

A Course in

FUNDAMENTALS OF COAL UTILIZATION AND CONVERSION PROCESSES

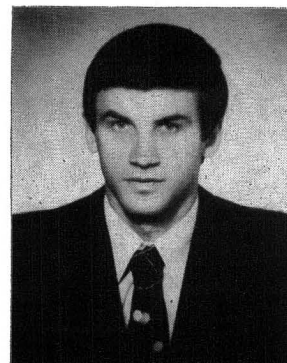
LJUBISA R. RADOVIC*

*University of Concepción
Concepción, Chile*

IT IS DIFFICULT TO think of a more interdisciplinary science than that of coal utilization (combustion) and conversion (pyrolysis, liquefaction, gasification). For decades combustion has been of equal interest to chemists as well as chemical, mechanical, and aerospace engineers. The recent world-wide renewal of interest in coal conversion technology has resulted in even greater heterogeneity of backgrounds among coal experts. Recent economic evaluations show that the commercialization of many conversion processes will only be feasible when significant reductions in their complexity are achieved. These, in turn, can be achieved only if significant advances are made in the fundamental understanding of coal chemistry. Coal structure, for example, is an elusive concept whose elucidation still represents a major research challenge to many organic chemists. In many cases, the determination of physical and chemical properties of coal and coal products, which is of equal interest to chemists, materials scientists, and engineers, is not a straight-forward application of classical techniques. Major improvements in instrumental methods of analysis (*e.g.*, cross-polarization, magic angle spinning NMR; Fourier transform IR; small-angle X-ray scattering) in the past decade are already contributing to a qualitative increase in understanding some of the above mentioned topics.

Recent economic evaluations show that the commercialization of many conversion processes will only be feasible when significant reductions in their complexity are achieved.

*Present Address: Department of Chemical Engineering, The Pennsylvania State University, University Park, PA 16802.



Ljubisa Radovic is a visiting assistant professor of chemical engineering at the University of Concepcion, Chile (1983-1984). He received his BSChE degree (1977) from the University of Belgrade, Yugoslavia, and his PhD degree in fuel science (1982) from the Pennsylvania State University. His research and teaching interests are in the general area of heterogenous kinetics and catalysis, particularly as applied to coal and carbon utilization and conversion.

This situation is responsible for the difficulties in bridging the gap between coal science and technology. It is, for example, quite common to find metallurgical-coke makers who are not familiar with the concept of mesophase. On the other hand, many coal scientists without "hands-on" experience (author not excluded) may have practical problems which can be as trivial as, for example, the "optimization of operation" of a barbecue "reactor." The design of a graduate course on coal utilization and conversion should attempt to contribute to alleviate some of these difficulties. It should also, of course, present a more or less critical review of the recent literature and indicate the major areas in which further research is most desirable and/or expected. The lack of textbooks with this orientation and the abundance of coal-related research publications (of widely varying value) appearing since the 1973 energy crisis, do not make this (in itself ambitious) task any easier.

COURSE STRUCTURE AND CONTENTS

Table 1 presents the outline of the one-semester (30 two-hour sessions) course that the author has

© Copyright ChE Division, ASEE, 1985

TABLE 1
Course Outline

INTRODUCTION: STRUCTURE AND PROPERTIES OF COAL [G1-G4] (4 sessions)

- Origin, traditional properties, and classifications
- Petrographic and mineralogical composition
- Structure [1, 2]
- Porosity and surface area [3-5]

COAL PYROLYSIS AND CARBONIZATION [G1-G4] (6 sessions)

- Fundamentals [6, 7]
 - Product yield and distribution
 - Kinetics [8-13]
 - Hydropyrolysis
- Processes of pyrolysis (COED, Rockwell, Occidental, etc.)
- Processes of carbonization (coke making)

COAL LIQUEFACTION [G1-G4, 1] (6 sessions)

- Fundamentals
 - Solubility
 - Product yield and distribution [14, 15]
 - Kinetics [16-18]
 - Catalysis [19-23]
- Processes (SRC, EDS, H-Coal, etc.)

COAL COMBUSTION AND GASIFICATION [G1-G4, 24] (12 sessions)

- Fundamentals
 - Thermodynamics
 - Kinetics [25-28]
 - Catalysis [29-31]
- Combustion processes (grate, fluidized-bed, pulverized-coal) [32, 33]
- Gasification processes (Lurgi, Koppers-Totzek, Winkler, Texaco, etc.)

SUMMARY: ECONOMIC AND ENVIRONMENTAL CONSIDERATIONS [G1-G4] (2 sessions)

developed and taught to engineering graduate students at the University of Concepción, Chile. As stated in the title and seen in Table 1, the emphasis is on fundamentals. The processes are discussed rather briefly, with the primary purposes of illustrating how the fundamental concepts are applied in practice on pilot-plant, demonstration, or commercial scale.

In the first session I present an overview and the philosophy of the course, together with the highlights of every topic. I consider this very important because it minimizes the danger of students "not seeing the forest for the trees" when some topics are subsequently dealt with in considerable depth. The introductory chapter exposes the students to basic coal terminology. The importance of both rank and petrographic composition in determining chemical and physical properties of coal is emphasized. The structure of

coal is introduced with the help of Given's and Wisser's models and is discussed in terms of basic aromatic and hydroaromatic units, cross-links, and functional groups. The typical structures and composition of these are discussed in turn as functions of coal rank. The origin and nature of mineral matter in coals of different rank are briefly reviewed. In the section on porosity, the molecular-sieve microporous structure of coal and chars (cokes) is presented. The often misunderstood implications of the presence of micropores for the measurement of surface areas are discussed. Dubinin's theory of volume filling of micropores is complemented (and contrasted) with the classical BET approach.

The following chapters on coal pyrolysis and carbonization, liquefaction, and gasification and

The processes are discussed briefly, with the primary purposes of illustrating how the fundamental concepts are applied in practice on pilot-plant, demonstration, or commercial scale.

combustion all have the same basic structure. The fundamentals are presented first in terms of thermodynamics, kinetics, and catalysis, and the most important processes are subsequently described and briefly discussed.

In the chapter on pyrolysis (fluids, primary products) and carbonization (solid, primary product), the necessity of empirical determination of product yields and distribution is emphasized. The effects of the principal process variables (bed density, temperature-time history, pressure, etc.) are discussed and the importance of secondary reactions of the primary volatiles is pointed out. The transformation of coal to coke is described and the importance of understanding meso-phase formation and growth for controlling coke strength and reactivity is briefly discussed. The various levels of sophistication in the treatment of the kinetics of rapid pyrolysis are discussed. The experimental techniques are presented and the difficulties in defining with precision the temperature-time histories of the devolatilizing coal particles are emphasized. In hydrolyrolysis the role of hydrogen in stabilizing the free radicals is discussed and the concept of nascent active sites is introduced to explain the enhanced yields of methane. The flow diagrams, reactor schemes, and typical operating conditions are discussed for representative processes.

Liquefaction fundamentals are introduced with

a brief analysis of coal solubility and a discussion of the problems associated with liquid product characterization and the definition of conversion. The classical preasphaltene-asphaltene-oil scheme as well as Mobil's SESC (sequential elution by specific solvents chromatography) technique is presented. The effects of solvent properties, coal rank, and reaction conditions on product yield and distribution are analyzed. The importance of hydrogen transfer and balance is emphasized. The various levels of kinetic treatment and modeling existent in the literature are discussed. As in pyrolysis, the difference between simple curve-fitting approaches and models which are based on knowledge of the actual chemistry is pointed out. The discussion on catalysis is limited primarily to the effect of inherent mineral matter, pyrite in particular. Flowsheets, typical operating conditions and product yields of representative direct liquefaction processes are briefly reviewed. The complexities involved are emphasized. The concept of indirect liquefaction is then introduced and briefly discussed as an alternative and also in order to bring up the importance of coal gasification, which is discussed extensively in the following chapter.

Coal combustion (in O_2) and gasification (in H_2O , CO_2 , H_2) are treated together because their fundamentals are, of course, essentially the same. In contrast to pyrolysis and liquefaction, the yield and distribution of products are discussed using thermodynamics. The consequences of the underlying assumption that char activity is equal to that of graphite are briefly analyzed. The kinetics of coal char gasification are introduced as a more or less straightforward application of the general gas/solid reaction theory. The difficulties in determining intrinsic (mass-transport-control-free) kinetic parameters for reactions of microporous chars are thoroughly analyzed. The surface mechanisms of adsorption, reaction, and desorption are also discussed. The concept of carbon active sites is introduced and the similarities and differences among carbonaceous solids of varying degree of crystallinity, from lignite chars to graphite, are emphasized. The effects of coal rank and pyrolysis conditions on char gasification reactivity are discussed in terms of variation of total and active surface area. A critical review of the recent kinetic models is presented. Catalysis of coal gasification is discussed as both inevitable (inherent) and desirable (induced). The inherent catalytic role of calcium in low-rank coals is point-

ed out. The mechanisms of catalysis are briefly discussed. The importance of, and difficulties in, measuring catalyst dispersion and determining turnover frequencies (necessary for meaningful comparison of catalysts) are analyzed. Both combustion and gasification processes are discussed in terms of conceptual differences between fixed-bed, fluidized-bed and entrained-flow reactors. In particular, the design of pulverized-coal combustors is discussed using two extreme simplifying approaches: plug-flow-reactor theory (Rosin equation) and perfectly-stirred-reactor theory. Representative gasification processes of first, second, and third generation (commercial, demonstration, and pilot scale, respectively) are described with particular emphasis on reactor type, gasifying medium and method of supplying heat. The effect of these characteristics on the composition and calorific value of the product gas is analyzed.

The final chapter on economic and environmental aspects addresses the fact that the selection of a coal conversion or utilization process is not based solely on the characteristics of the reactor. The main issues are presented with the objective of developing a feeling for the orders of magnitude of costs and environmental impact. Available economic evaluations from some of the most recent publications are briefly analyzed.

COURSE OBJECTIVES AND REQUIREMENTS

The topics included in the course cannot, of course, be presented and discussed all with the same depth. This is partly due to the time constraint and the extensiveness and dispersed nature of the literature available, but also to the instructor's own limitations. The presentation of the main issues in each area, rather than depth of analysis, is the primary goal. The fact that there exists only qualitative knowledge of many aspects of coal conversion is made clear and the importance of carefully designed experimental work is stressed. It is thought that this approach helps the students to appreciate in which direction the mainstream research efforts should be oriented. A point is made also of the necessity to combine experimental work, mostly performed by chemists and fuel scientists, with the process modeling efforts of chemical engineers. It is my conviction that by bridging this (yet another) interdisciplinary gap, many synergistic effects can be achieved.

The course has no formal prerequisites and no previous knowledge of coal is assumed. It can be taught, in a somewhat scaled-down version, at the

undergraduate level after the students have completed the courses on thermodynamics and chemical reaction engineering (or physical chemistry, for non-chemical engineering majors). Ideally, it is intended as an introductory graduate course for students interested in doing research in coal conversion or utilization.

The list of references in Table 1 is, of course, meant to be representative rather than comprehensive. The general references are used throughout the course. (Only selected chapters of G1 are discussed in some detail, namely chapters 3, 12, 19 and 23.) The material on (and the fate of) the various conversion processes is constantly updated on the basis of information published in *Chem. Eng. Progress*, *C&E News*, and similar journals.

The work requirements include rather extensive regular reading assignments, occasional homework problems, and a 20-minute seminar on a selected important research paper in the student's area of interest. The mid-term and final exam have the form of short essays. Five or six topics are given and the student is expected to address the basic issues of four or five of them in a concise but all-inclusive manner.

ACKNOWLEDGMENT

I appreciate the comments of Alfredo Gordon on the contents of this paper.

GENERAL REFERENCES

- G1 Elliott, M. A. (Ed.), *Chemistry of Coal Utilization*, 2nd Suppl. Vol., Wiley, New York, 1981.
- G2 Grainger, L. and J. Gibson, *Coal Utilization: Technology Economics and Policy*, Halsted Press/Wiley, New York, 1981.
- G3 Probst, R. F. and R. E. Hicks, *Synthetic Fuels*, McGraw-Hill, New York, 1982.
- G4 Wen, C. Y. and E. S. Lee (Eds.), *Coal Conversion Technology*, Addison-Wesley, Reading, MA, 1979.

SPECIFIC REFERENCES

- 1. Whitehurst, D. D., T. O. Mitchell, and M. Farcasiu, *Coal Liquefaction: The Chemistry and Technology of Thermal Processes*, Academic Press, New York, 1980.
- 2. Meyers, R. A. (Ed.), *Coal Structure*, Academic Press, New York, 1982.
- 3. Mahajan, O. P. and P. L. Walker, Jr., "Porosity of Coal and Coal Products," in *Analytical Methods for Coal and Coal Products*, Vol. I (C. Karr, Ed.), Academic Press, New York, 1978, p. 125.
- 4. Gregg, S. J. and K. S. W. Sing, *Adsorption, Surface Area and Porosity*, 2nd Ed., Academic Press, London, 1982.
- 5. Dubinin, M. M., *Carbon* 18, 355 (1980); 19, 321 (1981).
- 6. Anthony, D. B. and J. B. Howard, *AIChE J.* 22, 625 (1976).

- 7. Marsh, H. and P. L. Walker, Jr., "The Formation of Graphitizable Carbons via Mesophase: Chemical and Kinetic Considerations," in *Chemistry and Physics of Carbon*, Vol. 15 (P. L. Walker, Jr. and P. A. Thrower, Eds.), Marcel Dekker, New York, 1979, p. 229.
- 8. Badzioch, S. and P. G. W. Hawksley, *Ind. Eng. Chem. Process Des. Dev.* 9, 521 (1970).
- 9. Scaroni, A. W., P. L. Walker, Jr., and R. H. Essenhigh, *Fuel* 60, 71 (1981).
- 10. Nsakala, N. Y., R. H. Essenhigh, and P. L. Walker, Jr., *Combust. Sci. Technol.* 16, 153 (1977).
- 11. Solomon, P. R. and M. B. Colket, 17th Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, 1979, p. 131.
- 12. Golikeri, S. V. and D. Luss, *AIChE J.* 18, 277 (1972).
- 13. Gavalas, G. R., R. Jain, and P. H. K. Cheong, *Ind. Eng. Chem. Fundam.* 20, 122 (1981).
- 14. Neavel, R. C., *Fuel* 55, 237 (1976).
- 15. Yarzab, R. F., P. H. Given, W. Spackman, and A. Davis, *Fuel* 59, 81 (1980).
- 16. Curran, G. P., R. T. Struck, and E. Gorin, *Ind. Eng. Chem. Process Des. Dev.* 6, 166 (1967).
- 17. Cronauer, D. C., Y. T. Shah, and R. G. Ruberto, *Ind. Eng. Chem. Process Des. Dev.*, 17, 281 (1978).
- 18. Szladow, A. J. and P. H. Given, *Ind. Eng. Chem. Process Des. Dev.*, 20, 27 (1981).
- 19. Guin, J. A., A. R. Tarrer, J. W. Prather, D. R. Johnson, and J. M. Lee, *Ind. Eng. Chem. Process Des. Dev.* 17, 118 (1978).
- 20. Guin, J. A., A. R. Tarrer, J. M. Lee, L. Lo, and C. W. Curtis, *Ind. Eng. Chem. Process Des. Dev.* 18, 371 (1979).
- 21. Guin, J. A., A. R. Tarrer, J. M. Lee, H. F. Van Brackle, and C. W. Curtis, *Ind. Eng. Chem. Process Des. Dev.* 18, 631 (1979).
- 22. Brooks, D. G., J. A. Guin, C. W. Curtis, and T. D. Placek, *Ind. Eng. Chem. Process Des. Dev.*, 22, 343 (1983).
- 23. Garg, D. and E. N. Givens, *Ind. Eng. Chem. Process Des. Dev.* 21, 113 (1982).
- 24. Laurendau, N. M., *Prog. Energy Combust. Sci.*, 4, 221 (1978).
- 25. Smith, I. W., *Fuel* 57, 409 (1978).
- 26. Lewis, P. F. and G. A. Simons, *Combust. Sci. Technol.* 20, 117 (1979).
- 27. Mahajan, O. P., R. F. Yarzab, and P. L. Walker, Jr., *Fuel* 57, 643 (1978).
- 28. Radovic, L. R., P. L. Walker, Jr. and R. G. Jenkins, *Fuel* 62, 849 (1983).
- 29. McKee, D. W., "The Catalyzed Gasification Reactions of Carbon," in *Chemistry and Physics of Carbon*, Vol. 16 (P. L. Walker, Jr. and P. A. Thrower, Eds.), Marcel Dekker, New York, 1981, p. 1.
- 30. "Proceedings, Int. Symposium, Fundamentals of Catalytic Coal and Carbon Gasification," Amsterdam, The Netherlands, September 1982.
- 31. Radovic, L. R., P. L. Walker, Jr. and R. G. Jenkins, *J. Catal.* 82, 382 (1983).
- 32. Palmer, H. B. and J. M. Beer (Eds.), *Combustion Technology: Some Modern Developments*, Academic Press, New York, 1974.
- 33. Singer, J. G. (Ed.), "Combustion: Fossil Power Systems," *Combustion Eng.*, Windsor, CT, 1981. □