

PURDUE-INDUSTRY COMPUTER SIMULATION MODULES

2. The Eastman Chemical Reactive Distillation Process*

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As described in previous papers,^[1,2] a series of computer modules for use in the chemical engineering senior laboratory is being developed at Purdue University. The modules are meant to supplement, not to replace, traditional laboratory experiments. In our laboratory, for example, only one of three month-long experiments may be the use of a computer module. Computer simulated experiments have a number of advantages over traditional experiments:

- Processes that are too large, complex, or hazardous for the university laboratory can be simulated with ease on the computer.
- Realistic time and budget constraints can be built into the simulation, giving the students a taste of "real world" engineering problems.
- The emphasis of the laboratory can be shifted from the details of operating a particular piece of laboratory equipment to more general considerations of proper experimental design and data analysis.
- Computer simulation is relatively inexpensive compared to the cost of building and maintaining complex experimental equipment.
- Simulated experiments take up no laboratory space and are able to serve large classes because the same computer can run many different simulations.

EASTMAN CHEMICAL REACTIVE DISTILLATION PROCESS

The Eastman Chemical Reactive Distillation Process is part of a series of steps for obtaining acetic anhydride from coal. Acetic anhydride is an important chemical intermediate used in the production of cellulose acetate, which itself is used in the manu-

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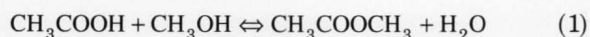
facture of photographic film base, fibers, plastics, and other products.

Each day the plant converts 900 tons of coal to acetic anhydride. Using conventional methodology, the chemicals produced would require the annual equivalent of one million barrels of oil. A brief description of the process is: synthesis gas produced from coal is used for methanol production; methanol (MeOH) is reacted with recycled acetic acid (HOAc) to produce methyl acetate (MeOAc) and then acetic anhydride; and finally, acetic anhydride is reacted with cellulose to form cellulose acetate. The process for formation of MeOAc was developed at the Eastman Chemical Company^[3] and patented. The reader is also referred to a paper by Agreda, Pond, and Zoeller^[4] for more details.

The formation of MeOAc is the focus of this project. In this process, methanol reacts with recycled acetic

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acid in the presence of sulfuric acid catalyst to form methyl acetate and water:



The reaction rate is given by

$$r_{\text{MeOAc}} = k_o A \exp(-E / RT) \left\{ C_{\text{HOAc}} C_{\text{MeOH}} - \frac{C_{\text{MeOAc}} C_{\text{H}_2\text{O}}}{K_e} \right\} \quad (2)$$

where

- k_o = preexponential factor
- A = catalyst acidity function ($0 \leq A \leq 1$)
- T = temperature
- E = activation energy

and the equilibrium constant is

$$K_e = \left\{ \frac{C_{\text{MeOAc}} C_{\text{H}_2\text{O}}}{C_{\text{HOAc}} C_{\text{MeOH}}} \right\} \quad (3)$$

Clearly, the maximum conversion of the reactants is equilibrium limited.

This Reactive Distillation Process relies on the fact that MeOAc is more volatile than water or the reactants. Thus, if the reaction mixture is distilled simultaneously, a significant amount of MeOAc product will vaporize, forcing the reaction to shift to the right and thereby allowing a much higher conversion than would be possible in the absence of distillation (conventional process). An additional consequence and advantage is that high purity MeOAc (> 99.5 wt%) is produced as the overhead product.

THE COMPUTER PROGRAM

The program is written entirely in the C language and uses some IMSL routines for solving systems of linear, non-linear, and ordinary differential equations. It can simulate

- A batch reactor
- An equilibrium cell
- A tray in the distillation column

The program can run on any machine that supports the X Window System. At Purdue, it runs on Sun Sparc workstations with 12 MB of memory. Each module uses less than 10 MB of disk space.

An important feature of the program is its menu-

TABLE 1
Expenses*

BATCH REACTOR	Cleanup	\$700
	Sample analysis	\$50 / sample
EQUILIBRIUM CELL	Cleanup	\$500
CONSULTATION		\$500

* All expenses are to be multiplied by 1.5 and 2 for Saturday and Sunday runs respectively.

driven graphical user interface. This enables anyone to use it, regardless of his or her knowledge of computers. An on-line help facility is provided to further assist the user in navigating through the program. The user can exit the program at any time.

STUDENT ASSIGNMENTS

Budget and Experiments

In the first part of the Eastman project, the students are required to determine the following:

1. Activation energy
2. Preexponential factor
3. Catalyst activity function
4. Wilson parameters for liquid activity coefficients

To determine these quantities, the students simulate a batch reactor and an equilibrium pressure cell, both described below. Also, a requirement that the students work within a budget of \$30,000 contributes a sense of realism to the module. Table 1 shows costs associated with operating the reactor and cell.

Laboratory Batch Reactor • A batch reactor is available for the students to study reaction kinetics for the determination of items 1-3 above: activation energy, preexponential factor, and the catalyst activity function. As seen in Eq. (2), the reaction is first order in the concentrations of each of the reactants and products. Preliminary data obtained using laboratory batch apparatus suggest that in the range of conditions used in the Eastman column, the equilibrium constant is independent of temperature and catalyst concentration. The catalyst acidity

function, A , depends on the sulfuric acid concentration, as shown in Figure 1.

The students are to design experiments to determine the activation energy E , the preexponential factor k_0 , and establish the functional dependence of A on the catalyst concentration. The equilibrium constant, K_e is known.

Equilibrium Cell • The purpose of this apparatus is to determine liquid phase activity coefficients in two-component systems. The cell is simply a closed vessel with a pressure gauge and a temperature sensor. Temperature control is provided, so isothermal runs can be made. The user can charge it with two components and record the equilibrium pressure. For all practical purposes, equilibrium can be assumed to have been established in four hours. There is no facility to measure or monitor the vapor or liquid phase mole fractions. However, since the vapor volume is very small compared to the volume of the liquid, it can be assumed that the concentrations of the components in the liquid phase at equilibrium are equal to the corresponding concentrations of the liquid charged into the cell. Note that there are five components of interest: the reactants, the products, and the catalyst, H_2SO_4 .

When the critical region is not approached (as in this case), we can assume that the liquid phase activity coefficients and standard fugacities are independent of pressure. If the standard fugacity is taken in the sense of the Lewis-Randall rule, we have for each component i

$$y_i^* \phi_i P = x_i \gamma_i P_i^o \phi_i^o \quad (4)$$

where for component i ,

- γ_i = liquid phase activity coefficient
- P_i^o = vapor pressure
- P = equilibrium pressure of the system
- x_i = liquid phase mole fraction
- y_i = vapor phase mole fraction
- ϕ_i, ϕ_i^o = fugacity coefficients of i , the latter calculated at the saturation vapor pressure.

Quite often, however, ϕ_i and ϕ_i^o are nearly equal, and Eq. (4) simplifies to

$$y_i P = x_i \gamma_i P_i^o \quad (5)$$

Since the total pressure equals the sum of the partial pressures of the components, adding Eq. (5) for each component results in

$$P = x_1 \gamma_1 P_1^o + x_2 \gamma_2 P_2^o \quad (6)$$

The vapor pressures, P_i^o , of the pure components

Catalyst Acidity Function

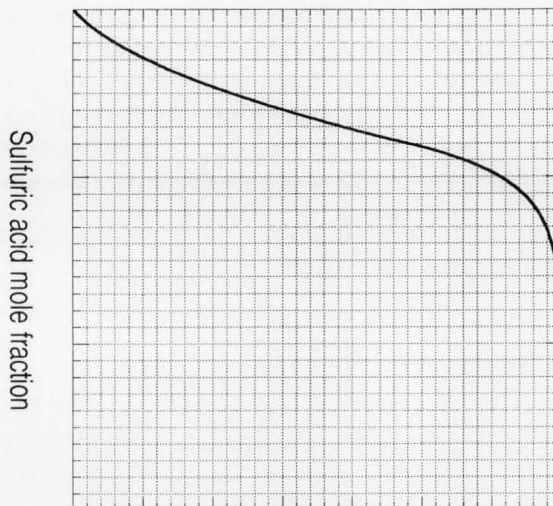


Figure 1. The catalyst activity function

may be calculated from the Antoine equation:

$$\ln P_i^o = A_i - \frac{B_i}{T + C_i} \quad (7)$$

where the Antoine constants, A_i, B_i, C_i , are known from the literature, and T is the temperature.

At low to moderate pressures, the Wilson equation^{5,6} may be used to predict the activity coefficients as a function of temperature and composition for a variety of liquid solutions comprising diverse chemical species. The Wilson equation for component i is

$$\ln \gamma_i = 1 - \ln \left(\sum_j x_j G_{ij} \right) - \sum_k \left(\frac{x_k G_{ki}}{\sum_j x_j G_{kj}} \right) \quad (8)$$

The summations are over all components present in the mixture. For an ij pair, there are two temperature-dependent parameters, G_{ij} and G_{ji} . For $i = j$, $G_{ij} = 1$. Over the narrow temperature range of interest, the temperature dependence of the parameters is weak enough to be ignored. The Wilson parameters for all of the component pairs except MeOH - MeOAc have been previously estimated and are known. The assignment given to students is to design a series of runs in the equilibrium cell to determine the two Wilson parameters for the MeOH - MeOAc pair. It should be noted that acetic acid was not chosen as a component in the binary pair since it exhibits vapor phase association and the simplification for Eq. (5) does not apply.

Application Problem—Tray Simulation

This part of the project involves analyzing trays of

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the column. Students do not run a tray to "obtain data," unlike the batch reactor or the equilibrium cell. Instead, they input the kinetic and phase equilibrium parameters to observe tray performance and use the results of the simulation to calculate the tray efficiency. In addition, for the same feed (vapor and liquid), they are asked to predict the conversion that will be obtained in a CSTR. It is to be observed that the tray is actually a CSTR with an additional operation, *e.g.*, distillation. It is instructive to see that the conversion obtained in a tray is much higher (for the current process) than in a simple CSTR. This is an important observation since the basic idea in carrying out the methyl acetate process in a distillation column was to increase the conversion.

Two representative trays, one in the upper portion of the column and the other in the lower portion, are simulated. The students must run both.

For the purpose of the current simulation, the tray is assumed to operate isothermally at a known temperature. Thus, material balance and equilibrium relationships are used to model the tray. A tray efficiency is incorporated in the model. Given the input flow rates of the vapor (from the bottom tray), the liquid (from the upper tray), the composition of the input streams, the pressure, temperature, tray efficiency, and the kinetic and phase equilibrium parameters, the model predicts the flow rates and compositions of the output liquid and vapor streams of the tray.

The tray model does not explicitly account for the dependence of the acidity function on the acid concentration. For the steady state, it suffices to provide the simulator with the acidity value corresponding to the steady-state acid concentration in the liquid phase (output). This value, however, is not known since the output acid concentration in the liquid phase is not known. The student must therefore resort to an iterative procedure. He must guess a value of the acid composition in the output liquid stream, calculate the value of A from his catalyst acidity function, and input this value to the simulator. The model solves the problem using this value of A and predicts the output liquid-phase acid concentration. This procedure must be repeated until the entered acidity function value agrees with the predicted acid concentration according to the student's function.

In the event that students are unable to evaluate the kinetic and phase equilibrium parameters within the assigned time, or that they come up with impractical values or cannot establish the acidity function curve, they have the option of using the

instructor's data (with the permission of the instructor, of course). In this case, the students do not have to input the kinetic and phase equilibrium parameters; furthermore, the acidity function dependence is implicitly taken into account in the model, so that iteration is not required.

CONCLUSION

Our experience with the Eastman module has been very positive. The module presents a challenging problem that helps prepare students for the kinds of problems they are likely to encounter in industry. The simulated budget is especially effective in making the project more true-to-life than conventional lab experiments. Although the Eastman problem is challenging, students report that the software itself is very user-friendly.

One advantage of computer simulations is their flexibility. The Eastman module was originally developed for the chemical engineering laboratory; however, it would also be useful in courses in thermodynamics, chemical kinetics, and separations.

AVAILABILITY OF THE MODULES

The Purdue-Industry ChE Simulation Modules are being made available for educational use by the CACHE Corporation. Anyone interested in obtaining more information should contact Professor Squires.

ACKNOWLEDGMENTS

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REFERENCES

1. Squires, R.G., G.V. Reklaitis, N.C. Yeh, J.F. Mosby, I.A. Karimi, and P.K. Andersen, "Purdue-Industry Computer Simulation Modules: The Amoco Resid Hydrotreater Process," *Chem. Eng. Ed.*, **25**(2), 98 (1991)
2. Squires, R.G., P.K. Andersen, G.V. Reklaitis, S. Jayakumar, and D.S. Carmichael, "Multi-Media Based Educational Applications of Computer Simulations of Chemical Engineering Processes," *Comp. Appns. Engr. Ed.*, **1**(1), 25 (1992)
3. Agreda, V.H., and L.R. Partin, U.S. Patent 4,435,595, March 1984 (Assigned to Eastman Kodak Co.)
4. Agreda, V.H., D.M. Pond, and J.R. Zoeller, "From Coal to Acetic Anhydride," *Chemtech*, 172 (1992)
5. Sandler, S.I., *Chemical and Engineering Thermodynamics*, John Wiley & Sons, New York, NY (1989)
6. Wilson, G.M., "Vapor Liquid Equilibrium. XI: A New Expression for the Excess Free Energy of Mixing," *J. Am. Chem. Soc.*, **86**, 127 (1964) □