COMMUNICATIONS TO THE EDITOR

The Effect of Using a Distillation Column Reactor on the Selectivity of a Complex Reaction

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The reaction of ethylene oxide and water to form ethylene glycol in a distillation column reactor was simulated on a 7094 computer. The purpose was to test the hypothesis that in such a reactor 100% selectivities to monoethylene glycol could be obtained. The performance of a distillation column reactor was not found to surpass the performance of a plug-flow reactor when the high feed ratios of commercial practice are used.

A distillation column reactor will exceed the performance of a plug-flow reactor at stoichiometric feed ratios, but the performance of the distillation column does not improve as rapidly with higher feed ratios. At the ratio of 20 moles of water/mole of ethylene oxide used in commercial hydration reactors, the selectivity to ethylene glycol obtained in a distillation column reactor is less than that of a tubular (plug-flow) reactor. Regardless of relative volatilities, the performance of a distillation column reactor for a series/parallel reaction does not exceed that of a plug-flow reactor at high mole ratios in the feed.

The major objective of the process is to maximize the production of monoethylene glycol and keep diethylene glycol to a minimum. To achieve this commercially, feed mole ratios of water to ethylene oxide of about 20:1 are used, and a longitudinal or tubular reactor would be preferable to a tank reactor to prevent backmixing. In spite of the high mole ratios, the yield of higher glycols is greater than desired.

United States Patent 2,839,588 (*1*) indicates that much higher selectivity could be obtained by carrying out the reaction in a distillation column. The reactants would be fed into a feed plate somewhere in midcolumn. The ethylene oxide would go up the column leaving a very high concentration of water in the immediate vicinity of the feed plate. This region would have an excessively high mole ratio of water to oxide, thus giving a high selectivity. The glycol having a relatively low volatility would immediately go down the column, thus preventing its further reaction. The expected effect would be an almost 100% selectivity.

This investigation tested this concept by simulating the system on a 7094 computer. Systems with both higher and lower relative volatilities were also tested.

Material balance calculations were made on each tray in conjunction with vapor-liquid equilibria and the kinetics equations of the reactions. Originally, the relative volatilities for ethylene oxide, water, monoethylene glycol, and diethylene glycol were used. Later, systems with both

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TABLE 1. COMPARISON OF COLUMN REACTOR WITH PLUG-FLOW REACTOR

Mole ratio in feed water to oxide	Selectivity* Column	Plug flow
1.0	0.881	0.382
2.33	0.917	0.668
9.0	0.886	0.900
20	0.900	0.960

* Selectivity is defined as moles of monoethylene glycol/total moles of glycol.

higher and lower relative volatilities were used.

The convergence was measured by taking a material balance over the column for each component. When a material balance closure was within 1%, the solution was accepted. The relative rate constant κ was obtained from data in the literature (*2*).

The results of this analysis are shown in Table 1 where they are compared with the results to be expected in a plug-flow and in a continuous stirred-tank reactor. It can be seen from Table 1 that at mole ratios of water to oxide greater than 2:1 (mole fraction of B greater than 0.7 in Table 1), the plug-flow reactor gives superior performance, and at mole ratios of 9:1 or greater, both the plug-flow and the continuous stirred-tank reactor give superior performance. The distillation column is superior only at low feed mole ratios.

At first it might be assumed that the greater the relative volatilities among the components of the system, the better the distillation column would work. However, this is not the case. Let us consider the extreme cases in a qualitative manner. If all four components had the same volatilities, there would be no separation at all in the column, the composition on all plates would be the same, and the system would tend to behave like a continuous stirred-tank reactor.

In the opposite case of infinite relative volatility, there would be immediate separation and the components could contact each other only on the feed tray. The system would behave as a single continuous stirred-tank reactor. The patent is concerned with only intermediate cases.

The relative volatilities were calculated by taking the ratio of the vapor pressure of each pure component at 40°C. to the vapor pressure of B at 40°C. The use of relative volatilities eliminates the need to know the pressures and temperatures in the distillation column to make the separation calculations, since it is assumed that relative volatility is independent of pressure and temperature. It was also assumed, in order to simplify the calculations, that the reaction rate constants were independent of temperature and pressure. In all cases only three theoretical trays were required because of the high relative volatilities.

Simulation of a distillation column reactor on a 7094 computer has shown that it will not exceed the performance of a tubular or continuous stirred-tank reactor operating at high ratios of water to ethylene oxide in the feed.

LITERATURE CITED

1. Parker, Almon S., U. S. Pat. 2,839,588 (June 17, 1958).
2. Sonawala, S. K., "Report on Kinetics of Ethylene Oxide-Water Reaction," Ohio State Univ., Columbus.

The Use of Green's Functions in the Solution of a Convective Diffusion Equation: Application to a Fuel Cell Battery

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The diffusion equation with a constant mass flow term to account for bulk transport of heat or chemical species occurs in many practical problems, such as in heat transfer in fuel cell batteries, in chromatographic work with appreciable diffusion in the direction of flow, and in dispersion studies in fluids with and without reaction. The methods of solving these problems include the classical separation of variables method, the Laplace and Fourier transform operational methods, and the moving source technique discussed by Carslaw and Jaeger (*1*). The complexity of some of these problems, especially those in three dimensions, is such that it is desirable to have additional simplifying techniques.

The principal simplifying technique for the usual diffusion equation widely used in heat transfer is the product theorem due to Newman (*1*, *2*). Recently the construction of three-dimensional solutions from one- and two-dimensional problems was extended by Goldenberg (*3*). For the case of the diffusion equation with a linear term, for example, for diffusion with a first-order reaction, the transformation of Danckwerts is useful (*1*, *4*). In this paper it is shown how a change of the dependent variable, similar to that employed in the Danckwerts method, together with the tabulated Green's functions for the simple diffusion equation, can rapidly lead to many new solutions of the convective diffusion equation with a constant velocity. Then various product properties useful for analytical and graphical representations of two- and three-dimensional problems are established for the general, second-order, parabolic partial differential equation with