

AN APPETIZING STRUCTURE OF CHEMICAL REACTION ENGINEERING FOR UNDERGRADUATES

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Chemical reaction engineering (CRE) is fun to teach, not only because it has extremely interesting subject matter and is one of the few courses that sets chemical engineering apart from other engineering disciplines, but also because it has a very logical structure. The six basic pillars that hold up what could be called the "Temple of Chemical Reaction Engineering" are shown in Figure 1.^[1] The four on the left are usually covered in the majority of undergraduate reaction engineering courses.^[2] But *diffusion* effects, which include mass transfer limited reactions, effectiveness factors, and the shrinking core model, are covered in only a small number of courses. *Contacting*, which includes reactor characterization (e.g., residence time distribution) and modeling non-ideal reactors, is normally left to graduate-level courses.

The pillar structure shown in the figure allows one to develop a few basic concepts and then to arrange the parameters (equations) associated with each concept in a variety of ways. Without such a structure, one is faced with the possibility of choosing, or perhaps memorizing, the correct equation from a *multitude* of equations that can arise for a variety of different reactions, reactors, and sets of conditions. We draw a loose analogy with dining at a Swedish smorgasbord where it is difficult to choose

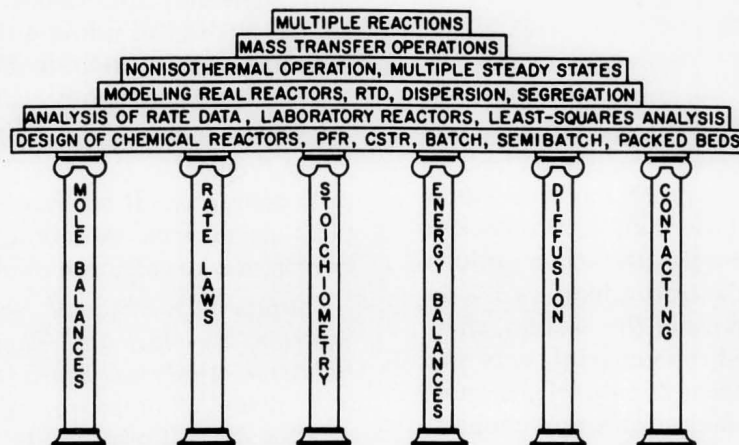


Figure 1. Pillars of the Temple of Chemical Reaction Engineering.

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from a *multitude* of dishes in order to end up with a satisfying, well-balanced meal that *fits together*. In CRE, consider the number of equations that arise in calculating the conversion in CSTRs, batch, plug flow, and semibatch reactor—for zero, first, second, and third order reactions—for both liquid and gas phase systems—with and without pressure drop. The number of equations (dishes) from all the above possible combinations which we must choose (memorize) is then $4 \times 4 \times 3 = 48$. If we also consider catalyst decay with either first, second, or third order decay laws, the number of dishes increases to 192. If Langmuir-Hinshelwood kinetics are included, the number of equations, or dishes (*i.e.*, equations in isothermal reactor design) increases to well over 1,000. Finally, if we add non-isothermal effects, the

number of dishes increases to such an extent that choosing the right dish, or dishes, becomes a task of unbelievable gastronomical proportions. The challenge is to put everything in an orderly and logical fashion so that we can proceed to arrive at the correct equation (dishes that fit together) for a given situation.

Fortunately, by structuring CRE using an algorithm analogous to a fixed-price menu in a fine French restaurant, we can eliminate virtually all memorization (see Figures 2 and 4) and proceed in a logical manner to develop the reaction engineering equation necessary to describe the given situation. The lower price (220 FF) menu corresponds to isothermal reactor design, while the higher price menu (280 FF) corresponds to non-isothermal design.

Here we start by choosing *one* dish from the appetizers listed. The analog is to choose the mole balance from one of four reactor types shown. Next, we choose our main course from one of four entrées: the main course analog in CRE is to choose the appropriate rate law. Continuing with our meal, we choose cheese or dessert; the analogy in CRE is stating whether the reaction is liquid or gas phase in order to use the appropriate equation for concentration.

The main difference between CRE and ordering and eating a fine French meal as we have just done is that in CRE we combine everything together at the end; such a mixing of the courses on a single plate before eating a wonderful French meal would be a disaster! The application of this structure to a first order gas phase reaction car-

ried out in a PFR (with a change in the total number of moles) is shown in Figure 3. As an example, we will follow the dark lines as we proceed through our algorithm. The dashed lines represent possible pathways for other situations. Here we choose

1. the mole balance on species A for PFR,
2. the rate law for an irreversible first order reaction,
3. the equation for the concentration of A in the gas phase, and then
4. combine to evaluate the volume necessary to achieve a given conversion or the conversion that can be achieved in a specified reaction volume.

For the case of isothermal operation with no pressure drop, we were able to obtain an analytical solution. In the majority of situations, however, analytical solutions of the resulting ordinary differential equations appearing in the **combine** step are not possible. Consequently, we include POLY-MATH⁽³⁾ in our menu. POLYMATH is analogous to *vin blanc ou rouge* in that it makes obtaining solutions to the differential equations much more palatable.

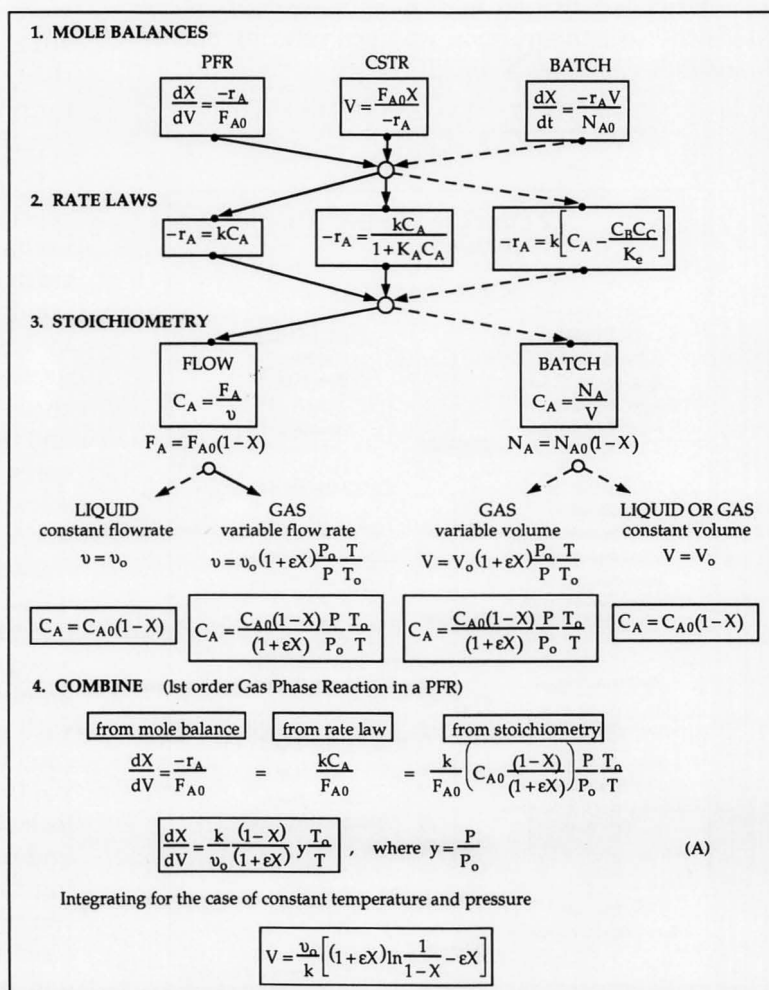
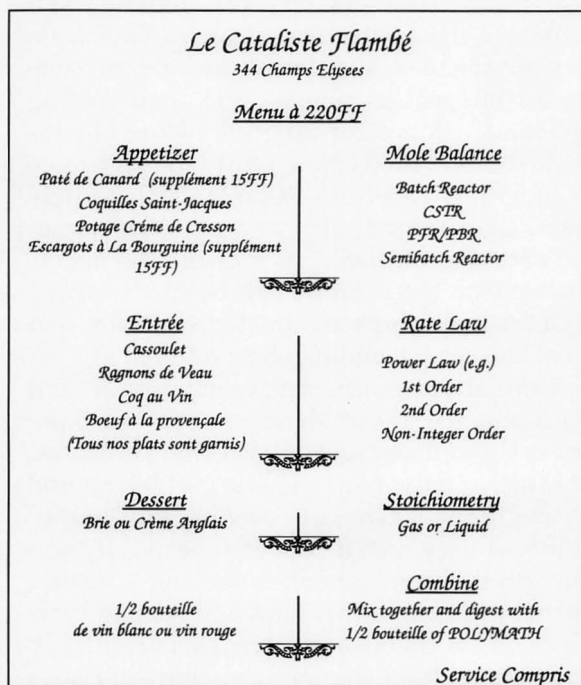


Figure 2. French Menu I: Isothermal reactor design Spring 1993

Figure 3. Algorithm for ISOTHERMAL reactors

HEAT EFFECTS

Studying non-isothermal reactor design is analogous to ordering from a more expensive (280 FF) French menu (see Figure 4) in which we have an extra category from which to make a selection. In CRE this corresponds to choosing which form of the energy balance to use (e.g., PFR, CSTR) and which terms to eliminate (e.g., $Q=0$ for adiabatic operation). The structure introduced to study these reactors builds on the isothermal algorithm by introducing the Arrhenius Equation, $k = A e^{-E/RT}$ in the **rate law** step, which results in *one* equation with *two* unknowns, X and T , when we finish with the **combine** step. The students realize the necessity of performing an energy balance on the reactor to obtain a second equation relating X and T . For example, using again the PFR mole balance and conditions in Figure 3 (Eq. A), we have, for constant pressure

$$\frac{dX}{dV} = \frac{A e^{-E/RT} (1-X)}{v_0(1+\epsilon X)} \left(\frac{T_0}{T} \right) \quad (A)$$

An energy balance on a PFR with heat exchange yields the second equation we need relating our independent variables X and T

$$\frac{dT}{dV} = \frac{[U A_c (T_a - T) + (r_A)(\Delta H_R)]}{F_{A0} C_{PA}} \quad (B)$$

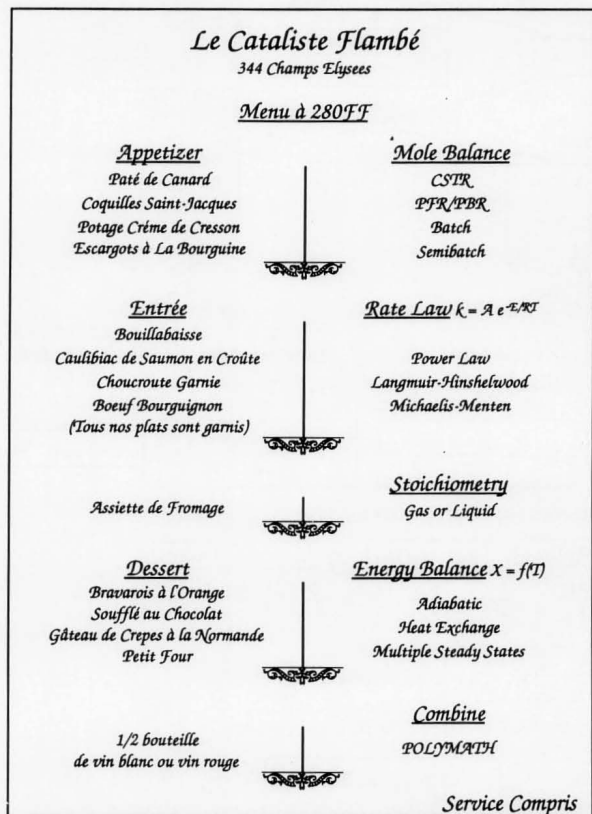


Figure 4. French Menu II: Non-isothermal reactor design

With the emergence of extremely user-friendly software packages, we can now allow students to explore the problem much more effectively, to develop an *intuitive feeling* for the reactor/reaction behavior, . . .

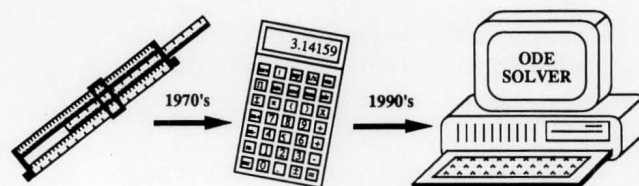


Figure 5. Paradigm shifts in chemical engineering education.

These simultaneous differential equations can be readily solved with an ODE solver, as discussed below.

A PARADIGM SHIFT

With the emergence of extremely user-friendly software packages (see Figure 5), we can now allow students to explore the problem much more effectively, to develop an intuitive **feeling** for the reactor/reaction behavior, and to obtain more practice in creative problem solving.

To illustrate this point, consider an exothermic reaction carried out in a plug flow reactor with heat exchange. Obtaining the temperature and concentration profiles requires the solution of two coupled non-linear differential equations such as those given by Eqs. (A) and (B). In the past, it would have been necessary to spend a significant amount of time choosing an integration scheme and then writing and developing a computer program before any results could be obtained. Now, with the available software programs (especially POLYMATH), it rarely takes more than ten minutes to type in the equations and obtain a solution.^[3] As a result, the majority of the time on the exercise can be spent exploring the problem through parameter variation and analysis of the corresponding observations. For example, in the above exothermic reaction in a PFR with heat exchange, the students can vary such parameters as the ambient and entering temperatures, the flow rates, and the heat transfer coefficient, and look for conditions where the reaction will "ignite" and conditions for which it will "run away." By trying their own different combinations and schemes, the students are able to carry out open-ended exercises which allow them to practice their creativity and better understand the physical characteristics of the system.

VARIATIONS ON A THEME

As a result of the paradigm shift in the ease of computation using ODE solvers, the study of a wide variety of chemical reaction engineering systems just becomes a variation on our main theme (menu?). Once the concepts of the four left-most pillars are mastered, many important extensions can be viewed as minor variations on the four basic steps in our isothermal reaction design algorithm. Table 1 shows the basic algorithm for solving CRE problems (including the energy balance), along with the steps that need to be examined to handle the individual variation.

To reinforce how many different CRE problems are minor extensions of the basic algorithm, we shall discuss three in greater detail below.

Pressure Drop

If pressure drop is not accounted for in gas phase reactions, significant under-design of the reactor size can result. This variation is handled in the **stoichiometry** step, where concentration is expressed as a function of conversion, temperature, and total pressure. The change in total pressure is given by the Ergun equation^[1]

$$\frac{dP}{dL} = -\frac{G(1-\phi)}{\rho g_c D_p \phi^3} \left[\frac{150(1-\phi)\mu}{D_p} + 1.75G \right] \quad (C)$$

This equation can be rearranged by lumping the constant parameters to arrive at the following equation, giving the variation of the pressure ratio ($y=P/P_o$) with either reactor volume

$$\frac{dy}{dV} = -\frac{\alpha_1(1+\epsilon X)}{2y} \quad (D)$$

or catalyst weight

$$\frac{dy}{dW} = -\frac{\alpha_2(1+\epsilon X)}{2y} \quad (E)$$

Either of these equations can be coupled with the combined mole balance, rate law, and stoichiometry and solved numerically (e.g., with an ODE Solver). For example, for isothermal conditions, Eq. (E) would be coupled with Eq. (A) adopted to an isothermal PBR

$$\frac{dX}{dW} = \frac{k(1-X)}{v_o(1+\epsilon X)} y \quad (F)$$

Catalyst Decay

For the case of separable kinetics, we simply include a catalyst decay law in the rate law step of our algorithm. For example, for a straight through transport reactor (STTR), the rate law might be given by

$$-r_A = a(t) \frac{kC_A}{1+K_A C_A} \quad (G)$$

where the catalyst activity, $a(t)$, is

$$a(t) = \frac{1}{1+\beta t^{1/2}} \quad (H)$$

The algorithm for studying a catalytic reaction in a straight through transport reactor is shown in Figure 6.


<u>Variations</u>	
MOLE BALANCE	
• _____	Reactive Distillation
• _____	Membrane Reactors
RATE LAW	
• _____	Catalyst Decay
• _____	Catalysis/CVD
STOICHIOMETRY	
• _____	Pressure Drop
• _____	Multiple Reactions
• _____	Membrane Reactors
COMBINE	
ENERGY BALANCE	
ADIBATIC	
NON ADIBATIC	
• _____	Multiple Steady States
PARAMETER EVALUATION	
ODE SOLVER	 What if . . .??
• _____	

Table 1. Variations on the basic algorithm

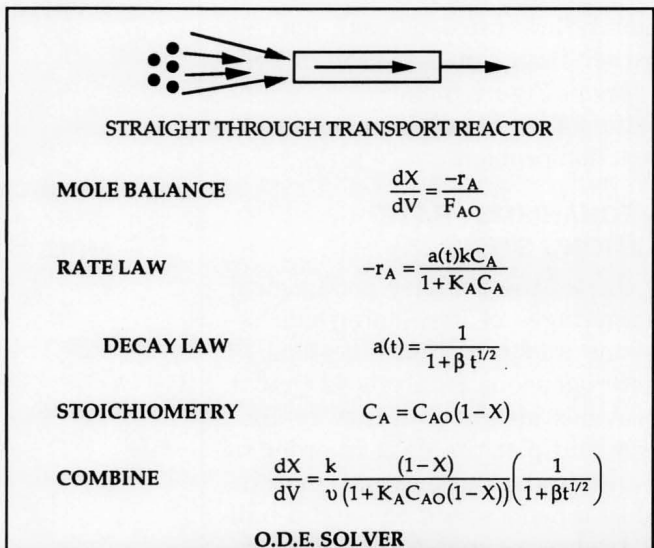
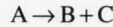


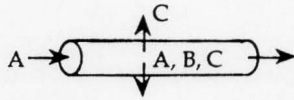
Figure 6. Variations on a theme: Catalyst decay in a STTR

Membrane Reactors

The only trick in studying membrane reactors is to make sure to write the equations in terms of molar flow rates rather than conversion, and to account for the products that are leaving the reactor through the sides of the membrane reactor in our **mole balance** step. Consider the reaction



taking place in a membrane reactor



For the product that exits through the side of the membrane reactor, C, the mole balance and stoichiometry steps are

$$\frac{dF_C}{dV} = -r_A - k_c C_c \quad (I)$$

$$C_i = \frac{F_i}{v} \quad (J)$$

$$v = v_0 \frac{F_T}{F_{T0}} = v_0 \left(\frac{F_{A0} + F_B}{F_{T0}} \right) \quad (K)$$

After writing a mole balance on A and B, the resulting set of non-linear ODEs is solved numerically. A sample POLYMATH solution is shown in Figure 7.

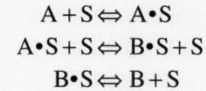
MULTIPLE REACTIONS

The steps that are varied when multiple reactions occur are **rate law** and **stoichiometry**. As with membrane reactors, we work in terms of the number of moles or molar flow rates of each species rather than concentration or conversion. Figure 8 shows the application of the *algorithm* to a sample reaction problem.

MECHANISMS / RATE LIMITING STEPS

One of the primary pedagogical advantages of developing mechanisms and rate limiting steps in heterogeneous catalysis is that it provides insight into how to analyze and plot the data in order to evaluate the rate law parameters. Most schools spend one-and-a-half to two weeks on heterogeneous catalysis. Once the basic concepts of

adsorption, surface reaction, and desorption are introduced in conjunction with the idea of a *rate limiting step*, one can derive many possible rate laws by varying the mechanism and rate limiting step. For example, consider the following dual site isomerization mechanism



One can write the rate laws for each step in this mechanism and then show that if the catalytic reaction ($A \rightarrow B$) in this example is surface reaction

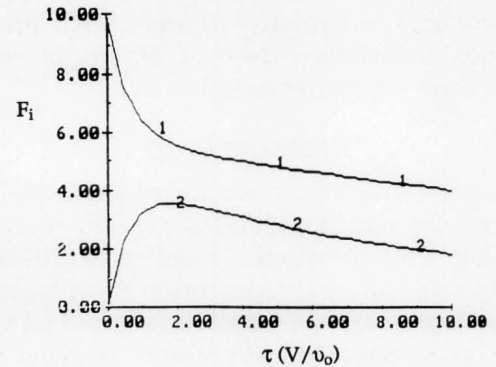


Figure 7. Composition profiles in a membrane reaction

MULTIPLE REACTIONS

STOICHIOMETRY

$A \rightarrow B \quad -r_{A1} = k_{A1} C_A$

$A \rightarrow C + D \quad -r_{A2} = k_{A2} C_A^2 \quad C_i = \frac{N_i}{V}$

$B + D \rightarrow E \quad -r_{B3} = k_{B3} C_B C_D$

RATE LAWS

$r_A = r_{A1} + r_{A2} = -k_{A1} C_A - k_{A2} C_A^2$

$r_B = r_{B1} + r_{B3} = k_{A1} C_A - k_{B3} C_B C_D$

$r_C = r_{C2} = k_{A2} C_A^2$

$r_D = r_{D2} + r_{D3} = k_{A2} C_A^2 - k_{B3} C_B C_D$

$r_E = r_{E3} = k_{B3} C_B C_D$

MOLE BALANCES

$\frac{dN_A}{dt} = r_A = -k_{A1} \frac{N_A}{V} - k_{A2} \frac{N_A^2}{V^2}$

•

•

$\frac{dN_E}{dt} = r_E = k_{B3} \frac{N_B N_D}{V^2}$

USE O.D.E. SOLVER

IT'S ONLY A MATTER OF BOOKKEEPING!

Figure 8. Variation on a theme: Multiple reactions

limited, a plot of the initial rate data in the form of

$$\left(\sqrt{\frac{P_{A0}}{-r'_{A0}}} \right)$$

versus P_{A0} should yield a straight line, as shown in Figure 9. By formulating different mechanisms and rate limiting steps, a variety of rate laws can be developed which provide a number of options on how to interpret the data and evaluate the rate law parameters.

Currently, there is an added incentive to study mechanisms in heterogeneous catalysis because of the emergence of chemical vapor deposition (CVD). CVD is widely used in the microelectronics industry, and the mechanisms for CVD are very similar to the mechanisms analyzed in heterogeneous catalysis. By developing fundamental laws and principles such as those in heterogeneous catalysis, the students will be prepared to analyze chemical reaction engineering problems in engineering technologies, e.g., CVD.

Other mechanisms and rate laws that can be easily incorporated into the original algorithm include:

- Enzyme kinetics (e.g., the Michaelis-Menten equations)

$$-r_s = \frac{\mu C_s}{1 + KC_s}$$

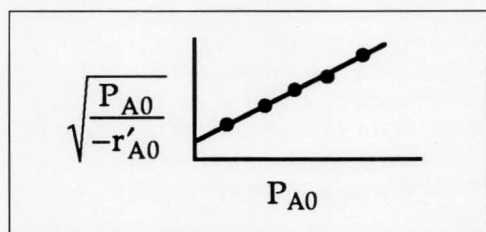


Figure 9. Gaining insight into how to analyze the data.

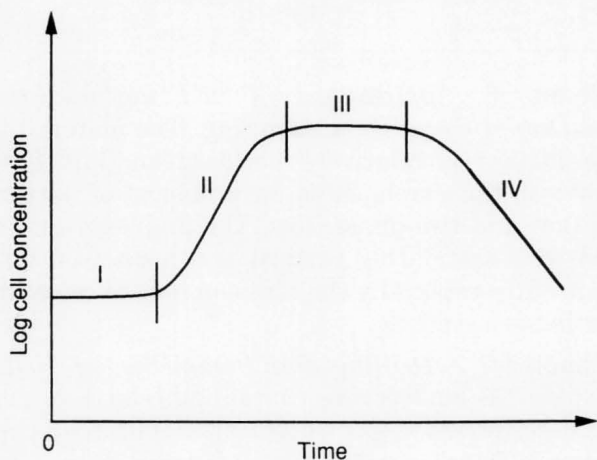


Figure 10. Phases of bacteria cell growth

- Bioreactors (e.g., the Monod equation for bacteria growth; see Figure 10)

$$r_g = \frac{\mu C_s}{1 + KC_s} C_B$$

- Pseudo Steady-State-Hypothesis

Reaction



Mechanism



$$-r_{A^* \text{ net}} = 0$$

$$-r_A = \frac{k_1 C_A^2}{1 + k_2 C_A}$$

- Polymerization (long chain approximation)

In studying these topics, rules are put forth to guide the student in the development of the underlying mechanism and of the rate law. Once the rate law(s) is formulated by analyzing the particular reaction mechanism, one can then use it (them) in step 2 of the algorithm (menu) to study the particular system of interest.

THINGS TO COME

Discussion of future directions in CRE with colleagues at Michigan and elsewhere is the same as discussion on other academic issues. Where n faculty members are gathered to express an opinion on an issue, there will be $1.5n$ opinions. But my feeling is that in the immediate future we will continue to focus on developing problems that exploit software packages such as POLYMATH, Maple, and Mathematica. We will see materials processing, environmental reaction modeling, reaction pathways and more applications on safety, batch processing, mixing, ecology (see Figure 11), and novel reactors (membrane batch reactors?) along with stochastic approaches for analyzing reacting systems.

Finally, in the not-too-distant future I see a greater emphasis on predicting the reactivity of different species, first perhaps by using empirical means but

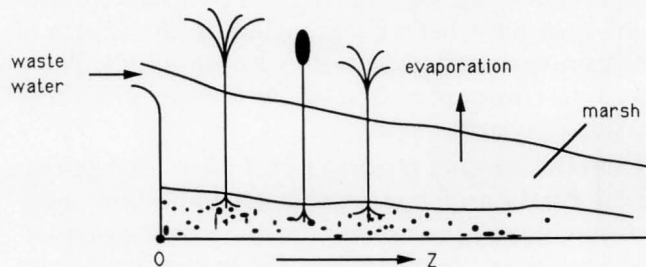


Figure 11. Using wetlands to degrade toxic wastes^[1,4]

KNOWLEDGE STRUCTURE

later on from first principles. This direction will lead us into what I would call molecular chemical reaction engineering. These and other topics not mentioned here may first be covered (and in some cases are *currently* covered) at the graduate level, but they will filter down to the undergraduate level. This filtering will occur much more rapidly than have analogous topics in the past.

SUMMARY

By arranging the teaching of chemical reaction engineering in a structure analogous to a French menu, we can study a multitude of reaction systems with very little effort. This structure is extremely compatible with a number of user-friendly ordinary differential equation (ODE) solvers. Using ODE solvers such as POLYMATH, the student is able to focus on exploring reaction engineering problems rather than on crunching numbers. Thus, one is able to assign problems that are more open-ended and to give students practice at developing their own creativity. Practicing creativity is extremely important, not only in CRE but also in every course in the curriculum, if our students are to compete in the world arena and succeed in solving the relevant problems that they will be faced with in the future.

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NOMENCLATURE

a catalyst activity

A	frequency factor, appropriate units
A_c	cross sectional area, m^2
C_i	concentration of species i (i = A,B,C,D), mol/dm^3
C_{pi}	heat capacity of species i, J/gK
D_p	particle diameter, m
E	activation energy, J/mol
F_i	entering molar flow rate of species i, mol/s
G	superficial gas velocity $g/m^2/s$
g_c	conversion factor
k	specific reaction rate (constant), appropriate units
K_e	equilibrium constant, appropriate units
L	length down the reactor, m
N_i	number of moles of species i, mol
P	pressure, kPa
r_i	rate of formation of species i per unit volume, $mol/s/dm^3$
r'_i	rate of formation of species i per unit mass of catalyst, $mol/s/g$
t	time, s
T	temperature, K
U	overall heat transfer coefficient, $J/dm^3 \cdot sK$
V	volume, dm^3
W	catalyst weight, g
X	conversion
y	pressure drop parameter, (P/P_0)
y_A	mole fraction of A

Subscripts

A	refers to species A
0	entering or initial condition

Greek

α	pressure drop parameter, g^{-1}
β	catalyst decay parameter, $s^{-1/2}$
ΔH_R	heat of reaction, $J/mole A$
δ	change in the total number of moles per mole of A reacted
ϵ	volume change parameter = $y_{A0} \delta$
ϕ	porosity
μ	viscosity, cp
ρ	density, g/dm^3
v	volumetric flow rate, dm^3/s
\square	

REVIEW: Natural Gas Engineering

Continued from page 109

There is a discussion of the compressibility of natural gases with an explanation of the various correlations that have been used, including the effects of nitrogen, carbon dioxide, and hydrogen sulfide. There are a few examples that show how to use these particular charts.

Chapter 5 • *Gas Hydrates and Their Prevention*. The formation of hydrates is an important issue associated with the production of natural gas, especially in colder circumstances. The discussion is quite complete.

Chapter 6 • *Applications of Flow Equations: Pressure Drop, Compression, Metering*. The material in this chapter is relatively standard on fluid flow. However, the emphasis is on problems of natural gas flow and two-phase flow. The problems associated with calculating vertical and horizontal flow are useful—especially the hints on how to calculate flow in such systems.

Chapter 7 • *Drilling and Completion of Wells*. Chapter 7 is an overview containing relatively concise descriptions of gas fracturing and acidizing operations. The discussion of well logging is a review of most of the various kinds of logs that are used.