

$e$  = base of natural logarithms  
 $f$  =  $\frac{\sqrt{2g}}{u_A} \cdot \frac{1 - \epsilon_o}{1 - \epsilon_A}$   
 $F$  = flow rate of particles, g./sec.  
 $g$  = acceleration due to gravity, cm./sec.<sup>2</sup>  
 $h$  = height of powder bed above apex of a hopper, cm.  
 $H$  = holdup of solids, g.  
 $i, j$  = coefficients defined by Equation 19  
 $k$  =  $\tan \frac{\theta}{2}$   
 $l$  = thickness of discoidal block, cm.  
 $m$  =  $\frac{27 f^2 D_o}{16 k} + 2$   
 $n$  = collapsing frequency, sec.<sup>-1</sup>  
 $p, P$  = solids pressure, g./cm. sec.<sup>2</sup>  
 $S$  = falling distance of particles, or height of dynamic arch above opening, cm.  
 $t$  = time, sec.  
 $u$  = velocity of solids, cm./sec.  
 $V$  = storage volume of a hopper, cc.  
 $\gamma$  = height above apex of a hopper, cm.

#### GREEK LETTERS

$\alpha$  =  $\tau_s/P$   
 $\epsilon$  = void fraction  
 $\theta$  = hopper cone angle, °  
 $\lambda$  = shape factor defined by Fowler's equation  
 $\mu$  = coefficient of internal friction  
 $\rho_b$  = bulk density of solids, g./cc.

$\rho_p$  = particle density, g./cc.  
 $\tau_s$  = shear strength of particle layer, g./cm. sec.<sup>2</sup>  
 $\tau_T$  = tensile strength of particle layer, g./cm. sec.<sup>2</sup>

#### SUBSCRIPTS

$A$  = at  $A$  section where dynamic arch is built  
 $o$  = at opening of hopper or bin  
 $n$  = natural loose packing  
 $t$  = tight packing

#### Literature Cited

- Aoki, R., *Kagaku Kogaku* **25**, 281 (1961).  
 Beverloo, W. A., Leniger, H. A., Van de Velde, J., *Chem. Eng. Sci.* **15**, 260 (1961).  
 Brown, R. I., Richards, J. C., *Trans. Inst. Chem. Engrs. (London)* **37**, 108 (1959).  
 Fowler, R. T., Glastonbury, J. R., *Chem. Eng. Sci.* **10**, 150 (1959).  
 Kvapil, R., "Theorie der Schüttgutbewegung," VEB Verlag Technik, Berlin, 1959.  
 Langmaid, R. N., Rose, H. E., *J. Inst. Fuel* **30**, 166 (1957).  
 Rausch, J. M., Ph. D. thesis, Princeton University, 1948.  
 Richmond, O., Gardner, G. C., *Chem. Eng. Sci.* **17**, 1071 (1962).  
 Shinohara, K., Tamura, K., Gotoh, K., Tanaka, T., *Kagaku Kogaku* **31**, 287 (1967).  
 Shirai, T., *Kagaku Kikai* **16**, 83 (1952).  
 Tanaka, T., Kawai, S., *Kagaku Kogaku* **20**, 144 (1956).  
 Wöhlbier, H., Reisner, W., *Chem. Ing. Tech.* **34**, 603 (1962).

RECEIVED for review July 24, 1967

ACCEPTED January 29, 1968

# EFFECT OF DISTILLATION ON A CHEMICAL REACTION

THOMAS E. CORRIGAN<sup>1</sup> AND JOHN H. MILLER<sup>2</sup>

Department of Chemical Engineering, Ohio State University, Columbus, Ohio

The reaction of ethylene oxide and water to form ethylene glycol in a distillation column reactor was simulated on a digital computer to test the hypothesis that 100% selectivities could be obtained in this type of reactor. It was found that a distillation column does not surpass the performance of a plug flow reactor if the latter uses a high mole ratio of water to ethylene oxide in the feed. At the high mole ratios used in commercial hydration reactors, the selectivity obtained in a distillation column reactor can be exceeded by either the plug flow or the perfect mixer reactor. Calculations show that over a wide range of relative volatilities, the performance of a distillation column reactor for a series parallel reaction does not exceed that of a plug flow reactor using a high mole ratio in the feed.

THE production of ethylene glycol by the reaction of ethylene oxide and water is a commercial example of a large scale series parallel type of reaction.

The major problem is to maximize the production of monoethylene glycol and keep the by-product, diethylene glycol and higher glycols, to a minimum. To achieve this goal, extremely high mole ratios of water to ethylene oxide are used in the feed. In commercial practice the ratio is about 20 to 1. The selectivity to monoethylene glycol is further improved if backmixing in the reactor is kept to a minimum. Thus, a

longitudinal or tubular reactor would be preferable to a tank reactor.

In spite of the high mole ratios used in commercial practice, the higher glycols exceed 10% of the total glycols formed. If higher selectivities could be obtained at lower mole ratios of water to glycol, it would not be necessary to recycle and evaporate such large quantities of water.

A recent United States patent (Parker, 1958) is based upon obtaining a much higher selectivity by using only stoichiometric ratios in the feed and carrying out the reaction in a distillation column. The principles of this patent would apply to any liquid-phase series-parallel reaction in which the relative volatilities increase significantly with increasing molecular weight of the adduct.

<sup>1</sup> Present address, Mobil Chemical Co., Edison, N. J.

<sup>2</sup> Present address, Wright Patterson Air Force Base, Fairborn, Ohio.

According to the theory presented in the patent, the more volatile component of the feed would immediately be separated at the feed plate, leaving a very high mole ratio of the nonrecurring reactant (water) at the feed plate. The ethylene glycol formed, having a very low volatility, would immediately pass down the column and, thus, be removed from the reaction zone, preventing its further reaction. The over-all effect was predicted in the patent to give a monoethylene glycol yield approaching 100%.

This paper tests the principles involved in carrying out a liquid-phase series-parallel reaction in a distillation column. The system was simulated on a digital computer. Selectivities at various feed compositions were calculated and compared with those of the plug flow and perfect mixer reactors. First the relative volatilities and relative rate constants for the ethylene oxide-water system were used. Then the scope was widened to consider both higher and lower relative volatilities.

### Theory

The basic method of this calculation was to make a material balance on each tray for each constituent of the system. For each, except the feed, top, and bottom trays, the inputs were the liquid from the tray above, the vapor from the tray below, and the amount formed on the tray by chemical reaction. The outputs were the liquid to the tray below, the vapor to the tray above, and the depletion by chemical reaction. To carry out these calculations, the following items had to be known:

- Vapor liquid equilibria for the four-component system.
- The kinetics equations of the reactions.
- The relative rate constant,  $\kappa$ , for the two reactions.

For this analysis the relative volatilities for ethylene oxide, water, monoethylene glycol, and diethylene glycol were used. It was assumed that the liquid-phase solutions were ideal—that is, all activity coefficients were taken as unity. The relative rate constant was taken as 2.0, based upon data in the literature.

### Procedure

The procedure uses a tray by tray calculation. After the vapor composition from the top tray is chosen by some arbitrary method, the procedure is a simple three-step process for each tray:

The liquid composition is calculated from the vapor composition by equilibrium equations.

The amount of reaction is computed from the liquid composition.

The vapor composition from the next tray is calculated from the material balance.

This procedure is repeated for each tray until the feed tray is reached. At this point the amount of feed is estimated and the three-step process is continued until the desired separation is obtained. The assumed values of the feed and the vapor composition from the top tray are checked by a material balance over the whole column. If the assumed values are not correct, another trial must be made. Repeated trials are carried out until the over-all material balance checks.

### Discussion of Results

The physical properties of the system were chosen to resemble the ethylene oxide-water system. The relative rate constant,  $\kappa$ , was needed, since the rate equations involved the product of the rate constants for the reactions and the height on the tray. Calculations were made for 1 square foot of tray area, and liquid height was left arbitrary. Thus, the absolute values of the rate constants were not necessary as long as the relative rate constant was known. The parameter used was

**Table I. Comparison of Column Reactor with Plug Flow and Perfect Mixer Reactors**

Feed Mole Ratio, Water/Oxide	Selectivity (Monoglycol/Total Glycols)			
	Column		Plug flow	Perfect mixer
	$k_1H = 0.0001$	$k_1H = 0.0003$		
1.0	0.8881	0.762	0.382	0.268
2.33	0.917	0.818	0.668	0.540
9.0	0.886	0.783	0.900	0.830

the product of the rate constant,  $k_1$ , and the liquid height on the tray.

The results of this analysis are shown in Table I, where they are compared with the results of the plug flow and the perfect mixer reactors. The selectivities in Table I for the plug flow and the perfect mixer reactors were calculated for 100% conversion based upon the methods presented by Levenspiel (1962). The selectivities are defined as moles of monoglycol divided by total moles of glycol.

At low mole ratios in the feed the distillation column reactor provides higher selectivities than either the plug flow or the continuous stirred tank reactor at the same low mole ratios. However, these mole ratios are too low for feasible commercial operation because of the low selectivities. At mole ratios of 10 to 1 or greater, both the plug flow and the continuous stirred tank reactor give superior performance. At stoichiometric mole ratios the distillation column is superior.

There are some optimum relative volatilities which give maximum performance. If all four components had the same volatilities, there would be no separation in the column and the composition would be equal on all the plates. The continual boiling would keep the contents well mixed and, therefore, the system would tend to behave like a single perfect mixer.

If the relative volatility were infinite and the reaction rate slow by comparison, there would be reaction on only one tray, the feed tray, with continuous removal of product. The selectivity would be determined by the relationship between reaction rates and mass transfer rates and not subject to the methods of the present calculations.

### Conclusions

The selectivity obtained by using a distillation column reactor for a series parallel reaction does not exceed that of the plug flow or perfect mixer reactors at high feed mole ratios. It does exceed the performance of these reactors if a stoichiometric mole ratio is used in the feed.

### Nomenclature

- $k_1H$  = reaction parameters, product of arbitrary reaction rate and tray height
- $k_2H$  = rate constant of first reaction
- $k_1$  = rate constant of second reaction
- $k_2$  =  $k_2/k_1$  ratio

### Literature Cited

- Levenspiel, Octave, "Chemical Reaction Engineering," Wiley, New York, 1962.
- Parker, A. S., U. S. Patent 2,839,588 (June 17, 1958).

RECEIVED for review July 25, 1967  
ACCEPTED January 29, 1968