Session 3513

The story of polyethylene garbage bags

Bruce A. Finlayson
University of Washington

Overview. The story of polyethylene garbage bags has been used as a structure around which to organize a course on numerical methods applied to chemical engineering problems. Starting with natural gas, a series of problems is posed that must be solved if one is to eventually end up with a garbage bag.

The course begins with a theme, written about some aspect of polyethylene: raw materials, production methods, uses, business trends, recycling, etc. These themes are then put on the course Web-site so that they can be read by all the class. It is also necessary to use many different computer tools (e-mail, anonymous ftp servers, local area networks) to accommodate the diverse needs of the students, some of whom have their own computers and different software. Most problems are solved using Microsoft EXCEL™ or Mathworks MATLAB™. After the standard problems are solved, the students prepare multimedia displays illustrating the mathematical problems a chemical engineer runs into in order to convert natural gas into garbage bags. Two displays are done: one for a technical audience (a prospective sophomore chemical engineer) and one for a general audience (middle school or high school students). Even the patent literature is used in lectures to display the role of innovation. Safety aspects in polyethylene plants can be addressed by using films prepared by SACHE (Safety and Chemical Engineering Education).

Course Objectives. The goal of the course is to learn to apply mathematical and numerical methods to chemical engineering problems. This goal involves learning to use existing software like EXCEL and MATLAB, learning some rudimentary programming in MATLAB, and especially learning to check your results numerically, since there are often no known analytical solutions for comparison. The instructor's task is to achieve those goals within a structure imposed by a case study. In this course the structure was provided by a series of problems arising when modeling processes to obtain natural gas, separate the ethane, react it to ethylene, polymerize it to polyethylene, and extrude it to make polyethylene garbage bags. This provides the story line of the course. The sequence of problems is: sets of algebraic equations, ordinary differential equations as initial value problems, ordinary differential equations as boundary value problems, and partial differential equations. This presentation describes the course activities that shape the learning environment and then gives a description of the mathematical models and problems assigned and solved in homework problems.

Course Activities. The first assignment is to write a theme about some aspect of making polyethylene garbage bags: raw materials, production methods, uses, business trends, recycling, etc. These themes are then put on the student's individual Web pages and a class directory points to them all. Thus, all students can read all the themes. This means that each student can benefit from what every other student has found, and in the process get a good overview of all aspects, not just the one they write about.

The computers and computer tools were diverse. A computer laboratory with 30 Macintosh computers is available with MATLAB accessible from any of them. Thus the instructor could send via e-mail program segments to the entire class. This was done sometimes to save the students' time in situations when little learning would occur for the time spent, or for problems which had already been solved as homework and discussed in class. Some students had IBM compatible computers at home, with their own copy of MATLAB, so it was necessary for them to learn how to connect to the University network to receive mail if they didn't know already. Anonymous ftp servers could be used to distribute documents in forms that were not computer specific, but this was not as successful as just using e-mail.

Most problems were solved using Microsoft Excel or Mathworks MATLAB. These tools, as powerful as they are, will not give correct answers if the engineering work is not correct. Thus considerable emphasis was placed on checking one's work, and this message was repeated and displayed over and over again. For example, if one wants to find the value of x making

$$f(x) = \frac{e^{-x}}{2 + \sin(x)} = 0.3$$

one can use either EXCEL or MATLAB to find the root, by typing in the equation

$$e^{-x} / (2 + \sin(x)) - 0.3$$

in one form or another. However, one must be sure the function is correct. The minus sign in e^{-x} might be left off, a relatively visible error. However, the syntax rules might be different from what a student expects. Thus they might write

$$e^{-x} / 2 + \sin(x) - 0.3$$

and obtain the wrong answer. Thus each problem requires that the student-generated part be examined term by term. In this case, evaluating the function for x=1 would detect the error when compared with a hand calculation (with presumably correct syntax). However, the instructor prefers never to use 1.0, but at least use 1.1, etc., because if the correct term is 2x and one use x=1, the same answer is obtained if the term is 2x or 2. These subtle distinctions and strategies are important to learn.

The next part of the computer tools one needs to learn is when to use which tool. It is easy to solve a single nonlinear algebraic equation in both MATLAB and EXCEL. Sets of nonlinear equations can be solved in both by developing an optimization function which is to be minimized, giving the value zero when the solution to all the equations is found. This often works. However, if one is not careful in specifying the error limits and number of iterations allowed, one can be misled into thinking the problem is solved when it isn't really.

One aspect of a case study approach is the lack of a suitable textbook. Since the author has written several books on mathematical methods, material from those could be included in class notes. These materials were augmented by examples solving problems using the computer codes and giving step-by-step instructions. The notes were then made available for purchase at a copy shop. This is a very cheap alternative to a textbook (about $7), but suffers from the difficulty in knowing what information is essential and what is background for the case study in question.

One part of the polyethylene story is the low pressure process to polymerize polyethylene. The patent literature is full of patents describing various aspects of the discover and commercialization of the low pressure process. These stories make interesting topics for lecture. As one example, in an early example of the reactor, the polymer would form in sheets, e.g. 1/4" x 10" x 3".[1] These sheets obstructed the flow in the fluidized bed. Eventually it was found that they were caused by an electrostatic charge building up on the particles near the wall, and this could be alleviated if one washed the reactor first with bis(cyclopentadienyl) chromium (II) dissolved in benzene or toluene. The patent description of the process used to deduce this is fascinating. The object lesson here is the process of discovery, the value of chemistry, and the knowledge that it is a complicated process to commercialize an invention.

Industrial feedback to Universities emphasize the importance of safety, and fortunately materials were available on the safety of polyethylene reactors. The tape, *Phillips 66 Company Explosion and Fire at Pasadena, TX*, available from SACHE, was used in class to emphasize that what we are doing deals not just with computers, or models, but results in equipment with life and death implications. This film shows the aftermath of an explosion and fire in a polyethylene plant in Houston. The film itself is qualitative, since it is based on newsreel footage shot during the disaster. The cause of the accident was air hoses re-hooked incorrectly after maintenance, so that valves were open but the signals said they were shut. Important safety lessons can be made when discussing this film, and the mood of students leaving class that day was very somber. When dealing with such a broad subject, there are occasionally questions raised in class that the instructor can't answer. Some of these can be answered with a bit of study, but some can't. In one such case, the instructor asked for help from a recruiter from Dow Chemical, which produces polyethylene. The message was sent by e-mail, forwarded to an operating engineer by e-mail, and answered in return e-mail. Naturally company secrets can't be revealed, but the engineers in the plant can still be helpful. This is an excellent example of industrial-University cooperation.

At the end of the course the students were divided into teams, and each team was asked to make a demonstration of how to make polyethylene garbage bags using either Web pages or Macromedia Director. Five groups did their stories on Web pages and one did theirs in Director. Each group needed two versions - one for engineers (e.g. sophomore chemical engineers) and one for grades 6-12. Students were imaginative in gathering material, thought through how to present it, and developed marvelous lessons.[2] These lessons can be, and are being, used in demonstrations and interactions with students in grades 6-12. One professor wrote: "Those are superb - how did you get the students to do it?" The way was very simple. At the start of the quarter, the instructor spent 5 minutes showing how to set up a simple home page – with one sentence in it. Later in the course figures were added, and the theme was added. Pointers to html tools/instruction on the University of Washington Web site were also given. Then the students were let loose. The instructor likens this to: give them some tools and then get out of the way. In addition to learning communication skills the students also have fun. Samples of the student work are shown in Figures 1-3 and the Web[2].

Typical Problems. Given here is a sample of problems used as homework assignments in the course. Additional problems were of course used, and the objective of this list is to show that the entire course can be covered (i.e. all mathematical types of equations treated) even though one is restricted to solving only problems arising in the production of polyethylene garbage bags.

<u>Problem 4</u> requires solution of a single nonlinear algebraic equation, the Rachford-Rice equation.[3]

$$f(v) = \sum_{i=1}^{NC} \frac{(K_i - 1)\, z_i}{(K_i - 1)\, v + 1} = 0$$

Such equations are easily solved in either EXCEL or MATLAB by simply typing in the equation.

4. A reservoir in Northern Louisiana contains a volatile oil. The reservoir conditions at discovery were 246 °F, 4836 psia, supposedly at the fluids bubble point. The composition was

Component	Mole Fraction
Nitrogen	0.0167
Methane	0.6051
Carbon Dioxide	0.0218
Ethane	0.0752

CHEMICAL ENGINEERING - WE'RE ALMOST EVERYWHERE!

People are always asking us, "What do Chemical Engineers do?" And we always answer, "Just about everything."
Chemical engineers are involved in all sorts of things, from helping to destroy pollution in the environment, to designing huge reactors, to manufacturing household items.
Today we're going to talk about something that you probably

wouldn't even associate with engineering, and yet chemical engineers are involved every single step of the way. What are we going to talk about?

Making garbage bags!

Doesn't sound too exciting, does it? But just wait....there's more here than meets the eye...

To begin our story, press one of the following buttons:

This story was prepared by

Christine Haswell
Joe Brule
Ismael Icantu
Katty Hui

as part of Chem. Eng. 475, Mathematical Modeling of Chemical Engineering Systems.

Figure 1. Introduction

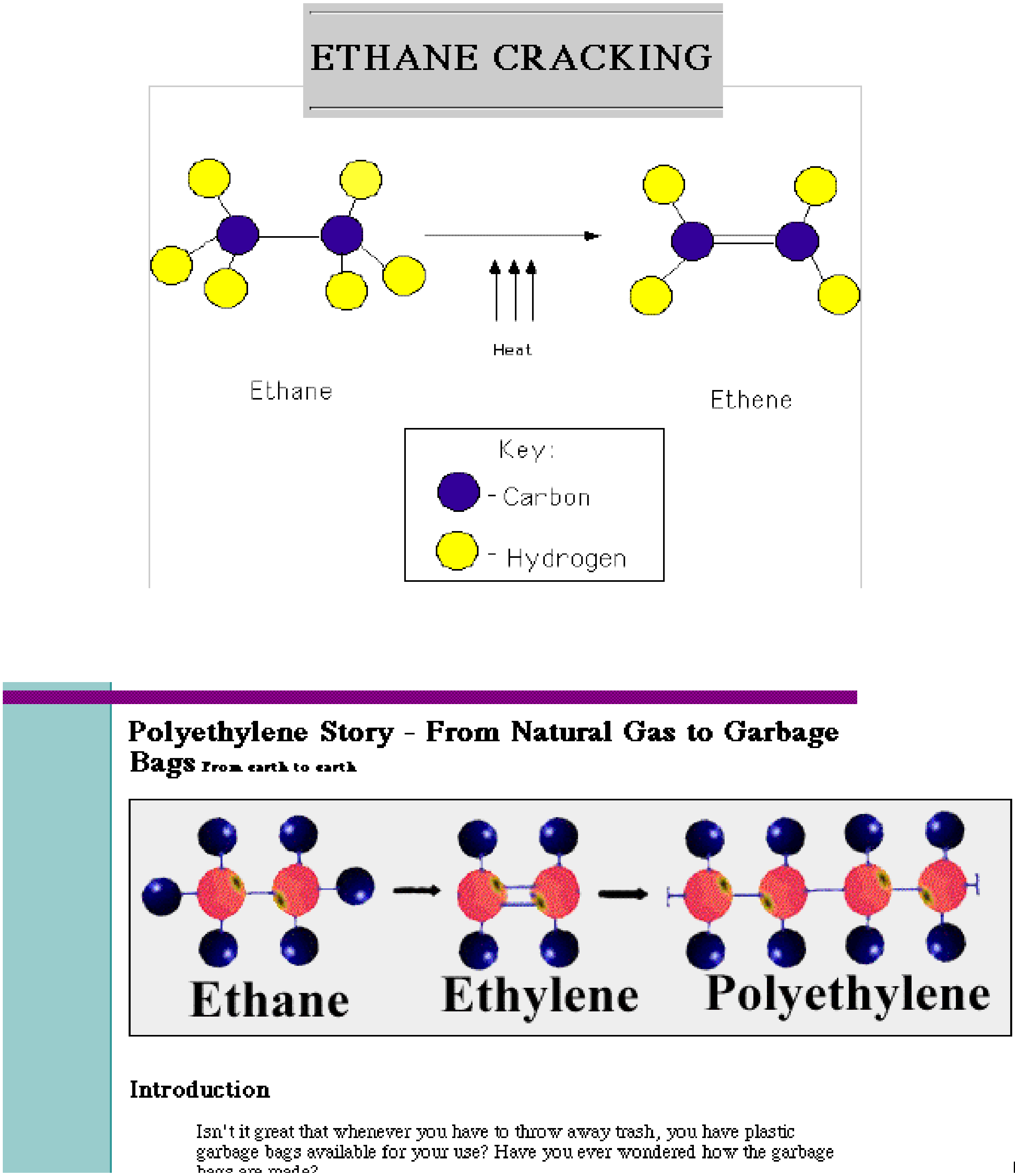
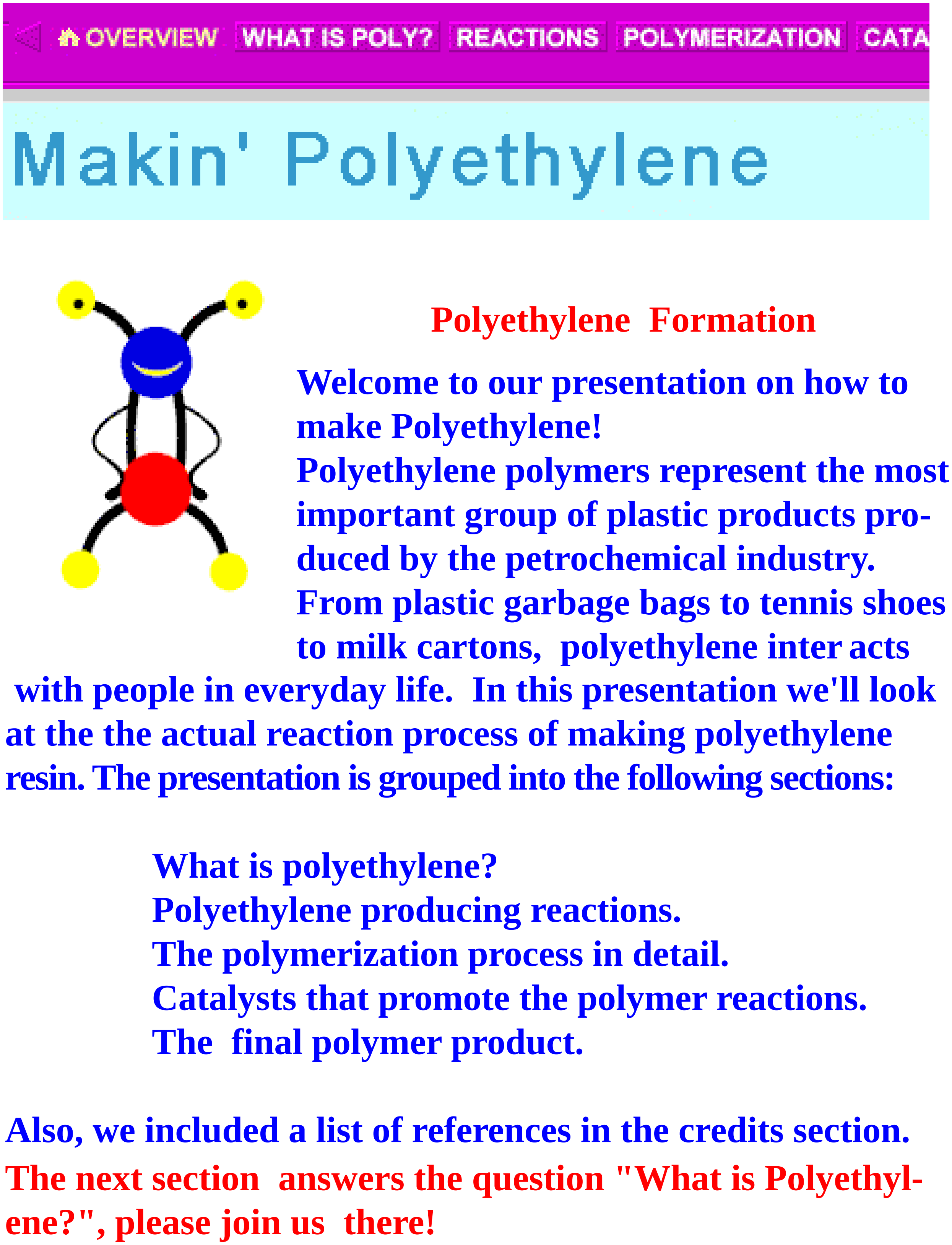


Figure 2. Molecular View


OVERVIEW WHAT IS POLY? REACTIONS POLYMERIZATION CATA

Makin' Polyethylene

Polyethylene Formation

Welcome to our presentation on how to make Polyethylene!
Polyethylene polymers represent the most important group of plastic products produced by the petrochemical industry. From plastic garbage bags to tennis shoes to milk cartons, polyethylene inter acts with people in everyday life. In this presentation we'll look at the the actual reaction process of making polyethylene resin. The presentation is grouped into the following sections:

What is polyethylene?
Polyethylene producing reactions.
The polymerization process in detail.
Catalysts that promote the polymer reactions.
The final polymer product.

Also, we included a list of references in the credits section.
The next section answers the question "What is Polyethylene?", please join us there!

Figure 3. Polyethylene Page

Propane	0.0474
Butanes	0.0412
Pentanes	0.0297
Hexanes	0.0138
Heptanes plus	0.1491

a) The gas-liquid separator at the surface is at 500 psia, 65 °F. Find the composition of the gas and liquid streams and the vapor fraction using the program DISTILL or ASPEN.

b) The liquid is taken to the stock tank, which is at 14.7 psia, 70 °F. Find the vapor fraction at these conditions.

c) Take the K-values from part (a) and use them in the Rachford-Rice equation. Solve this equation for the vapor fraction using EXCEL, or MATLAB, or a program of your choosing (not DISTILL or ASPEN).

Problem 8 is also a single nonlinear equation: solve the cubic equation of state for either the compressibility factor or the specific volume. The constants A, B, a, and b can be determined from the values for the individual components and the composition, and the values for the individual components depend on the critical temperature and pressure.[4]

$$Z^3 - Z^2 + Z\,[A - B\,(1 + B)\,] - AB = 0$$

$$\hat{v}^3\,p - \hat{v}^2\,RT + \hat{v}\,(-p\,b^2 - RT\,b + a\,) - ab = 0$$

8. In order to size a pipe, it is necessary to compute the specific volume of a mixture of hydrocarbons.

Component	lb.moles/hr
Ethane	200
Propane	223
Butanes	214

Do so using the Redlich-Kwong equation of state at 100 °F, and pressures of 100, 200, and 300 psia. For liquids use an optimal pipe diameter set by u = 7 ft/sec. For gases use 70 ft/sec. Give the diameters of pipes needed in the three cases.

Problem 11 involves solving sets of ordinary differential equations in a relatively straight forward problem.

$$\frac{dF_i}{dV} = R_i,\ i = 1,\ldots,5$$

$$r_1 = -\,k_1\,c_1,\ r_2 = -\,k_2\,c_1$$

$k_1 = 1.535 \times 10^{14} \exp(-70{,}200 / RT)$

$k_2 = 2.58 \times 10^{16} \exp(-86{,}000 / RT)$

R = 1.98, T in K

This class of problems involves solution of ordinary differential equations as initial value problems, which is easily done in MATLAB using ode45, which is a version of a fourth-order Runge-Kutta method (rfk45) with automatic control of the error by adjusting the step size. Thus concepts of methods (Euler, Runge-Kutta), errors, stability, and step-size choice can all be addressed, and the variation of error with mesh size (and resulting extrapolation techniques) can be treated.

11. Take the stream coming from the top of the column in Problem 5 and feed it to a thermal cracker operating at the constant temperature of 1311 K.
(a) Design a thermal cracker to convert 95% of the ethane to ethylene. The design should say how many tubes and their diameters and lengths, as well as give the overall mass balance.
(b) How much does the molecular weight of the gas change from inlet to outlet?

Problem 17 involves solving an ordinary differential equation combined with an algebraic equation. Thus the skills learned in solving nonlinear algebraic equations and those learned in solving ordinary differential equations are combined. This problem is one that is difficult to do in EXCEL, and MATLAB is the preferred software.

17. Find the reactor length that will result in 65% of the ethane feed being reacted using the following model derived in class:

$$C_p \, F_{tot} \frac{dT}{dV} = \sum_{i=1}^{2} (-\Delta H_{rxn,i}) \, r_i + \phi \, \sigma \, (T_r^4 - T_w^4) \frac{A_w}{A_c}$$

$$\phi \, \sigma \, (T_r^4 - T_w^4) = h_i \frac{T_w - T}{1 + h_i \, d / k}$$

The feed rate is 571 lb.moles/hr. of ethane and 0.2 lb. steam / lb. ethane, and the inlet temperature is 350 K while the inlet pressure (constant) is 50 psia. Other values are:

C_p = 20.9 Btu/lb.mole.°F

ϕ = 1.3

$\sigma = 18.0 \times 10^{-9}$ Btu/hr.ft.^{2} K^4 (= 1.713×10^{-9} Btu/hr.ft^2 °R^4)

R_t = 0.125 ft

T_r = 1311 K

$\Delta H_{rxn,1}$ = 58,900 Btu/lb.mole, $\Delta H_{rxn,2}$ = 15,500 Btu/lb.mole

h_i = 70 Btu/hr ft^2 °F, d = tube wall thickness = 0.25 in., k = 12.5 Btu/hr ft °F

Problems 19-21 are all based on polymerization equations suggested by Hoftyzer and Zwietering[5] as a preliminary model for ethylene polymerization. The concentration of ethylene is kept constant, but the temperature and initiator concentration change in time. This model allows introduction of the concepts of multiple steady states as well as stiff equations. Multiple steady states again allows reinforcement of methods of solving nonlinear algebraic equations (now there is more than one answer!) and stiff equations allows discussion of implicit methods as an alternative to explicit methods like the Runge-Kutta method. The model is:

$$\frac{dC}{dt} = - B\, C \exp(-E_i/RT) + \frac{G}{V}(C_0 - C)$$

$$\rho C_p \frac{dT}{dt} = q\, A\, c^n \exp(-E_i/RT) + \frac{G\rho C_p}{V}(T_0 - T) - \frac{Ah}{V}(T - T_w)$$

C = concentration of initiator

T = temperature

B = rate constant for initiator

A = rate constant for main reaction

G = feed rate

V = reactor volume

Ah = area x heat transfer coefficient

q = heat of reaction

$n = \frac{1}{2}$, $E_i \neq E$

Problem 22 provides two boundary value problems, one an easy one using a Newtonian fluid and one a more difficult one using a non-Newtonian fluid. These problems are solved using a shooting method and also using a finite difference method. In the shooting method one uses the techniques learned to solve ordinary differential equations as initial value problems with the techniques (specifically Newton-Raphson) used to solve nonlinear equations. In the process one learns how to derive and use sensitivity equations involving the derivative of the solution with respect to a parameter. In the finite difference method, one learns how to solve tridiagonal systems quicker than by inverting a complete matrix, and various iterative strategies for sets of nonlinear equations are invoked. Quadrature formulas are also needed in this problem. The methods, errors, and convergence with mesh size are all studied in these problems.

22. LLDPE is flowing in a die that has a height of 1 mm, a width of 30 mm, and is 60 mm long. The viscosity of the fluid is governed by the Carreau equation:

$$\eta = \frac{\eta_0}{[1 + (\lambda\dot{\gamma})^b]^c}$$

$\eta_0 = 8818$ Pa s

$\lambda = 0.1813$ sec

b = 0.975

c = 0.428

Use the shooting method to find the the flow rate that will occur if the pressure difference is
820 psi over a length of 60 mm under the following conditions.
(a) Assume a Newtonian fluid with a viscosity of 8818 Pa s.
(b) Use the Carreau model.

Partial Differential Equations. In this course, none of the important models required the solution of partial differential equations. The topic was introduced, though, because partial differential equations can be solved using a combination of techniques for ordinary differential equations as initial value problems and boundary value problems, leading to the method of lines. The main topic is then how the interpretations and guidelines developed in each case are applied in the combined case. In particular using the method of lines, as suggested here, leads to stiff equations, so the concept of stiff equations is reinforced. The solution of elliptic partial differential equations was not covered.

Conclusion. The outline above shows that nearly all the important classes of problems can be treated, even when the course is organized around a chemical process. The inclusion of polyethylene garbage bags as a story line makes the course more interesting, and provides a context that the students can remember even if the details of the mathematical method are hazy. Throughout the discussion of homework problems the emphasis is on showing that your numerical work is correct, and that you have solved the problem you want within some accuracy. Without that checking, the numerical work becomes problematic at best. The students have come away with that clear concept, and they carry it forth into other courses. The instructor has even had former students send e-mail and give anecdotes about how they used those skills in their jobs, whereas their coworkers did not and went astray. The downside is that it is much harder to organize the course, and it requires great effort on the part of the instructor. If the instructor does his/her job well, the students are unaware of how the course has been shaped: they discover everything themselves! Some of the numerical topics are not covered in as much depth as the instructor would like, because they are unimportant to the process being studied. On the whole, the course objectives are satisfied for a larger number of students (of various abilities) than in more traditional formats.

References

[1] Fulks, B. D, *et al.*, U. S. Patent No. 4,792,592, Dec. 20, 1988, “Process for reducing sheeting during polymerization of alpha-olefins”.

[2] See the internet: http://weber.u.washington.edu/~chemeng/Polyeth/

[3] Henley, E. J. and J. D. Seader, *Equilibrium-Stage Separation Operations in Chemical Engineering*, Wiley, New York, 1981, p. 273.

[4] *ibid*, p. 171.

[5] Hoftyzer, P. J. and Th. N. Zwietering, “The characteristics of a homogenized reactor for the polymerization of ethylene,” Chem. Eng. Sci. 14 241-251 (1961).

Biographical Information

BRUCE A. FINLAYSON obtained a B.A. in 1961, a M.S. in 1963 from Rice University and a Ph.D. in 1965 from the University of Minnesota. He is the Rehnberg Professor of Chemical Engineering and Chair at the University of Washington, a member of the National Academy of Engineering, a Fellow of the American Institute of Chemical Engineers, and received the Martin Award from the Chemical Engineering Division of the ASEE, and and was a winner of the Undergraduate Computational Engineering and Science Award of the Department of Energy, 1996.