PURDUE-INDUSTRY COMPUTER SIMULATION MODULES

The Amoco Resid Hydrotreater Process

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The senior chemical engineering laboratory is a required part of most accredited chemical engineering programs and is considered a "capstone" course, drawing as it does on students' previous technical work. Furthermore, the senior laboratory typically requires the students to use their written and oral communication skills and, since lab projects are often group efforts, their interpersonal skills as well.

In Purdue's laboratory course students work together in groups of three, consisting of a group leader, an experimentalist, and a design engineer. Each group works on three month-long projects chosen from a list of about a dozen experiments which involve processes such as extraction, filtration, distillation, gas- and liquid-phase reaction, ion exchange, heat transfer, fluid flow, mixing, and diffusion.

In our view, the ideal laboratory experiment should duplicate a real industrial process. The students would use modern equipment to investigate a complex problem, and would do so under realistic time and budget constraints. Since universities can hardly afford to construct or operate industrial-scale plants, the next best alternative is to devise experiments which closely *simulate* the operation of industrial processes. With this in mind, we are developing a series of computer simulations intended for use in undergraduate chemical engineering laboratories. These simulations model actual industrial chemical processes and are being produced with the assistance of various corporate sponsors. The first five are listed in Table 1.

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TABLE 1
Process Simulations and Industrial Sponsors

Company	Process
Amoco	Hydrodesulfurization
Mobil	Catalytic Reforming
Dow Chemical	Latex Emulsion Polymerization
Tennessee Eastman	Methyl Acetate from Coal
Air Products	Process Heat Transfer

AMOCO RESID HYDROTREATER

The first simulation that we have completed models a hydrodesulfurization pilot plant (see Figure 1) built by Amoco in its Naperville, Illinois, research facility. The hydrotreater takes a mixture of heavy, high-sulfur hydrocarbons (called "resid oil") and upgrades it by

- **breaking the long carbon chains to form smaller chains**
- **adding hydrogen to increase the saturation**
- **removing sulfur in the form of H_2S gas**

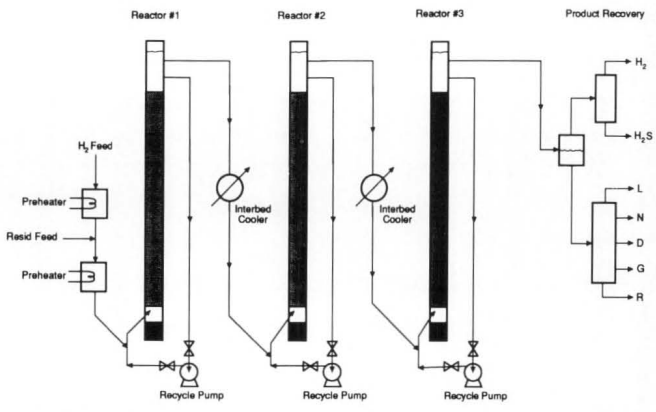
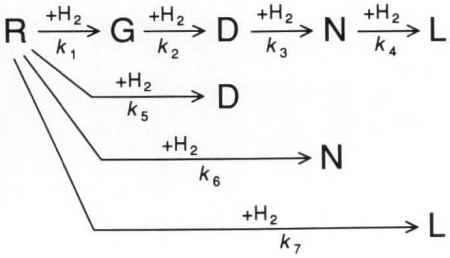


Figure 1. *Amoco hydrodesulfurization pilot plant. The three ebullated-bed columns are well mixed by the recycle streams.*

[1] Amoco Corporation; [2] Northwestern University

Non-Catalytic Reactions



Catalytic Reaction

$$\text{Sulfur} + H_2 \xrightarrow{k_8} H_2S$$

Figure 2. *Hydrodesulfurization reaction scheme. Each of the components R, G, D, N, and L is a mixture of many different compounds, lumped together by boiling point.*

The reaction scheme is shown in Figure 2. Each of the components R, G, D, N, and L is a complicated mixture of many different chemical species, the actual composition of which would be very difficult to specify exactly. R, G, D, N, and L are characterized by their average boiling points and their sulfur content (see Table 2).

The hydrogenation reactions (reactions 1 through 7) are modeled as a set of sequential and parallel first-order reactions. The net generation rates are given by

$$r_R = -\left(k_1 + k_5 + k_6 + k_7\right)R$$
$$r_G = -k_2 G + C_{RG} k_1 R$$
$$r_D = -k_3 D + C_{RD} k_5 R + C_{GD} k_2 G$$
$$r_N = -k_4 N + C_{RN} k_6 R + C_{DN} k_3 D$$
$$r_L = C_{NL} k_4 N + C_{RL} k_7 R$$

where R, G, D, N, and L are the weight fractions of the sulfur-free components; k_1, k_2, . . . , are rate constants, and C_{RG}, C_{RD}, . . . , C_{RL} are stoichiometric coefficients.

The desulfurization reaction (reaction 8) is catalytic. It is first order in hydrogen, second order in sulfur, and inhibited by resid:

$$-r_s = \frac{Ak_8 \pi S^2}{1 + K_9 R}$$

Here A is a catalyst deactivation factor (A = 1 for fresh catalyst), π is the partial pressure of hydrogen, k_8 is a kinetic rate constant, and K_9 is an equilibrium constant.

The rate constants for reactions 1 through 8 are given by Arrhenius-type relations

$$k_i = a_i \exp\left(-E_i / RT\right), \qquad i = 1, \ldots, 8$$

where a_i is the pre-exponential factor and E_i is the activation energy for the i^{th} reaction.

The reactions are carried out in well mixed, ebullated-bed reactors, which are modeled as continuous stirred-tank reactors (CSTRs). Under some conditions, the simultaneous solution of the mass and energy balances for a CSTR may exhibit multiple steady states (see Figure 3). The reactors usually operate at the intermediate steady state, which is unstable with respect to temperature; at the lower steady state the conversion is too low and at the upper steady state the temperature is too high.

THE COMPUTER PROGRAM

The program consists of more than 10,000 lines of FORTRAN and C code. It can simulate the steady-state behavior of one, two, or three reactors in series,

TABLE 2
Reactants

Component	Average B.P. (°F)	Sulfur (wt. %)
Resid (R)	>1200	5.0
Gas Oil (G)	827	2.0
Distillate (D)	514	1.0
Naphthas (N)	280	0.5
Light Gas (L)	<200	0.0

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or the dynamic behavior of a single reactor. The program currently runs on the Sun 3/60 workstation, although it can be readily modified to run on any machine that supports the X Window System.

A graphical user interface makes the program easy to use, even for students having minimal experience with Sun computers. The user employs a mouse to select from options presented on "pull-down" menus. Should the user get lost or forget what to do, he or she can get help from the program itself.

USE OF THE MODULES AT PURDUE

Eight three-hour lab periods are allotted to each project. In preparation for the first scheduled lab period, the students are asked to study a written description of the process and to view a short videotaped "plant tour" supplied by the corporate sponsor. They also attend an orientation meeting with the instructor, where general questions about the process, the simulation, and the lab are answered.

THE INITIAL ASSIGNMENT

In keeping with our attempt to provide realism in the project, the students are given their assignment on official Amoco stationery. They are required to do the following things:

- **Determine the values of the pre-exponential factors for the hydrogenations**
- **Check activation energy for one of the hydrogenations**
- **Determine the pre-exponential factor a_8 and activation energy E_8 for the desulfurization**
- **Check the form of the catalyst deactivation equation and measure the catalyst deactivation rate**

The assignment letter authorizes the students to run the Naperville pilot plant and two small laboratory reactors.

BUDGETARY LIMITATIONS

Contributing to the sense of realism in this module is a requirement that the students work within a budget. Initially they are given $150,000 (simulated money, of course!) with which to work. Table 3 lists the time and money required for various tasks involving the pilot plant and laboratory reactor. Note that the students are charged a fee each time they seek help from the "consultant" (*i.e.,* the instructor).

THE PLANNING CONFERENCE

The students spend the first two lab periods preparing a plan of attack, which they must present to the instructor in a planning conference before the third period. In this conference the instructor asks the students to describe, in order, the experiments they intend to carry out. At each step they must justify their plans. The instructor asks questions and gives hints where necessary, but is careful not to reveal too much about the solution to the problem.

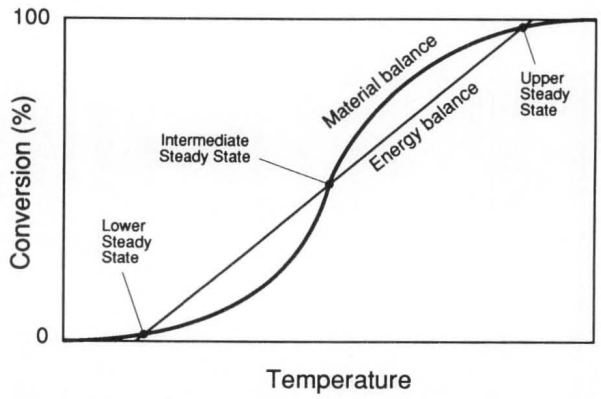

Figure 3. *Mutiple steady states in a CSTR. The system usually operates at the intermediate steady time.*

The students are faced with a number of choices regarding the type and number of reactors, the catalyst age, the feed composition, and the reactor temperature. In making these choices, they have to keep in mind a number of constraints:

- **It takes five days[1] and $75,000 (half the budget) to clean and prepare the pilot plant.**
- **It costs another three days[1] and $50,000 to replace the catalyst in the pilot plant; obviously, the students cannot afford to change their minds on the catalyst selection.**
- **Each pilot plant run takes twenty-four hours.[1]**
- **The pre-exponential factors $a_1, \ldots, a_7$ must be measured in the pilot plant.**
- **Other constants can be obtained from the lab reactor, but their values must be checked in the pilot plant.**

It makes sense to use the lab reactors as much as possible, since they are considerably cheaper to operate than the pilot plant. Furthermore, the lab reactors are easily refilled with catalyst, permitting the students to take data related to catalyst age. However, all constants that are determined from laboratory data *must* be checked in the pilot plant. (By "checked" we mean that four or five points over a reasonable range should agree with the previously determined values.)

STEADY-STATE SIMULATION

Once the students have demonstrated to the instructor's satisfaction that they have a good grasp of the problem, they are shown how to operate the computer program in the steady-state mode. This enables them to simulate the operation of the labo-

[1] Simulated time

ratory reactors and the pilot plant, from which they can obtain the required kinetic constants.

The students are permitted to take data from the third through the sixth lab period. During the sixth period the group leader is required to give a fifteen-minute oral progress report, which is videotaped and critiqued in private with the speaker.

DYNAMIC SIMULATION

After the group leader's progress report, the instructor shows the students how to run the simulator in the dynamic mode. The students are then given a second assignment letter informing them that they have been selected to act as consultants during the start-up of a resid hydrotreater at Amoco's Texas City refinery. They are asked to simulate the start-up of a single reactor, controlling the operating conditions manually to reach steady state. Then they are to cease controlling the system and to note the time that elapses before automatic shutdown occurs.

The start-up problem is especially challenging because the operating conditions within the reactor can only be controlled indirectly, by setting the temperature, flow rate, and composition of the feed stream. Furthermore, instantaneous changes in these variables are not permitted; the students must wait fifteen minutes between changes in the feed settings, and they are limited to changing feed temperature by no more than 100 F at a time. Finding a suitable control strategy is typically a trial-and-error process. (Dynamic simulation runs are not charged against the students' budgets.)

Two lab periods are allotted for the start-up problem. The students then have one week to produce a full written report, including the results of their steady-state experiments and an outline of their recommended start-up procedure.

TABLE 3
Expenses

Initial preparation and start-up of pilot plant (includes cost of initial charge of catalyst	5 days	$75,000
Replacement of catalyst in pilot plant	3 days	$50,000
One pilot plant run (includes labor, materials, analysis, etc.)		
Three reactors in series	24 hours	$4,500[1]
Two reactors in series	24 hours	$4,000[1]
One reactor	24 hours	$3,500[1]
One laboratory reactor run (includes catalyst replacement)	24 hours	$500[1]
Consultation	?	$500

[1]Multiply by 1.5 for Saturday runs; by 2.0 for Sunday runs

ROLE OF THE INSTRUCTOR

The instructor has four important parts to play in a simulation project:

1. ***Mother Nature*—sets the mean values and random variability of all parameters used in the simulation**
2. ***Boss*—receives the oral and written reports from the group**
3. ***Consultant*—helps with specific technical questions, but charges a fee that must be paid from the budget.**
4. ***Instructor*—assigns the grades, of course.**

COMPUTER SIMULATIONS FOR EDUCATION

Although it would be possible to design a senior laboratory made up entirely of computer-simulated experiments, we believe that students should also gain "hands-on" experience by working with real laboratory equipment. For this reason, we allow only one of the three required experiments to be a computer project.

We have used the Amoco module here at Purdue for five semesters, with great success. As an alternative to traditional lab experiments, computer simulation offers a number of significant advantages:

- **Processes that are too large, complex, or hazardous for the university lab can be readily simulated 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 (which may not be representative of current industrial practice) to more general considerations of proper experimental design and data analysis.**
- **Computer simulation is relatively inexpensive compared to the cost of building and maintaining 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.**

AVAILABILITY OF THE MODULES

Anyone interested in obtaining more information on the Purdue-Industry ChE Simulation Modules should contact Professor Squires. An NSF-sponsored workshop on the modules will be held at Purdue on July 26-28, 1991.

ACKNOWLEDGMENTS

This work has been supported by the National Science Foundation (Grant No. USE-888554614). Technical assistance was provided by Amoco Oil Company and the CACHE Corporation. ❐