INFLUENTIAL PAPERS IN CHEMICAL REACTION ENGINEERING

ROBERT L. KABEL
Pennsylvania State University
University Park, PA 16802

THIS PAPER DESCRIBES the genesis, development, implementation, and evaluation of a graduate level kinetics course based upon selected influential papers in chemical reaction engineering. The starting point was the following letter of January 1976.


No doubt you have your own favorites. So I am asking you along with a number of our colleagues to send me the references to a few papers that you consider to be of special importance.

One should not conduct a survey without sharing the results with the respondents. Also you may be interested in the cumulative opinion of your peers. So I will send a tabulation of the responses to everyone who contributes. Thank you for your help.

Twenty-two such letters were sent to individuals prominent in chemical reaction engineering. Sixteen responses were received including four from the researchers surveyed outside of the United States. All responses came from academic researchers although one industrial person was solicited. The list, shown in Table I, comprises the suggestions of fourteen of the respondents. Two respondents referred only to chapter bibliographies in their books. These responses, while useful, would produce an even longer list. Papers are listed first by frequency of mention and second by date of publication.

*Presented at the Summer School for Chemical Engineering Faculty held at Snowmass, Colorado, 1977.
This paper describes the genesis, implementation, and evaluation of a graduate level kinetics course based upon selected influential papers in chemical reaction engineering.
THE RESULTS OF THE survey led to a very nice course structure with very little artificial juggling. The papers selected for the course included all multiply mentioned ones except those which overlapped other selected papers. For practical reasons, extremely long papers were omitted. With one exception [Flory, P. J., "The Mechanism of Vinyl Polymerization," J. Am. Chem. Soc. 59, 241-253 (1937)] all papers selected came from the list of Table I. Table II presents the selected topics

and source papers in the order in which they were taken up in the course. It can be seen that the selected papers yield a reasonably coherent and comprehensive course according to subject matter. The most obvious omission is in the area of fluidized beds where none of the papers appeared to be quite suitable. Thermodynamics also is not mentioned in Table II, but it does play a role in a number of papers. Comments follow on the individual papers selected and their roles in the course.

Hougen and Watson (1943) was treated first for several reasons. Its emphasis on catalytic kinetics was a good starting point. As a very comprehensive paper, it gave a good introduction to

### TABLE II

<table>
<thead>
<tr>
<th>Course Organization by Subject</th>
<th>TOPIC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalytic Kinetics and Reactors</td>
<td>Hougen and Watson (1943)</td>
</tr>
<tr>
<td>Laboratory Reactors</td>
<td>Weekman (1974)</td>
</tr>
<tr>
<td>Flow Reactors (esp. CSTR's)</td>
<td>Denbigh (1944)</td>
</tr>
<tr>
<td>Residence Time Distribution</td>
<td>Danckwerts (1953)</td>
</tr>
<tr>
<td>Mass Transfer with Chemical Reaction</td>
<td>van Krevelen and Hoftijzer (1948)</td>
</tr>
<tr>
<td>Polymerization</td>
<td>Flory (1937)</td>
</tr>
<tr>
<td>Multiple Steady States and Stability</td>
<td>van Heerden (1958)</td>
</tr>
<tr>
<td>Stability and Control</td>
<td>Aris and Amundson (1958)</td>
</tr>
<tr>
<td>Pore Diffusion</td>
<td>Thiele (1939)</td>
</tr>
<tr>
<td>Effectiveness Factors</td>
<td>Weiz and Hicks (1962)</td>
</tr>
<tr>
<td>Heat Transfer in Packed Beds</td>
<td>Singer and Wilhelm (1950)</td>
</tr>
<tr>
<td>Coke Formation on Catalysts</td>
<td>Voorhies (1945)</td>
</tr>
<tr>
<td>Selectivity and Yield</td>
<td>Carberry (1966)</td>
</tr>
<tr>
<td>Commercial Reactors</td>
<td>—</td>
</tr>
<tr>
<td>Optimization</td>
<td>Chu and Hougen (1961)</td>
</tr>
</tbody>
</table>
much of what was to follow. Their original derivation of the plug flow reactor mass balance could well have appeared later in the course sequence. Nevertheless, it was desirable for me to present this paper first to set an example for the students and to allow them time to prepare their material (see Class Organization).

Weekman (1974) discussed selection of laboratory reactors. This paper is perhaps not a classic but it served well to introduce the various kinds of reactors. The students were asked to “Choose a chemical reaction of commercial importance and, utilizing the decision process suggested by Weekman, discuss the type of reactor best suited to study the reaction.” Toward the end of the course commercial reactors were considered.

Denbigh (1944) is surely a landmark paper in the quantitative treatment of flow reactors. We used it especially in relation to continuous flow stirred tank reactors; however, its treatment of plug flow was compared to Hougen and Watson’s. Denbigh also analyzed by-passing effects, selectivity and yield, and temperature programming of reactors. These subjects all arose again in subsequent papers.

Danckwerts’ (1953) paper on residence time distribution followed naturally after Denbigh’s. An important and unique class of heterogeneous reactions, gas-liquid, was powerfully influenced by van Krevelen and Hoftijzer (1948). To bring in more kinetics and the important subject of polymerization, we selected the 1937 paper by Flory on the mechanism of vinyl polymerization. Van Heerden’s work on multiple steady states is so well known that no further comment is required to demonstrate its influence. No one in the class discovered that 35-40 years earlier Liljenroth, F. G., “Starting and Stability Phenomena of Ammonia-Oxidation and Similar Reactions,” Chem. Met. Eng. 19, 287-293 (1918) had made many of the same points. Aris and Amundson (1958) provided a culmination of the treatment of homogeneous reaction systems with a seminal paper in the area of reactor control.

The most mentioned paper was Thiele (1939) on pore diffusion. This served as a basis for much of the work on the ubiquitous effectiveness factor and its ramifications, of which the paper of Weisz and Hicks (1962) is a foremost example. Way ahead of their time were Singer and Wilhelm (1950) on heat transfer in packed beds. This paper was chosen for the course but a sister paper [Bernard, R. A., and Wilhelm, R. H., “Turbulent Diffusion in Fixed Beds of Packed Solids,” Chem. Eng. Progr. 46, 233-244 (1950)] should be acknowledged. Voorhies (1945) was so successful in correlating coke formation on catalysts that very few papers appeared on this subject for twenty years. You might call its influence adverse.

Carberry’s (1966) article induced a good look back over our earlier papers in addressing the important and complex topic of selectivity and yield. This moved the class closer to the consideration of the details of commercial reactors. Finally the paper of Chu and Hougen (1961), though not very influential, served as a comprehensive example of design and intuitive optimization.

### TABLE III

Some General Characteristics of Chemical Reaction Engineering

<table>
<thead>
<tr>
<th>I. Types of Technical Activity</th>
<th>III. Other Important Aspects</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. Determination of Effect of Process Variables on Reactor Performance</td>
<td>A. Uniqueness</td>
</tr>
<tr>
<td>1. Variables 2. Performance</td>
<td>B. Quality Specifications</td>
</tr>
<tr>
<td>Temperature Conversion</td>
<td>C. Optimization</td>
</tr>
<tr>
<td>Pressure Yield</td>
<td>D. Scale Up</td>
</tr>
<tr>
<td>Composition 3. Analysis</td>
<td>E. Communication</td>
</tr>
<tr>
<td>Reactor Type Input + Process → ?</td>
<td>F. Integration</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>II. Some Related Subject Areas</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>A. Thermodynamics</td>
<td>A. Uniqueness</td>
</tr>
<tr>
<td>B. Thermostatics</td>
<td>B. Quality Specifications</td>
</tr>
<tr>
<td>C. Stoichiometry</td>
<td>C. Optimization</td>
</tr>
<tr>
<td>D. Chemical Kinetics</td>
<td>D. Scale Up</td>
</tr>
<tr>
<td>E. Economics</td>
<td>E. Communication</td>
</tr>
<tr>
<td>F. Statistics and Distribution</td>
<td>F. Integration</td>
</tr>
</tbody>
</table>

In addition to the source material, another uncommon aspect to this course was the designation of each student as a specialist with regard to one of the central papers. The student was responsible for advance study of the assigned article including references to earlier work.

---

FALL 1978
TABLE IV  
Quantitative Structure of  
Chemical Reaction Engineering

I. Some preliminary considerations
   A. Reaction stoichiometry
   B. Determine thermodynamic feasibility
   C. Heat effects
   D. Physical and chemical properties
   E. Analytical techniques
   F. Mass balances
   G. Energy balance

II. Kinetics
   A. Reaction mechanism
   B. Find rate equation
   C. Effect of temperature and pressure
   D. Experimentation
   E. Data handling and error analysis
   F. Flow ramifications
   G. Selectivity

III. Engineering aspects
   A. Catalyst selection
   B. Select reactor(s) type (simple or combination)
   C. Heat and mass transfer in heterogeneous and
      homogeneous systems
   D. Effectiveness factors
   E. Residence time distribution
   F. Process dynamics
   G. Optimization

IV. Other aspects
   A. Safety
   B. Pollution control
   C. Preprocessing and subsequent operations
   D. Further recommendations
   E. Admission of inadequacies

For each article there was an introductory lecture of about 15 minutes and assignment of homework. At the next class, the specialist gave his main lecture, discussed the homework, and made new assignments. In the following class period about 30 minutes were devoted to wrapping up all aspects of a given topic. The student also reviewed (as did the instructor) the homework, providing constructive criticism. Sometimes the specialist would assign required or optional supplementary reading. In this course structure each student served as a specialist in one area, studied all of the primary source papers and occasional supplements, worked homework assignments, lectured and reviewed homework papers, and took two written exams prepared and graded by the instructor.

For each article there was an introductory lecture of about 15 minutes and assignment of homework. At the next class, the specialist gave his main lecture, discussed the homework, and made new assignments.

CLASS ORGANIZATION

THE EARLY CLASSES were spent organizing the course and discussing the nature of chemical reaction engineering. Two results of these discussions are shown in Tables III and IV. It can be seen that most of these aspects could be expected to come up in the study of the central papers and their literary kin.

In addition to the source material, another uncommon aspect to this course was the designation of each student as a specialist with regard to one of the central papers. The student was responsible for advance study of the assigned article including references to earlier work. In this way he would understand the circumstances in which the article appeared. Further by checking the citation index and recent textbooks he could discover the influence of the assigned article on subsequent work. With consultation with the instructor, the specialist prepared lectures and homework assignments for the class.

For each article there was an introductory lecture of about 15 minutes and assignment of homework. At the next class, the specialist gave his main lecture, discussed the homework, and made new assignments. In the following class period about 30 minutes were devoted to wrapping up all aspects of a given topic. The student also reviewed (as did the instructor) the homework, providing constructive criticism. Sometimes the specialist would assign required or optional supplementary reading. In this course structure each student served as a specialist in one area, studied all of the primary source papers and occasional supplements, worked homework assignments, lectured and reviewed homework papers, and took two written exams prepared and graded by the instructor.

One final activity of the specialist was the preparation of a summary of his area with special attention to the documentation of key references. These summaries were reviewed by the instructor, typed, and distributed to the class. To give a more concrete picture of the course; the assignments, exam question, and summary relating to Hougen and Watson (1943) are given as an appendix to this article.

EVALUATION

At the end of the term, class members were asked to evaluate the course. Of the twelve respondents, eight were enthusiastic about the course structure (i.e. the use of student specialists), two preferred that the instructor handle it in a conventional manner, and two were neutral. Several students suggested that early in the term (but after the specialty topics have been assigned) instruction should be given in effective teaching.

The students were asked to indicate which two
INFLUENTIAL PAPERS
Continued from page 162
articles they liked best and which two they liked least. The results are given in Table V. Perhaps there is a message here, perhaps not.

My opinion is that the course was less efficient than a conventional textbook course in teaching facts, concepts, methods, etc. Still it was much more effective in conveying a comprehensive view of chemical reaction engineering than anticipated. The dynamics of history are not so easily and dramatically conveyed via technical texts. Also, with this course format, it was natural to bring each topic right up to date. With one or two exceptions only, these “influential papers” were excellently written. The students enjoyed a realistic teaching experience. Because of the nature of their involvement, they were surely provided with a strong feeling for the flow of research and technology.

There is much more to be said about the central and related papers than can be accommodated by this article. At the suggestion of one respondent, Michel Boudart, it is my intention to prepare an annotated collection of “Influential Papers in Chemical Reaction Engineering.” Your suggestions on papers to be included will be appreciated.

ACKNOWLEDGMENTS

I would like to acknowledge the contributions of the respondents to the original survey and the students in the course. Special thanks go to Mr. Deepak Perti for his assistance in the large amount of library work necessary to develop this course and for his service as a specialist in an area where he had unique expertise.

APPENDIX

CHEMICAL ENGINEERING 535
Assignments
Monday 28 March 1977
Read Hougen and Watson (1943)
Work #1 and 2 below.
Wednesday 30 March 1977
Read Weller (1956) and Boudart (1956). Photocopies of these two articles are available in the ChE Reading Room and on reserve in the Physical Sciences Library. In addition the AIChE Journal is available in both of these locations.
Optional reading—Weller (1975) gives excellent up-to-date perspective on the topic of catalytic kinetics. Copies of this article are also located in the reading room and the library.
Work #3 and 4 below.

TABLE V
Article Preference

<table>
<thead>
<tr>
<th></th>
<th>(most − least = net)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hougen &amp; Watson</td>
<td>(6 − 0 = 6)</td>
</tr>
<tr>
<td>Thiele</td>
<td>(3 − 0 = 3)</td>
</tr>
<tr>
<td>Carberry</td>
<td>(3 − 1 = 2)</td>
</tr>
<tr>
<td>Danckwerts</td>
<td>(3 − 1 = 2)</td>
</tr>
<tr>
<td>Denbigh</td>
<td>(2 − 0 = 2)</td>
</tr>
<tr>
<td>Weisz &amp; Hicks</td>
<td>(2 − 0 = 2)</td>
</tr>
<tr>
<td>van Krevelen &amp; Hofijzer</td>
<td>(2 − 0 = 2)</td>
</tr>
<tr>
<td>van Heerden</td>
<td>(1 − 0 = 1)</td>
</tr>
<tr>
<td>Weekman</td>
<td>(1 − 1 = 0)</td>
</tr>
<tr>
<td>Voorhies</td>
<td>(1 − 2 = −1)</td>
</tr>
<tr>
<td>Flory</td>
<td>(1 − 2 = −1)</td>
</tr>
<tr>
<td>Singer &amp; Wilhelm</td>
<td>(1 − 4 = −3)</td>
</tr>
<tr>
<td>Aris &amp; Amundson</td>
<td>(0 − 6 = −6)</td>
</tr>
<tr>
<td>Chu &amp; Hougen</td>
<td>(0 − 9 = −9)</td>
</tr>
</tbody>
</table>

1. The vapor phase hydrogenation of ethylene (C₂H₄ + H₂ → C₂H₆) on a well dispersed platinum catalyst (0.05% Pt on SiO₂) is described by Sinfelt, J. Phys. Chem., 68, 856 (1964). The overall reaction is virtually irreversible and is considered to occur according to the following mechanism.

   C₂H₄ + l ⇌ C₂H₅l
   H₂ + 2l ⇌ 2 H⁺l
   C₂H₅l + H⁺l → C₂H₄⁺l + l
   C₂H₄⁺l + H⁺l → C₂H₆⁺l + 2l

Reaction (4) is very rapid. Reaction (3) is the rate determining step.

a) Use the methods of Hougen and Watson (1943) to derive an equation for the rate of reaction of ethylene. The equation should contain only rate and equilibrium constants and partial pressures of the reaction components.

b) It is known that hydrogen adsorption, although significant (Kₜ is finite) and necessary, is slight. Use this information to simplify your rate equation.

c) At rather low temperatures the rate of reaction at constant ethylene partial pressure will be directly proportional to the square root of the hydrogen partial pressure and at constant hydrogen partial pressure will be inversely proportional to the ethylene partial pressure. Explain why these experimental observations are consistent with your rate equation from part (b).

2. Write a three dimensional, unsteady state mass balance on a differential element of a fixed bed catalytic reactor. Show how to reduce this equation to the one dimensional, steady state form for a plug flow reactor, given by equation (56) in Hougen and Watson (1943).

3. Refer back to the system of problem #1. For experiments conducted at constant P_H₂ but over a wide range of P_C₂H₄, sketch a graph of log r vs log P_C₂H₄. Indicate quantitative features on the graph where you can.
4. Akers and White, Chem. Eng. Progr. 44, 553 (1948) reported the following data for the synthesis of methane from CO and H₂ over a nickel-kieselguhr catalyst at 1 atm and approximately 800°C with a feed gas containing 44.5% CO, 53.9% H₂, 0.4% CO₂ and 1.2% inert.

<table>
<thead>
<tr>
<th>In catalyst-hr/mol feed</th>
<th>mol CH₄ in product/mol feed</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.13</td>
<td>0.187</td>
</tr>
<tr>
<td>2.97</td>
<td>0.154</td>
</tr>
<tr>
<td>1.68</td>
<td>0.120</td>
</tr>
<tr>
<td>0.38</td>
<td>0.045</td>
</tr>
</tbody>
</table>

Determine the specific rate and tabulate as a function of the mol CH₄/mol feed.

Examination #1 (Take home)
1. In Hougen and Watson (1943)* equation (12) gives the rate of a catalytic reaction in terms of adsorbed phase concentrations and the concentration of vacant sites, c_v. In equation (14) the adsorbed phase concentrations are gone and fluid phase concentrations appear. During our study of this paper, one student asserted that there was an error in equation (14). Show in complete detail how equation (14) is obtained from equation (12). If there is an error in equation (14), give the correct result and compare it to equation (14).

**SUMMARY OF STUDY ON HOUGEN AND WATSON (1943)**

This excellent paper was a remarkably comprehensive, trendsetting, and futuristic paper. It dealt effectively with many of the topics which have proved to be important in the more than thirty years since its appearance. Among these are catalytic kinetics, catalyst deactivation, effectiveness factors, external mass transfer, and fixed bed reactor analysis and design. One can see that many of the topics now considered crucial in research, teaching, and practice of chemical reaction engineering were anticipated by Hougen and Watson. This review chooses those two items in which the impact of this 1943 paper has been greatest: catalytic kinetics and the tubular reactor mass balance.

The above equation provided a quantitative basis for rational tubular reactor design. Before its appearance semi-quantitative scale up procedures were used. A rather sophisticated illustration of this earlier mode of thought can be provided by reference to an article by Emmett and Kummer (1943). There they give 9 graphs of % NH₃ in the exit gas versus space velocity for three temperatures, three pressures, and three N₂:H₂ feed ratios. From such graphs (which might come from the laboratory or pilot plant) encompassing the processing conditions of interest, one can find the space velocity to achieve a specified conversion. With the assumed analogy between tubular and batch reactors, the intuitive argument that the space velocity is inversely proportional to the contact time (imperfect for reactions like ammonia synthesis in which there is a change in the total moles), and the hypothesis that only contact time determinants were present, such equations could be scaled up directly by calculating the commercial reactor volume from the space velocity and the specified commercial feed rate. It would remain to determine the reactor shape (usually characterized by the length to diameter ratio) from previous experience with similar systems. Major factors in this determination would be catalyst characteristics and heat transfer. Among other things, it was the physical processes like heat and mass transfer and mechanical characteristics of catalysts and reactors that made scale up from small to large reactors so uncertain.

Apart from its design application, the tubular flow reactor mass balance enabled the isolation of reaction kinetics from reactor characteristics. This in turn allowed much better reaction rate data to be obtained in catalytic reactions and led ultimately to improved characterizations (rate equations) of catalytic kinetics.

*Some errata in Hougen and Watson (1943) are as follows: Equation (9), C_v should be C_v'.

Eqn (14), K_a C_{A1} C_i should be K_a a_{A1} C_i

p. 533, left side, line 25 should be 27

p. 538, right side, line 10, unabsorbed should be unadsorbed

My opinion is that the course was less effective than a conventional textbook course in teaching facts, concepts, methods, etc. Still it was much more effective in conveying a comprehensive view of chemical reaction engineering than anticipated.
derived from a Hougen and Watson kinetic analysis of the rate data agreed quite well with the corresponding constants obtained directly from independent adsorption experiments. Their results generated other papers by Lapidus and Peterson (1965), Kabel (1968), and Mezaki and Kittrell (1968).

Almost 20 years after his original article Weller (1975) has written a very comprehensive analysis of the state of catalytic kinetics. It is recommended reading for those wishing an up-to-date perspective.

REFERENCES


FUEL CELLS


Reviewed by Robert D. Walker, University of Florida

This small book of thirteen chapters presents a reasonably adequate discussion of the major aspects of fuel cells at a quite elementary level. It will be useful, therefore, for introducing new students or casual readers to the subject without confusing them with unnecessary details. In spite of this advantage, however, it appears to this reviewer that the book suffers from a number of shortcomings. In the first place, the author includes no references to sources of the data used; indeed, there are no references to any other publications. The reader is, therefore, left with no suggestions as to more advanced literature. Secondly, the case for fuel cells as energy sources is consistently presented too optimistically; the efficiency and performance described are substantially in excess of those achieved practically. Finally, the usefulness of the book for the American reader is diminished by the author's discussion of British fuel cells alone; no American (or other) fuel cells are described.