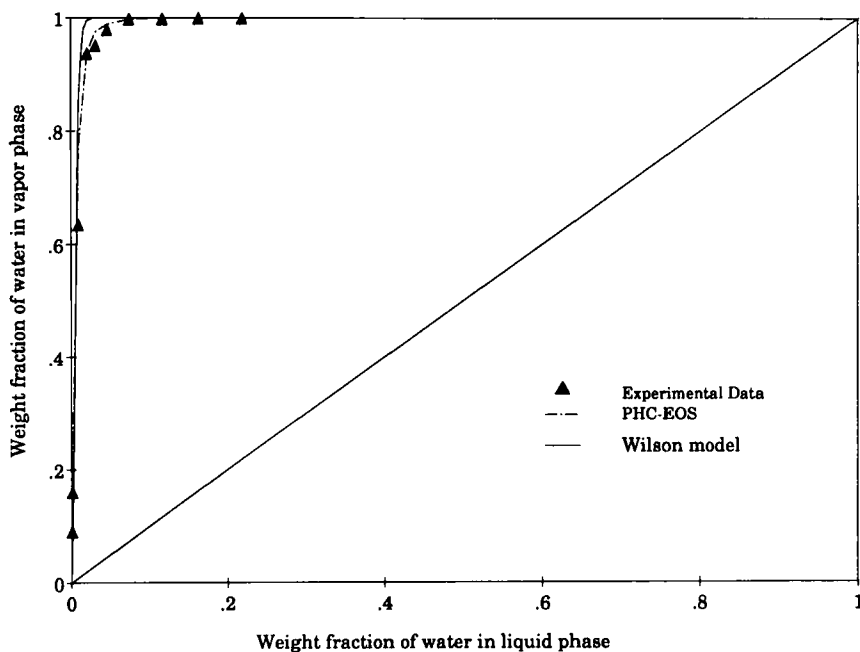

FIG. 3. Calculated and experimental VLE for water–glycerol binary system at 13 mbar.
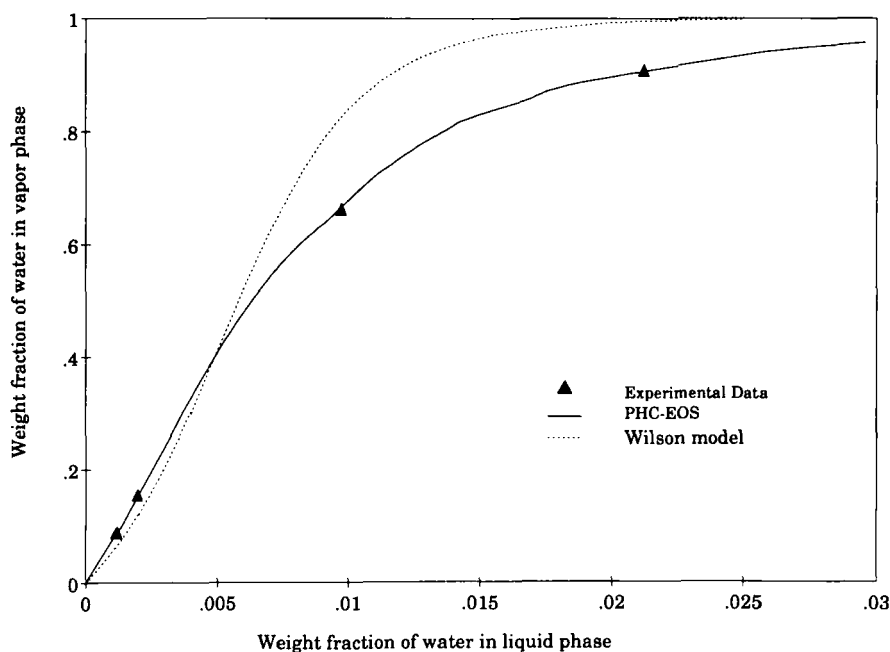
FIG. 4. Calculated and experimental VLE for water–glycerol binary system at 13 mbar in liquid-phase concentration range of 0–3.0 wt% water.

the best fitted dual model. Furthermore, being capable of calculating all thermodynamic properties needed, accurately predicting VLE at both low and high pressures, and using only one binary interaction parameter, the PHC-EOS is very well suited for the simulation of distillation processes used for refining different crude glycerol feedstocks.

The VLE of multicomponent systems must be known since separations of binary mixtures are rare in practice. The PHC-EOS is able to predict the behavior of multicomponent systems on the basis of binary interaction parameters obtained from binary VLE data as outlined above.

The distillation process, shown in Fig. 1, was simulated using the *Aspen Plus* flow-sheeting program (*8*) and the PHC-EOS. The crude glycerol mixture was simulated as a three-component system consisting of glycerol, stearic acid, and water. The fatty acid component was chosen to represent a group of unidentifiable organic compounds. As mentioned earlier, the main distillation column is divided into four sections, each packed with Montz-pac material. The column is also provided with a reboiler and two heat exchangers used in the condensation sections. Through the use of

plant operating data supplied by a major Swedish fatty acids and glycerol producer, the stripping section was first simulated to calculate the number of trays equivalent to the packing height in that section. The outlet data were then used in the other sections, and consequently the packed distillation column was considered to be equivalent to a total of 15 trays. On the other hand, the distillation still is equivalent to two trays, representing a reboiler and a partial condenser.

The simulation results for the integrated distillation unit are shown in Figs. 5–8, where the flow rate of both liquid and vapor streams, liquid and vapor phase composition, and temperature profiles are plotted as functions of the tray number. Some measured operating data are also plotted for comparison. Figure 5 shows a considerable increase in the flow rate of both liquid and vapor streams flowing in the condensation sections. Compared to the feed flow rate F, the mass flow rate of glycerine solutions circulating over primary and final condensors are approximately $15F$ and $8F$, respectively. These large quantities are required to condense all glyc-
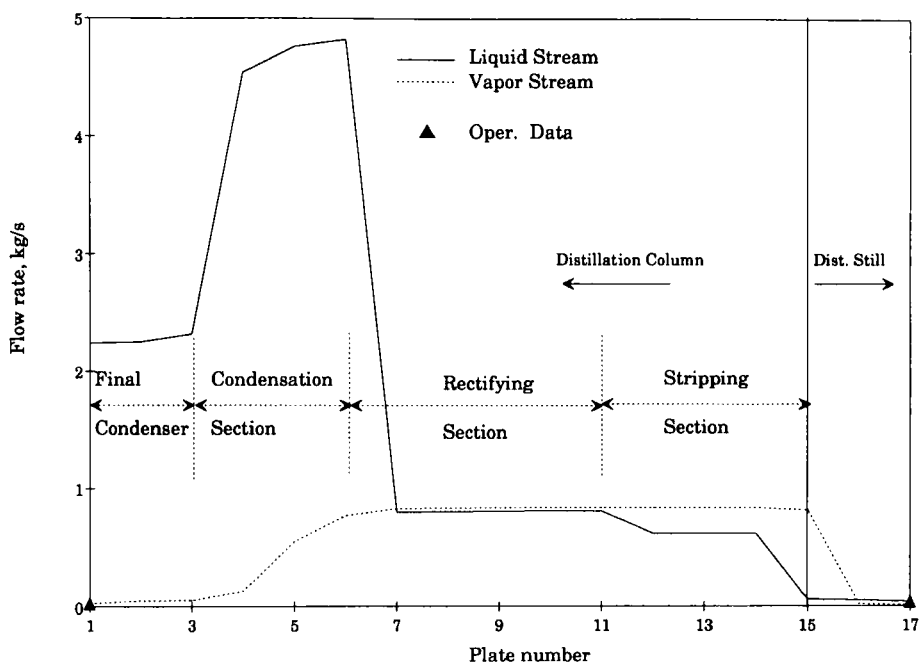

FIG. 5. Plant operating data and calculated flow rate profiles.

erol vapor flowing upward in these sections. Both heat exchangers used to cool the circulating streams have a total cooling duty of 320 kW. The increase in vapor phase flow rate is attributed to the flashing of all water content in the circulating streams as explained earlier. At Trays 12 and 15, a decrease in liquid phase flow rate takes place due to the withdrawal of the main distillate D1 and the bottom stream, respectively.

Figures 6 and 7 show the concentration profiles for the liquid and vapor phases, respectively. As an indication of the ease of separation of the water–glycerol system, glycerol concentration in both phases is practically constant on Trays 4–14. Entering the main distillation column at a concentration of 85 wt%, glycerol separation takes place in the final condensation section. The distillation unit is operated at a pressure range of 5–13 mbar, corresponding to a temperature range of 40–185°C as indicted by the temperature profile shown in Fig. 8.

As can be observed, the comparison between simulated and measured plant data is very good for flow rate (Fig. 5), liquid and vapor phase
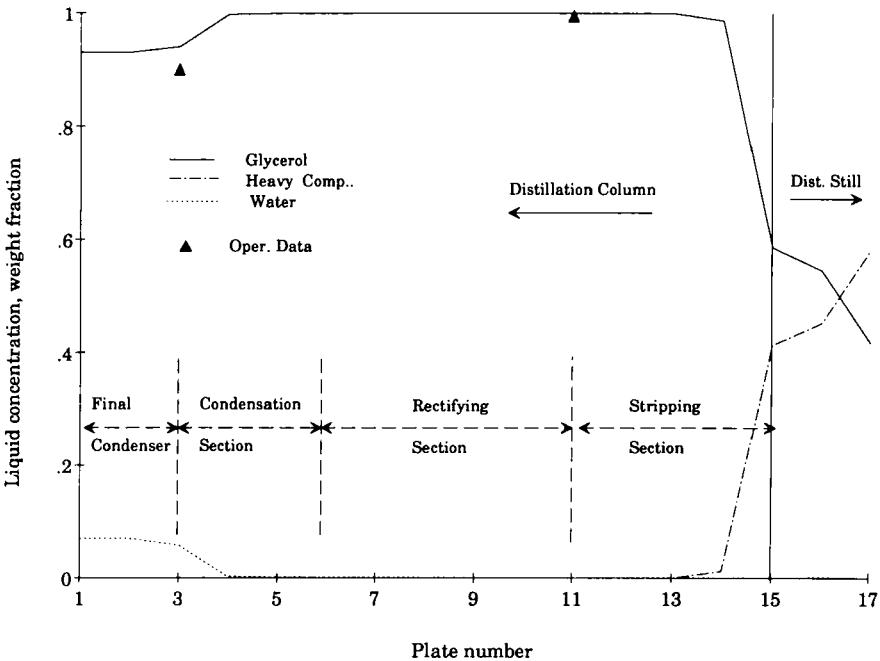

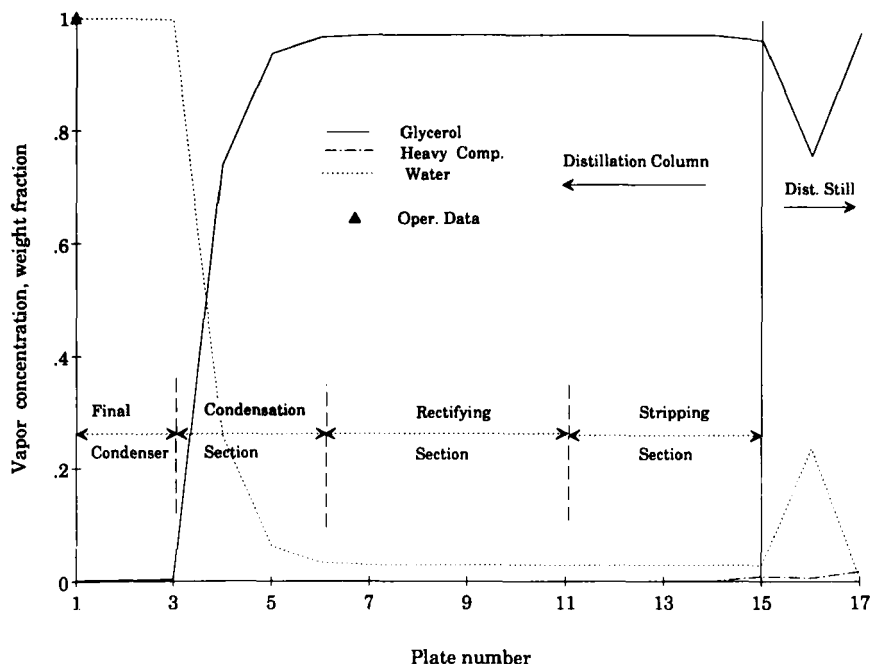FIG. 6. Plant operating data and calculated liquid concentration profiles.

FIG. 7. Plant operating data and calculated vapor concentration profiles.

compositions (Figs. 6 and 7), and reasonably good for temperature (Fig. 8). At maximum and average relative temperature deviations of 4.5 and 2.8%, respectively, the slight discrepancy in temperature can be attributed to the choice of stearic acid to represent the unidentifiable high-boiling compounds. Entering the distillation unit with a concentration of 10 wt%, the stearic acid component would only affect the temperature profile.

In conclusion, the results obtained from the PHC-EOS are very good, especially in view of the fact that only one binary interaction parameter has been fitted to the binary vapor–liquid equilibrium data. Both thermodynamic and process simulations clearly indicated that this equation of state is very well suited for simulating different distillation processes for the purification of crude glycerine feedstocks.
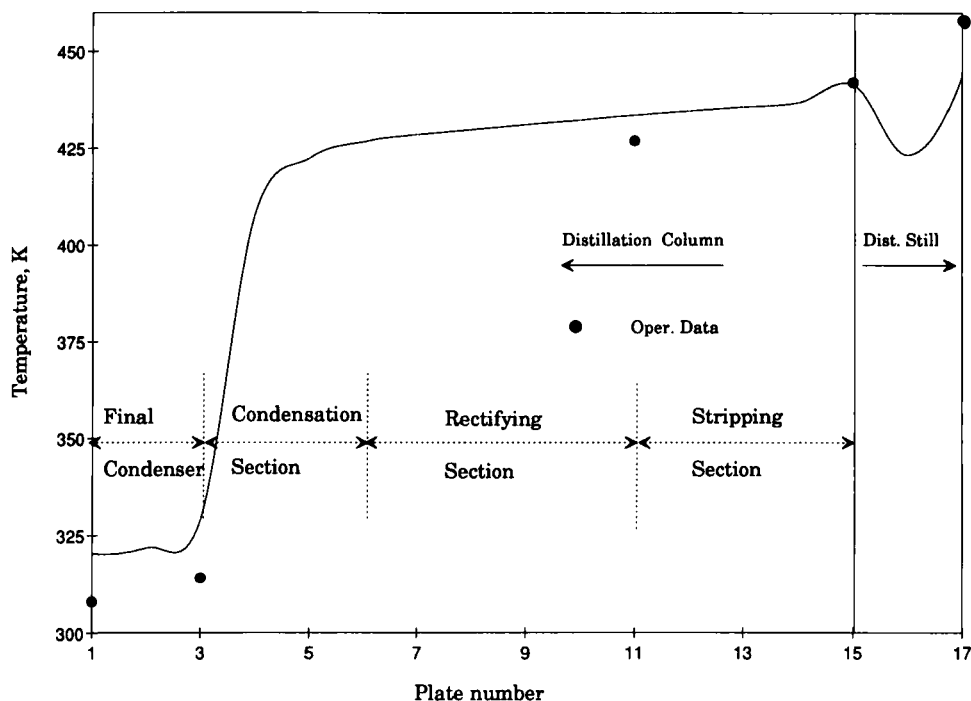
Acknowledgments

FIG. 8. Plant operating data and calcualted temperature profile.

ation, for supplying the necessary process data, and for their kind permission to publish the results.

REFERENCES

1. G. Aly and I. Ashour, "Applicability of the Pertubed Hard Chain Equation of State for Simulation of Distillation Processes in the Oleochemical Industry. Part I: Separation of Fatty Acids," *Sep. Sci. Technol.*, 27, 955 (1992).
2. A. J. Kaufman and R. J. Ruebusch, *INFORM*, 1(12), 1034 (1990).
3. B. D. Smith and R. Srivastava, *Thermodynamic Data for Pure Compounds, Part B*, Elsevier, 1986.
4. J. Gmehling, U. Onken, and P. Grenzheuser, *Vapor–Liquid Data Collection*, Vol. I, Part 5, Dechema, Frankfurt am Main, 1982.
5. N. M. Sokolov, L. N. Tsygankova, and N. M. Zhavoronkov, *Khim. Prom. (Moscow)*, 48, 96 (1972).
6. G. Aly and G. Zacchi, *Report LUTKDH/TKKA-3003)/1-38/(1979)*, Department of Chemical Engineering I, Lund Institute of Technology, 1979.
7. G. M. Wilson, *J. Am. Chem. Soc.*, 86, 127 (1964).
8. *Aspen Plus*, Aspen Technology, Inc., Cambridge, Massachusetts.