LBL-15295
UC-13 c.2

Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

ENERGY & ENVIRONMENT DIVISION

RECEIVED
LAWRENCE
BERKELEY LABORATORY
AUG 10 1983
LIBRARY AND
DOCUMENTS SECTION

FY 1982 Annual Report

CHEMICAL PROCESS RESEARCH AND DEVELOPMENT PROGRAM

June 1983

TWO-WEEK LOAN COPY
This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 6782.

ENERGY
AND ENVIRONMENT
DIVISION

Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

LBL-15295 c.2

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

LBL-15295

ENERGY & ENVIRONMENT DIVISION ANNUAL REPORT

CHEMICAL PROCESS RESEARCH AND DEVELOPMENT PROGRAM

FY 1982

Elton J. Cairns
Program Leader
Head, Energy & Environment Division
and
Associate Director, LBL

Report Coordinator

Maya Osowitt

Energy and Environment Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

Prepared for the U.S. Department of Energy Under Contract No. DE-AC03-76SF00098

CONTENTS

CHEMICAL PROCESS RESEARCH AND DEVELOPMENT PROGRAM STAFF 1–iv

INTRODUCTION 1–1

Chemical Liquefaction of Biomass

THE DIRECT LIQUEFACTION OF BIOMASS
H.G. Davis, C. Figueroa, R. Gansley, L. Schaleger, and D. Watt 1–2

Fuels from Biomass by Biochemical Processes

BIOCONVERSION OF CELLULOSE
H.W. Blanch, C.R. Wilke, A.F. Sciamanna, K. Murphy, D. Wiley, and H. Wong 1–6

PRODUCTION OF SUGARS FROM CELLULOSE
C.R. Wilke, H.W. Blanch, N. Hendy, B. Maiorella, A. Mancuso, K. Murphy, S. Orichowskyj, and A. Sciamanna 1–11

Oil Shale and Petroleum–Related Research

HOMOGENEOUS CATALYTIC HYDROGENATION: REGIOSPECIFIC REDUCTIONS OF POLYNUCLEAR AROMATIC AND HETEROAROMATIC NITROGEN COMPOUNDS CATALYZED BY TRANSITION–METAL CARBONYL HYDRIDES
R.H. Fish, A.D. Thormodsen, G.A. Cremer, T. Vermeulen, and H. Heinemann 1–19

MOLECULAR CHARACTERIZATION AND FINGERPRINTING OF VANADYL PORPHYRIN AND NON–PORPHYRIN COMPOUNDS FOUND IN VARIOUS HEAVY CRUDE PETROLEUMS AND THEIR ASPHALTENES
R.H. Fish, J.J. Komlenic, B. Wines, and T. Vermeulen 1–24

SYNTHESIS, STRUCTURAL ELUCIDATION, AND STEREOCHEMISTRY OF FIVE–COORDINATE ORGANOARSENIC CATECHOLATES
R.H. Fish and R.S. Tannous 1–31

ORGANOMETALLIC GEOCHEMISTRY: ISOLATION AND IDENTIFICATION OF ORGANOARSENIC COMPOUNDS FROM GREEN RIVER FORMATION OIL SHALE
R.H. Fish, R.S. Tannous, W. Walker, C.S. Weiss, and F.E. Brinckman 1–34

Coal–Related Research

PROCESSING OF CONDENSATE WATERS FROM COAL GASIFICATION
C.J. King, J. MacGlashan, D. Mohr, P. Mackenzie, R. Thompson, and J. Bixby 1–38

Electrochemical Energy Storage Research

TECHNOLOGY BASE RESEARCH PROJECT FOR ELECTROCHEMICAL ENERGY STORAGE
E.J. Cairns and F.R. McLarnon 1–43

BATTERY ELECTRODE STUDIES
E.J. Cairns, F.R. McLarnon, J.H. Flatt, M. Isaacson, M.H. Katz, P. Lessner, K.G. Miller, and J.T. Nichols 1–45

CHEMICAL PROCESSES RESEARCH AND DEVELOPMENT PROGRAM STAFF

Elton Cairns, Program Leader
Harvey Blanch, Deputy Program Leader

Myra Baker
James Bixby
Kathy Boyer
Patricia Bronnenberg
Garth Burns
Joni Buttke
Robert Chung
Gregg Cremer*
Hubert Davis
Robert Demyanovich
Morton Denn
Jesse Dobson
Michael Eames
Betsy Elzufon
Sabri Ergun
Mark Featherstone
Carlos Figueroa
Richard Fish
James Flatt
Alan Foss
Raymond Gansley
Robert Goldberg
Edward Grens
Donald Hanson
Neil Hendy
Mark Isaacson
Cihan Karatas
Marc Katz
Eileen Keefe
C. Judson King
John Komlenic
Phillip Lessner
Gary Lipscomb
Scott Lynn
John MacGlashan
Patricia MacKenzie
Frank McLarnon
Brian Maiorella
Anthony Mancusco
Kenneth Miller
Donald Mohr
Robert Moore
Curtis Munson
Thomas Murphy
Stuart Naftel
James Nichols
Steven Oblath
Timothy Oolman
Stephan Orichowsky
Michael Pedersen
Javier Perez
David Robinson
Larry Schaleger
Aldo Sciamanna
John Senetar
Mohindar Singh
Kathy Streibel
Raja Tannous
Rodney Thompson
Arne Thormodsen*
Theodore Vermeulen
Bruce Vickroy
James Walter
David Watt
Dale Wiley
Charles Wilke
Brian Wines
Harry Wong
Nasser Yaghoubzadeh
Rafael Zamora

---

*Materials and Molecular Research Division Staff

CHEMICAL PROCESS RESEARCH AND DEVELOPMENT PROGRAM

INTRODUCTION

The Chemical Process Research and Development Program has four main projects applying chemistry and chemical engineering to problems in the production of unconventional new fuels, their environmental impact, and energy storage. These projects are:

(a) Production of synthetic fuels, predominantly by coal liquefaction
(b) Processing of effluent gases and liquids resulting from such synthetic-fuel production, to provide acceptable waste or recycle streams
(c) Production of liquid fuels from biomass
(d) Electrochemical energy storage.

Each of these projects focuses on transport-process principles, chemical kinetics, thermodynamics, separation processes, and organic and physical chemistry.

The first project is the liquefaction of coal. Selective hydrogenation achieves a substantial conversion of coal to liquid at moderate temperatures. Homogeneous metal-organic catalysts have interesting selectivities with respect to their ability to promote different types of hydrogenation and cracking involved in liquefaction. Another aspect of this work involves examining metal impurities in fossil fuels, especially crude petroleum and shale oil. These impurities have been shown to be metallo-organic compounds. Their isolation and identification is necessary if means are to be devised to separate them from the fossil fuels. One approach is to use metal-organic complexing to separate these impurities.

The second project involves the development of novel and improved methods for processing synfuel condensate waters to make them suitable for recycle, thereby minimizing process-water requirements. The main emphasis is on physiochemical methods, particularly solvent extraction and stripping, to remove organics. Identification of the contaminating organics is difficult, but necessary to permit development of appropriate solvents for their removal. LBL studies have successfully examined simultaneous solvent extraction in removal of ammonia and acid gases by stripping.

The conversion of biomass to liquid fuels has been an area of considerable research and development within the Chemical Process Program over the past several years. Two main approaches have been taken. The first is the liquefaction of biomass and peat. A bench-scale continuous liquefaction unit has been developed to evaluate the process steps and to determine the relevant engineering parameters and optimal conditions for reduction of the biomass with synthesis gas or H_2-CO mixtures. Catalytic hydrogenation has been used to increase the value of the product oils. The second approach is the biological conversion of wood and agricultural residues to ethanol. An enzymatic hydrolysis of these cellulosic materials has been developed to yield monomeric hexose and pentose sugars. These can be subsequently fermented to produce ethanol. Various high-rate fermentation processes have been developed, and novel processes for ethanol recovery that are less energy intensive than conventional processes are being examined.

The electrochemical energy storage program provides research to develop advanced battery systems for electric vehicle and stationary energy storage applications. General problem areas include identification of new electrochemical couples for advanced batteries, determination of technical feasibility of the new couples, improvements in battery components and materials, establishment of engineering principles applicable to electrochemical energy storage and conversion, and the assessment of fuel-cell technology for transportation. Major emphasis is on applied research that will lead to superior performance and lower life-cycle costs.

THE DIRECT LIQUEFACTION OF BIOMASS*

H.G. Davis, C. Figueroa, R. Gansley, L.L. Schaleger, and D. Watt

The usual objective of synthetic liquid fuel programs has been the production of high-quality distillate fuels. This has not been the case with biomass (primarily wood) liquefaction. Here the product that arises most readily is a heavy, bituminous material, pumpable as a liquid but generally suitable only as boiler fuel. Because of a high content of oxygenated compounds, there have been fears (not always warranted) about its stability and corrosiveness.

The advantages of this "crude" product over raw biomass as a fuel lie in its effective densification (improvement in heating value per unit weight and per unit volume), dewatering, and conversion into a form that can be stored and pumped as a liquid. However, we currently question whether this product is valuable enough to justify commercial development.

Revamping the liquefaction program to focus on the goal of a distillate fuel has been difficult for both technical and economic reasons, but as the Biomass Group's FY 1982 program progressed, elements of a possible process appeared. Besides discussing our success in defining the limitations and possibilities of previously tested liquefaction processes, we will present the new approach, primarily as a basis for future effort.

ACCOMPLISHMENTS DURING FY 1982

In FY 1982, our continuous liquefaction unit (CLU) was operated successfully to obtain operating conditions and product-yield distributions for the LBL, or water-slurry, liquefaction process. By comparing these results with those for the PERC, or wet-oil recycle, process, we established the strengths and failings of the two approaches. As the year progressed, however, we were more and more impressed with the disadvantages of both processes. We also explored the use of solvolysis (dissolution of wood by appropriate solvents), studied since 1979.[1-5] We outlined a process based on this approach and studied some of its key elements through batch experiments.

Our ability of characterize the products of liquefaction improved considerably. We modified the SESC technique[6] of sequential elution, which we adapted to biomass oils in 1981, to improve speed and reproducibility.[7] It is proving to be a useful tool for following product changes that result from changes in operations. We have also applied various forms of high-performance liquid chromatography (HPLC) to improve our characterization of water-soluble products, molecular-weight distributions, and other features.

Comparison of CLU and PERC Operations

The operation of the CLU and its results have been described in detail in several publications.[8-10] We give here only a brief summary of the findings, comparing them with those for the wet-oil recycle process.

(1) At best—from Douglas fir wood with product oils having oxygen contents of 15-16%— the yield distribution by the water-slurry process is as follows: oil, 40% by weight; water-soluble organics (about half carboxylic acids or their anions), 25 wt.%; CO_2 and water, 35 wt.%. If char forms, the oil yield is reduced further. On the basis of data from the Albany process development unit (PDU), the oil-recycle or PERC process can result in 53% oil, 8% water solubles, and 39% CO_2 + water. The differences are the result of the high recycle of product oil, especially product-water solubles, and of the high ratio of oil to water in the PERC process.

(2) Aspen is a better raw material or substrate than Douglas fir. Oil yields can be about

*This work was supported by the Assistant Secretary for Conservation and Solar Energy, Office of Solar Applications for Industry, Biomass Energy Systems Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098 and was funded through Battelle Pacific Northwest Laboratory, Lead Laboratory for the U.S. Department of Energy, Biomass Energy Systems Division, Thermochemical Conservation Program under Contract No. DE-AC06-76RL01830.

10% higher and water-soluble organic yields about 10% lower. The oil product is more fluid and contains less oxygen at comparable severities (e.g., 13 wt.% vs. 16 wt.%.

(3) Little or no reducing gas is consumed in the water-slurry process—again in contrast to the PDU-PERC result. Hence the gas can be CO, H_2, synthesis gas (syngas), or probably an inert gas like nitrogen. CO-steam liquefaction is largely pyrolysis under a pressure of steam and a reducing gas.

(4) In the range studied (initial aqueous slurry ~6 to 9), pH made little difference in product distribution, except to affect the yield of formic acid.

(5) About 350-360°C with about 20 minutes reaction time is a good operating range. Above 360°C, there is a danger of slurries going dry as the critical temperature and pressure of water are approached.

The CLU has now been modified so that slurry pyrolysis, catalytic hydrogenation with either a trickle bed or a CSTR, or a modification of the original CO-steam can be studied as needed.

Observations on LBL and PERC Processes

Our observations on the state of the existing processes come from our own CLU studies (single-pass water-slurry or LBL process) and from a careful review of the Albany, Oregon, PDU (wet-oil recycle or PERC) operation. (The PDU was operated for DOE by Rust Engineering.) Data on Rust Engineering's[11,12] Test-Run 12 (TR-12), supplemented by additional data from Rust, were statistically analyzed. We were able to reach credible atom balances for a range of reaction severities.

The results of this study verify Rust Engineering's experimental oil yield of 53%. They indicate that, over the full range of temperatures used by Rust, yields and consumption vary as follows:

- oil—53 wt.% to 51 wt.%
- H_2O—7% to 8%
- CO reacted—0.3 mol/100 lbs wood feed to 0.6 mol
- Water-soluble organics—9% to 7%
- CO shifted to CO_2—~1.2 mol/100 lbs wood feed, independent of temperature, but dependent on CO/wood ratio.

This yield distribution is better than that we found with the water-slurry process. The cost of obtaining this improvement, however, is great. These costly steps are required:

- Grinding of wood feed to flour
- Drying of wood
- High recycle of product oil (in TR-12, on the order of 19 parts recycled for each part new oil generated).
- High recycle of water and water-soluble organics.
- Substantial usage of CO (0.5 mol/100 lbs feed = 179 scf/100 lbs $\cong$ 1300 scf/barrel oil produced).
- Shift reaction that converts ~3100 scf/bbl CO to hydrogen.

Our general conclusion is that the oil-recycle process is operable on the basis of the TR-12 results, and that the water-slurry process probably can be made operable on the basis of our CLU work. But economic or commercial feasibility of either route cannot be achieved without great and far from obvious improvements. TR-12 demonstrated the operability of several necessary components of an ultimate process—notably the ability to heat the oil-wood mix to 360-370°C in a direct-fired preheater and the stability of the oil during recycle. But a much better process than either PERC or LBL is needed.

Characterization of Products

Methods developed during FY 1981 were applied throughout the year to characterize our products and follow changes in variables.

The SESC (sequential elution by solvent chromatography)[13] procedure was especially valuable. A substantial improvement in its speed and reproducibility was obtained by applying the recently developed "flash chromatography" technique. By this method, a whole, crude biomass oil product is divided into 8 (sometimes 9) fractions, mainly according to polarity. The reproducibility of the modified procedure is shown by the results of Table 1. In a recent publication,[7] we give detailed discussion of the method and the results found with our products.

Several high-performance liquid chromatography (HPLC) techniques were developed or improved dur-

Table 1. SESC fractionation of TR-7 oil.

Fraction		Amount (%)	Std. Dev.
F1,2	15% Benzene-hexanes	3.5	± 0.4
F3	Chloroform	16.8	± 2.3
F4	6% Ether-chloroform	44.1	± 3.7
F5	4% Ethanol-ether	21.2	± 3.0
F6	Methanol	6.5	± 1.3
F7	4% Ethanol-$CHCl_3$	1.0	± 0.4
F8	4% EtOH-THF	2.5	± 1.7
F9	HOAc	4.2	± 0.6

ing the year. With size-exclusion chromatography (HPSEC), we obtained molecular-weight distributions of our product samples. With ion-exchange chromatography (HPIEC), we obtained quantitative yields of the light carboxylic acids and ions. Using Douglas fir as substrate, we found that one such acid, glycolic, was the largest single product of the reaction.

Proposed Use of Solvolysis

We have developed[14] a conceptual schematic of a process based on solvolysis (Fig. 1). Biomass feed, with only incidental drying or grinding, is heated with a phenolic recycle oil at about 240°C. Separated water, if any, is removed by decantation, and the solvolysis product—effectively a solution of the biomass in recycle oil—is catalytically hydrogenated, or otherwise partially depolymerized at temperatures around 360°C.

The final product is distilled, at atmospheric pressure if possible, or under some variation (≥50 mm pressure). The overhead material is the product. This is further stabilized by hydrogenation to remove reactive oxygen groups like carboxyl and olefinic double bonds. If necessary for the end use, phenol hydroxyl is converted to ether by alkylation.

The kettle product is the recycle solvolytic agent. If insolubles (chars) are formed in the process, the kettle liquid must be drawn off and used as fuel or gasifier feed.

Preliminary experiments have been carried out with several forms of biomass.[14] They indicate that lower-boiling material is indeed formed during hydrogenation, oxygen content is reduced, and the product remains a solvolytic agent. But a large amount of research needs to be done.

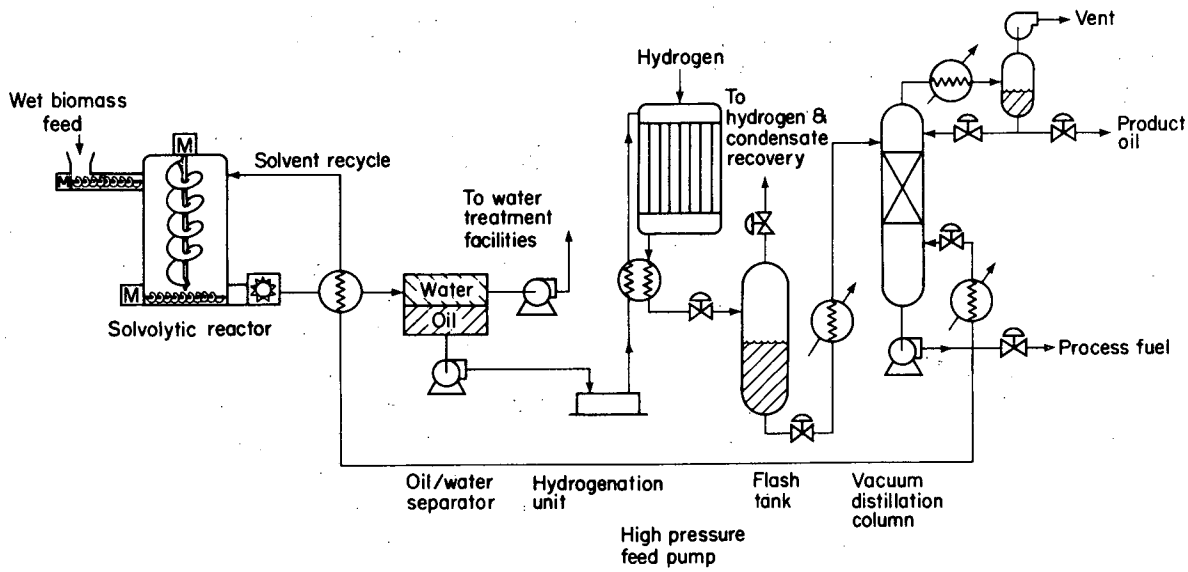


Figure 1. Schematic of solvolysis/ hydrogenation process. (XBL 827-7096)

PLANNED ACTIVITIES FOR FY 1983

(1) We will institute basic studies of the chemistry of solvolysis, using such model feeds as wood components (cellulose, xylan, lignin), lignin monomers, glucose, etc. Phenol will be used as a model solvolytic agent, but recycle oils must also be studied.

(2) The chemistry of catalytic hydrogenation of (a) crude solvolytic product and (b) distillate from the product of primary hydrogenation will be studied. Commercial hydrogenation and hydrocracking catalysts will be tried as well as cheap homemade catalysts like precipitated, high-surface-area iron sulfide.

(3) Basic studies of the roles of the water-gas shift reaction and of formate ion and formate esters in the chemistry of reduction by carbon monoxide will be performed.

(4) The possible role of supercritical solvents in solvolysis, liquefaction, or product separation will be investigated. This should include fundamental phase-rule studies with model compounds.

(5) The organic chemistry of upgrading the distillate product, e.g., of alkylation with fuel-grade methanol or ethanol, will be studied.

REFERENCES

1. Yu, S.-M. (1982), *Solvolytic Liquefaction of Wood under Mild Conditions*, Ph.D. Dissertation, Lawrence Berkeley Laboratory Report LBL-14096.
2. Seth, M., et al. (1981), "Catalytic Liquefaction of Biomass," in *Chemical Process Research and Development Program, FY 1980*, Lawrence Berkeley Laboratory Report LBL-10319.
3. Yu, G., Vermeulen, T., and Davis, H. (1982), "The Solvolysis of Douglas Fir Wood in Acidified Organic Solvents," in *Chemical Process Research and Development Program, FY 1981*, Lawrence Berkeley Laboratory Report LBL-11983.
4. Davis, H.G., Schaleger, L.L., and Yaghoubzadeh, N. (1982), "Chemistry and Mechanisms of Wood Liquefaction," in *Energy and Environment Division Annual Report, FY 1981*, Lawrence Berkeley Laboratory Report LBL-13500.
5. Davis, H.G., et al. (1981), *Research and Development Activities on Direct Liquefaction Technology*, April-June 1981 Quarterly Report, Lawrence Berkeley Laboratory Report LBID-426.
6. Schaleger, L.L., and Davis, H.G. (1982), "Progress in the Characterization of the Products of Direct Liquefaction of Douglas Fir," presented at the Workshop/Review Meeting on Biomass Liquefaction Research, National Research Council of Canada, Saskatoon, Saskatchewan, February 16–17, 1982, Lawrence Berkeley Laboratory Report LBL-14017.
7. Davis, H.G., et al. (1982), "The Products of Direct Liquefaction of Biomass," presented at the International Conference on Fundamentals of Thermochemical Biomass Conversion, Estes Park, Colorado, October 18–22, 1982, Lawrence Berkeley Laboratory Report LBL-15143.
8. Figueroa, C., Schaleger, L.L., and Davis, H. G. (1981), "LBL Continuous Bench-Scale Liquefaction Unit, Operation and Results," presented at the 6th Annual Conference on Energy from Biomass and Wastes, Lake Buena Vista, Florida, January 25–29, 1982, Lawrence Berkeley Laboratory Report LBL-13709.
9. Davis, H.G., Figueroa, C., Kloden, D., and Schaleger, L.L. (1982), *Research and Development Activities on Direct Liquefaction Technology*, October-December 1981 Quarterly Report, Lawrence Berkeley Laboratory Report LBID-470.
10. Davis, H.G., Figueroa, C., and L.L. Schaleger (1982), "Research and Development Activities on Direct Liquefaction Technology," presented at the 14th Biomass Thermal Chemical Conversion Contractors Meeting, Arlington, Virginia, June 23–24, 1982, Lawrence Berkeley Laboratory Report LBL-14595.
11. Thigpen, P., and Berry, W. (1982), "Liquid Fuels from Wood by Continuous Operation of the Albany, Oregon Liquefaction Facility," presented at the 6th Annual Conference on Energy from Biomass Wastes, Lake Buena Vista, Florida, January 25–29, 1982.
12. Berry W., and Thigpen, P. (1981), "Operation of the Biomass Liquefaction Facility, Albany, Oregon," in *Proceedings of the 13th Biomass Thermochemical Conversion Contractors' Meeting*, Arlington, Virgina, October 1981.

13. Farcasiu, M. (1977), "Fractional and Structural Characterization of Coal Liquids," *Fuel 56*, p. 9.
14. Davis, H.G., et al. (1982), *Research and Development Activities on Direct Liquefaction Technology*, July-September 1982 Quarterly Report, Lawrence Berkeley Laboratory Report LBID-638.

FUELS FROM BIOMASS BY BIOCHEMICAL PROCESSES

BIOCONVERSION OF CELLULOSE*

H.W. Blanch, C.R. Wilke, A.F. Sciamanna, K. Murphy, D. Wiley, and H. Wong

STUDIES OF THE MECHANISM AND KINETICS OF CELLULOSE HYDROLYSIS

Most studies of enzyme kinetics have been concerned with homogeneous systems: the action of soluble enzymes on soluble substrates. The minority of studies focusing on heterogeneous systems have largely been confined to the action of insoluble (immobilized) enzymes on soluble substrates. Much less research has looked at soluble enzymes on insoluble substrates. The enzymatic hydrolysis of cellulose falls in this latter area. Its interest is thus both practical (for its applications in saccharification technology) and theoretical (as an investigation into this lesser-known area of enzyme kinetics).

The kinetics of enzymatic hydrolysis of cellulose depends on the structural features of cellulose, the nature of the enzyme system, and the interaction of substrate and enzyme. Structural features pertinent to the development of a model for cellulose hydrolysis include particle size and degree of crystallinity. These influence both the surface available for enzyme binding and the rate of reaction, since amorphous regions are degraded readily, while hydrolysis of crystalline regions proceeds only slowly. The nature of the cellulase system is described by the relative amounts of the constituent enzymes—endoglucanases, exoglucohydrolases, cellobiohydrolases and β-glucosidases. The interaction of substrate and enzymes includes adsorption, reaction, and product-inhibition phenomena. Development of a mechanistic model incorporating all three groups of factors is the objective of this work.

Accomplishments During FY 1982

The scheme for the purification of components of the cellulase complex obtained from *Trichoderma reesei* has been modified (Fig. 1). In this scheme, changes were made in the composition of eluting buffers to optimize the separation, and steps were added to remove salts that interfered with separation. Results of the ion-exchange step (the second step of the purification scheme shown in Fig. 1) appear in

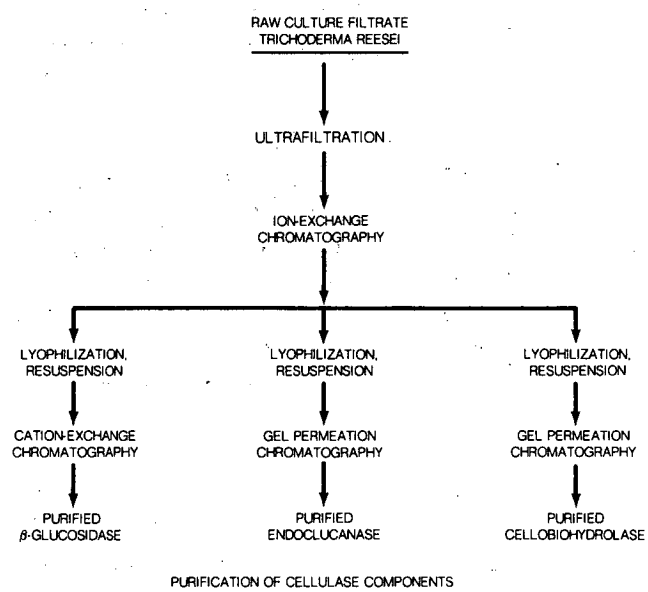


Figure 1. Purification of cellulase components. (XBL 8111-12529B)

*This work was supported by the Director of Energy Research, Office of Basic Energy Sciences, Division of Chemical Science of the Department of Energy under Contract No. DE-AC03-76SF00098.

Fig. 2. Gel permeation chromatography of the cellobiohydrolase has demonstrated that this component was purified to homogeneity.

Planned Activities for FY 1983

Determination of Langmuir isotherms for the adsorption of purified endoglucanase and purified cellobiohydrolase, separately and in varying proportions, is the first step in developing a model to describe the interaction of these enzymes from *T. reesei*.

Kinetic and inhibition constants for the action of β-glucosidase and association constants for glucose-endoglucanase and cellobiose-cellobiohydrolase will be obtained from kinetic studies on the action of β-glucosidase in the presence of variable amounts of cellobiohydrolase, endoglucanase, cellobiose, and glucose. This will characterize the homogeneous reactions in enzymatic hydrolysis of cellulose and, in conjunction with adsorption data, will comprise the kinetic model being devised.

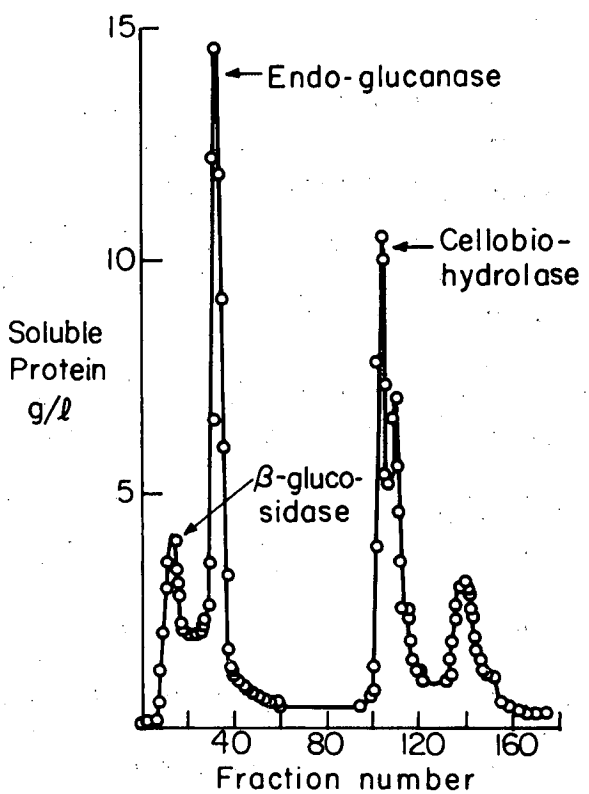


Figure 2. Ion-exchange chromatography of cellulase components. (XBL 8111-12529A)

FUNDAMENTAL STUDIES OF HIGH-PRODUCTIVITY FERMENTATIONS: YEAST NUTRITION

A basic study of nutrient requirements for yeast fermentation of sugars to ethanol is important because nutrients are a significant part of ethanol production costs and because complex sources such molasses and corn-steep liquor provide many of the minerals, the growth factors, and the major effects of ethanol-producing processes in media.

Up to now, little effort has been devoted to defining the active components of these complex sources in yeast fermentation and to defining their optimal ratios for a balanced medium. A balanced medium will eliminate the cost of excess components and prevent their inhibitory effects on build-up in recycle processes with selective ethanol removal. Batch and continuous fermentations are therefore being carried out with synthetic and semisynthetic media to define quantitatively how all major media components are used for cell growth and ethanol production.

Accomplishments During FY 1982

The most important growth factors were identified in batch fermentation, and continuous cultures were used to determine the optimum levels of all medium components in ethanol fermentation. The case considered was a medium with only 10–15 g/l glucose to eliminate the effects of ethanol inhibition and glucose inhibition on the medium requirements.

A novel procedure extending developments by Nateles and Battat[1] was employed. Each medium component is made the limiting substrate in terms of cell and ethanol yields. The limiting nutrient is first determined by observing which component, when injected as a concentrated pulse directly into the fermentor, produces a transient increase in cell mass or ethanol. The yields of cell mass and ethanol with respect to the limiting nutrient can then be determined from the known continuous or steady-state feed rate of the limiting nutrient and from the known productivity rates of cell mass and ethanol prior to the injection. When this limiting nutrient is found, its concentration in the feed reservoir, which has been feeding at a steady-state dilution rate, is increased so that the nutrient is no longer yield-limiting up to a given level of cell mass and ethanol. This component

can then be eliminated from further testing while the next component in the chain is made yield-limiting.

The minimal medium (no vitamins added) showed low cell and ethanol productivities with only about one-third of the available glucose consumed. Biotin added as a pulse gave a very positive response; when added continuously to the feed, it increased cell and ethanol productivities about three times.

Pantothenic acid was the next growth factor to show a positive pulse response after the biotin requirement was met. In fact, previous studies had shown that unless the biotin requirement was met first, pantothenic acid and pyridoxine did not show positive responses, which implies that biotin is needed for a critical reaction before pantothenic acid or pyridoxine can be utilized in subsequent reactions. The addition of pantothenic acid to the feed medium increased ethanol and cell production to the point where the glucose was almost entirely consumed so that the glucose itself became the limiting substrate.

Pyridoxine produced positive pulse and steady-state responses. A combination of thiamine, inositol, nicotinic acid, and p-aminobenzoic acid was pulsed into the fermentor with a positive response. After steady state was re-established, thiamine was pulsed with a positive response. However, the steady-state response to thiamine addition to the feed showed no significant change. Subsequent injections of the rest of the combination—inositol, nicotinic acid, and p-aminobenzoic acid—to the fermentor also showed no response. Yeast extract then gave a positive pulse response, indicating there were still nutrient limitations.

To observe the growth-limiting concentrations of the nutrient minerals, the medium was diluted to 10 g/l glucose and to two-thirds of the previous minimal and growth-factor concentrations for this glucose level. An injection of a mineral mixture gave a positive response, as did a subsequent injection of $(NH_4)_2SO_4$, which indicated that it was the limiting component responsible for the earlier positive response. The steady-state response for $(NH_4)_2SO_4$ addition to the feed showed a significant cell increase but a smaller ethanol increase.

With a recycle process that can produce high cell densities, high specific ethanol productivity will result in high total productivity. However, the cost of ethanol production will be largely determined by its yield with respect to its sugar substrate. Sugar should therefore be made the limiting substrate. This requires that the usage or, inversely, the yield of ethanol with respect to all other medium components must be known so that they will not become limiting.

Planned Activities for FY 1983

Future work will be directed at scale-up of the low-glucose, low-ethanol conditions to higher glucose (100 g/l) and correspondingly higher ethanol. As a basis for comparison, yeast extract as a general nutrient source will be studied at varying concentrations. Then the effects of varying individual mineral and vitamin concentrations in a highly synthetic medium and in a semisynthetic medium with an inexpensive complex component—for example, corn-steep liquor—will also be investigated. Finally, when we have determined the usage requirement of each medium component from studies of synthetic or highly synthetic media, the best composition of the inexpensive complex component of the medium, and all costs, we will then determine the optimum blend of components for the medium through a linear program. This program can be used to give the economically optimum medium as prices change for various components.

MODELS OF YEAST GROWTH, ETHANOL PRODUCTION, AND OXYGEN UPTAKE UNDER FERMENTATION CONDITIONS

Under aerobic conditions, yeast demand for oxygen can be determined from the overall reaction for aerobic growth given by Harrison[2]:

$$\begin{array}{ccccccc} 0.55556\ C_6H_{12}O_4 & + & 0.30017\ NH_3 & + & 1.45729\ O_2 & \rightarrow & \\ 100.00\ g & & 5.10\ g & & 46.63\ g & & \\ 0.30017\ C_6H_{10}O_3N & + & 2.28276\ H_2O & + & 1.53234\ CO_2 & & \\ 43.23\ g & & 41.08\ g & & 67.42\ g & & \end{array} \quad (1)$$

Almost all of the oxygen consumed by this reaction goes into the catabolic function of respiration as the terminal electron acceptors in oxidative phosphorylation. This use of oxygen for respiration is well understood and large enough to be easily measured.

However, oxygen is also required for less well understood biosynthesis under both aerobic and fer-

mentative conditions. It has been shown repeatedly that complete anaerobiosis results in very low cell and ethanol productivity.[3,4] Adding both ergosterol and unsaturated fatty acids to the medium gives relatively high cell yields even under anaerobiosis.[2] This suggests that oxygen is required for the synthesis of ergosterol and unsaturated fatty acids. Both are important components of yeast lipid, the bulk of which is required for cell membranes. However, the biosynthesis requirement for oxygen is very low and difficult to measure. It is even ignored by Harrison[2] in his overall reaction for fermentation:

$$\begin{array}{ccccc} 0.55556\ C_6H_{12}O_6 & + & 0.01214\ NH_3 & \rightarrow & \\ 100.00\ g & & 0.21\ g & & \\ 0.01214\ C_6H_{10}O_3N & + & 0.05697\ C_3H_8O_3 & & \\ 1.748\ g & & 5.241\ g & & \\ +\ 0.01204\ C_4H_6O_4 & + & 0.00071\ C_4H_{10}O & & \\ 1.42\ g & & 0.05\ g & & \\ +\ 0.01164\ H_2O & + & 1.03076\ CO_2 & & \\ 0.21\ g & & 45.32\ g & & \\ +\ 1.00380\ C_2H_6O & & & & \\ 46.17\ g & & & & \end{array} \qquad (2)$$

The objective of this research was to determine the fermentative oxygen requirement and its relationship to cell and ethanol productivities.

Accomplishments During FY 1982

All yeast fermentations are linear combinations of the approximate reactions (1) and (2) of Harrison. Thus it is possible to calculate the fermentative oxygen demand by measuring the total oxygen uptake and subtracting out the oxygen uptake from aerobic growth. The relative extent of aerobic growth to fermentation can be determined from the respiratory quotient, which is the ratio of the carbon dioxide evolution rate to the oxygen consumption rate.

Using a continuous culture, we determined the carbon dioxide evolution rate by measuring the total gas outlet rate from the fermentor and by measuring its CO_2 composition by gas chromatography. The oxygen consumption rate was measured by the dynamic method described by Taguchi and Humphrey.[5] This method requires measuring the dissolved oxygen concentration (D.O.) in the fermentor as a function of time with a dissolved oxygen probe. After a steady-state D.O. is reached, the gas inlet containing the O_2 source is turned off. The slope of the D.O. decline gives the O_2 consumption rate. A typical trace is shown in Fig. 3. The initial steady D.O. level is varied by changing the agitation rate.

The yeast metabolism is assumed to be still predominantly fermentative even with the D.O. raised, mainly because of glucose repression of respiration and also because of the short time exposure to the higher D.O. level in some cases. According to Suomalainen, Nurminen, and Oura,[6] glucose concentrations over 50-100 mg/l result in a mainly or partly fermentative metabolism, even with intense aeration. Ferdouse et al.[7] observed that mitochondria and aerobic cytochromes appeared in yeast between 3 to 6 hours after the transition from anaerobiosis to aerobiosis in the presence of only 0.02 to 1.66 m*M* glucose.

The maximum possible specific oxygen consumption rate for a given specific growth rate is q_{O_2} max. However, it is achieved only when the dissolved oxygen concentration is high enough to provide sufficient driving force for transport or for reaction, whichever is rate-limiting. The linear relationship in Fig. 4 between q_{O_2} max and the dilution rate implies that a constant quantity of oxygen is used per unit yeast

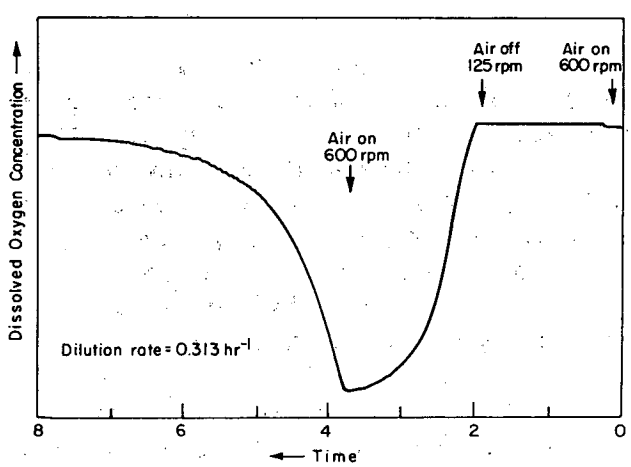


Figure 3. Typical dissolved oxygen trace for q_{O_2} and K_La. (XBL 822-5278)

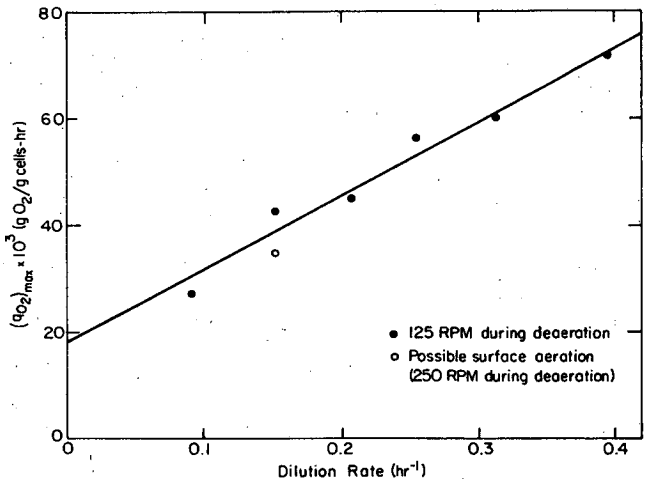


Figure 4. Maximum specific oxygen consumption versus dilution rate. (XBL 822-5286)

mass. This relationship can best be quantified as follows:

$$q_{O_2} \max (hr^{-1}) = 0.0175 + 0.140 \times \text{dilution rate } (hr^{-1})$$

The slope of this equation implies that 0.140 g O_2/g cells is the maximum required for growth for dilution rates up to 0.39 hr^{-1}. The intercept gives the maintenance requirement of 0.0175 g O_2/g cells/hr.

Planned Activities for FY 1983

Other Models of Yeast Growth and Ethanol Production

Future work will be directed at explaining the unaccounted-for use of oxygen during fermentation and investigating the transport mechanism for oxygen into the cells. Preliminary calculations indicate passive diffusion is sufficient to satisfy oxygen requirements for the fermentative conditions used.

In addition to studying the effects of oxygen uptake, the effects of varying dissolved oxygen tension will be studied to determine if there is an optimum value for maximum ethanol productivity and yield. The dissolved oxygen range to be studied will be from below the detectable limits of current probes to the toxic levels much above atmospheric conditions. As a method for determining dissolved oxygen from measurements of the gas-phase oxygen concentration, fermentor mass transfer characteristics for oxygen will be studied. In particular, the effects of CO_2 on the degree of mixing in the gas phase will be examined.

Other environmental effects to be studied further are the inhibition of glucose, ethanol, and carbon dioxide. Glucose inhibition will be studied in batch culture with initial concentrations from 100 g/l to 400 g/l. The ethanol inhibition study will first check Bazua's model[8]; the inhibition effects of the previously minimal medium supplemented with biotin, pantothenic acid, pyridoxine, and thiamine will then be determined. The effect of carbon dioxide will be examined at concentrations from about 10% to about 90% by volume in the fermentor headspace.

By-Product Inhibition in Cell Recycle and Vacuum Fermentation

Inhibition by secondary fermentation products may limit the ultimate productivity of glucose in ethanol fermentation processes.[9] New processes are under development whereby ethanol is selectively removed from the fermenting broth to eliminate ethanol inhibition effects, but these processes can concentrate minor secondary products to the point where they become toxic to the yeast. Vacuum fermentation selectively concentrates nonvolatile products in the fermentation broth; membrane fermentation systems may concentrate large molecules that are sterically blocked from membrane transport; and extractive fermentation systems, employing nonpolar solvents, may concentrate small organic acids. Production rates and inhibition levels in continuous fermentation with *Saccharomyces cerevisiae* have been determined for many by-products, including acetaldehyde; glycerol; formic, lactic, and acetic acids; 1-propanol; 2-methyl-1-butanediol; and 2,3-butanediol, to assess their potential effects on new fermentation processes. Mechanisms for the various inhibition effects observed were proposed. These mechanisms will be described in forthcoming publications.

REFERENCES

1. Mateles, R.J., and Battat, E. (1974), "Continuous Culture Used for Media Optimization," *Appl. Microbiol. 28*(6), p. 901–905.

2. Harrison, J.S. (1971), "Yeast Production" in *Progress in Industrial Microbiology 10,* D.J.D. Hockenhull, Ed., Churchill Livingstone, Edinburgh, p. 129–177.
3. Haukeli, A.D., and Lie, S. (1971), "Experimental Conditions Affecting Yeast Growth," *J. Inst. Brew. 77,* p. 253–258.
4. Cysewski, G.R., and Wilke, C.R. (1976), "Fermentation Kinetics and Process Economics for the Production of Ethanol," Ph.D. Thesis, Department of Chemical Engineering, University of California, Berkeley.
5. Taguchi, H., and Humphrey, A. (1966), "Dynamic Measurement of the Volumetric Oxygen Transfer Coefficient in Fermentation Systems," *J. Ferm. Tech. 44*(12), p. 881–889.
6. Suomalainen, H., Nurminen, T., and Oura, E. (1973), "Aspects of Cytology and Metabolism of Yeast," in *Progress in Industrial Microbiology 12,* D.J.D. Hockenhull, Ed., Churchill Livingstone, Edinburgh, p. 109.
7. Ferdouse, M., et al. (1972), "Quantitative Studies of the Development of *S. cerevisiae* Mitochondria," *Biotechnol. Bioeng. 14,* p. 1007–1026.
8. Bazua, C.D., and Wilke, C.R. (1977), "Ethanol Effects on the Kinetics of a Continuous Fermentation with *Saccharomyces cerevisiae,*" *Biotechnol. Bioeng. Symp. No. 7,* p. 105–118.
9. Maiorella, B., Blanch, H.W., and Wilke, C.R. (1981), "By-Product Inhibition Effects on Ethanol Fermentation by *Saccharomyces cerevisiae,*" presented at the American Chemical Society Annual Meeting, New York City, August 17, 1981, Lawrence Berkeley Laboratory Report LBL-13343.

PRODUCTION OF SUGARS FROM CELLULOSE*

C.R. Wilke, H.W. Blanch, N. Hendy, B. Maiorella, A. Mancuso, K. Murphy, S. Orichowskyj, and A.Sciamanna

This research has focused on the hydrolysis of lignocellulosic materials to sugars and their subsequent fermentation to ethanol and other fuel-grade chemicals. Applied studies have examined the kinetics of enzymatic hydrolysis of cellulose and hemicellulose fractions for optimal sugar production; the physical and chemical nature of the raw materials; the optimal production and recovery of enzymes; and the use of new organisms for converting polymeric pentosans and hexosans to sugars. Optimization of the continuous ethanol removal and recovery process, as well as alternative methods of fermentation to ethanol, have also been studied. In all this work, the economic impact of each process change is evaluated.

ACCOMPLISHMENTS DURING FY 1982

Process Development Studies

Enzymatic Hydrolysis of Corn Stover

The hydrolysis of acid-treated corn stover with cellulase from *Trichoderma reesei* Rut-C30 was

*This work was supported by the Assistant Secretary for Conservation and Solar Energy of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098 and by the Solar Energy Research Institute under Contract No. DR-0-9058-1.

evaluated.[1] Experiments were conducted with substrate concentrations of 5% to 25% by weight, enzyme activities of 0.5–7 International Units (IU) per milliliter, and residence times of 28–48 hours. The maximum conversion of available carbohydrates to fermentable sugars was 55% at a cellulase activity of 25–30 IU/g. Optimum cellobiase activity for minimum cellobiose production was approximately 1.8 cellobiase units to 1 filter paper activity (FPA) unit.

Hydrolysis experiments with steam-exploded corn stover, however, led to a maximum conversion of 80%, significantly higher than the results obtained for acid-treated substrate. In addition, steam-exploded corn stover was shown to be a suitable carbon source for growth of *T. reesei* in submerged cultures.

Computer-aided process evaluations were conducted for several processing alternatives, including steam explosion or dilute-acid pretreatment; equilibrium solid-liquid contacting or ultrafiltration for enzyme recovery; and batch, continuous, or continuous with cell-recycle culture for enzyme production. With dilute-acid-pretreated materials, glucose may be produced for 12–22 cents per pound at corn stover costs ranging from $0 to $30 per ton. This constitutes a 33% reduction over previous processing schemes employing cellulase from *T. reesei* QM9414. Enzyme production is the single most expensive processing step, accounting for 40% of processing costs. Preliminary evaluation of processing with steam-exploded corn stover leads to a glucose cost of 10–15 cents/pound for corn stover costing $0–$30 ton, with further improvement possible. The dominance of raw-material costs, however, tends to dampen the effect of process improvements on the cost of manufacturing ethanol.

Economic Evaluation of Alternative Fermentation Processes

A computer package (FERMEC) was developed, this being a comprehensive library of routines for the design and evaluation of alternative fermentation schemes. These schemes are compared on identical bases, using a single kinetic model of fermentation (based on the data of Bazua[2]) and identical economic assumptions. The entire fermentation plant, including feed preparation, fermentation, distillation, stillage processing, and feed and product storage is designed and costed (Fig. 1).

With this computer package, optimized designs were developed for batch, simple-continuous, series-continuous, plug flow, tower, cell-recycle, immobilized-cell fermentations, and fermentations coupled with selective ethanol removal processes. A high fermentor-cell density is most important for

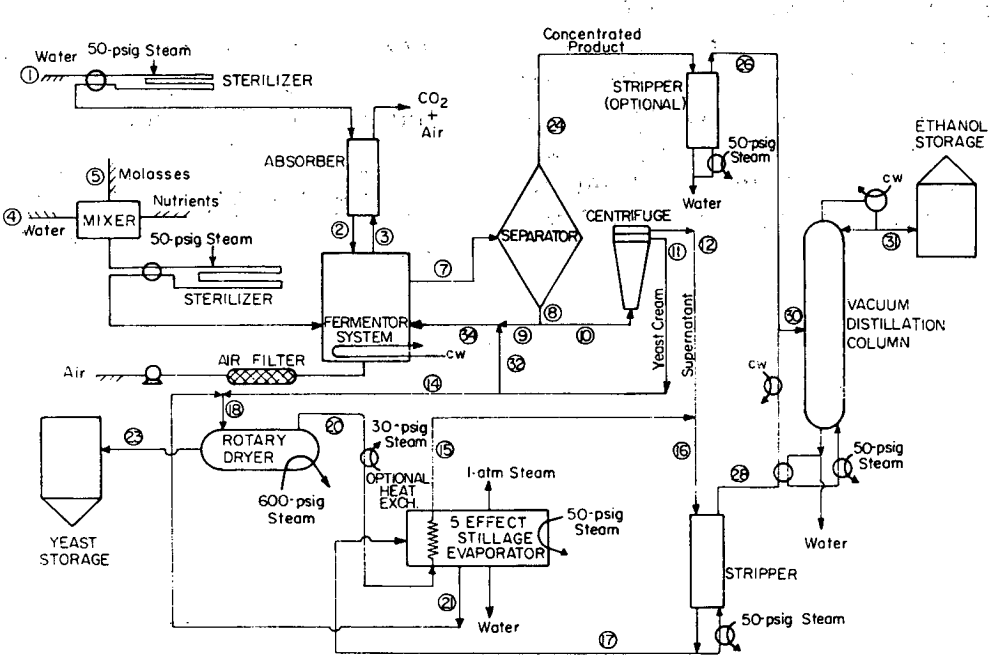


Figure 1. Flow model of fermentation plant for ethanol production. (XBL 825-5695)

achieving reduced costs. Excluding the selective ethanol removal processes, the recycle and tower fermentor processes are the most favorable, with similar economics. For ethanol produced from molasses containing approximately 50% fermentable sugars and priced at $85/ton, with a credit for yeast of 11.4 cents/kg and a 15% after-tax return on investment, the minimum charge is 48.2 cents/l, compared to 52.8 cents/l for the optimum conventional batch design.

For a selective ethanol removal process with a high separation factor (such as flash fermentation), the charge for ethanol, excluding the separator cost, is reduced to 42.9 cents/l, for a saving of 5.4 cents/l, the maximum achievable with a separator of the specified characteristics. This results not primarily from a reduction in fermentation or distillation costs, but from a reduction in the cost of auxiliaries such as stillage handling. If a dilute sugar source (such as glucose hydrolyzate) is used instead of molasses, then the cost of feed concentration offsets these savings.

With the FERMEC package, we evaluated possible fermentation cost savings from the use of genetically modified fermentation organisms. The yeast microorganism *Saccharomyces cerevisiae* (ar anamensis), grown in continuous culture with centrifuge recycle, was taken as a base case. We then used the economic model to assess the cost savings if each of four kinetic parameters could be raised by 15% through organism improvement techniques.

The results indicate that the greatest cost savings would be achieved by developing high-yielding, ethanol-tolerant organisms. A very high fermentation rate is of only secondary significance. The bacterium *Zymomonus mobilis* should be of particular interest because of its high product yield (approaching 0.49 g/g).

Documentation of the FERMEC package for use by other groups in evaluating alternative fermentation processes is nearing completion.

Evaluation of the High-Pressure Hydrogen Chloride Process

Saturating wood particles with HCl gas under pressure before subjecting the wood to dilute-acid hydrolysis was found to be an effective pretreatment—the glucose yield was doubled. The HCl gas makes the wood more susceptible to hydrolysis, which is otherwise inhibited by the tight lattice structure of cellulose.

The saturation was most effectively performed in a fluidized-bed reactor, with pure HCl gas fluidizing equal volumes of ground wood and inert particles, as shown in Fig. 2. The fluidized bed effectively dissipated the large amount of heat released upon HCl absorption into the wood. Batch reaction times of one hour at 314.7 psia gave glucose yields of 80% and xylose yields of 95% after dilute-acid hydrolysis. A noncatalytic gas-solid reaction model, with gas diffusion into the solid as the rate-limiting step, was found to describe this HCl-wood reaction.

Hydrogen chloride formed a stable adduct with the lignin residue in the wood, in a ratio of 3.33 moles

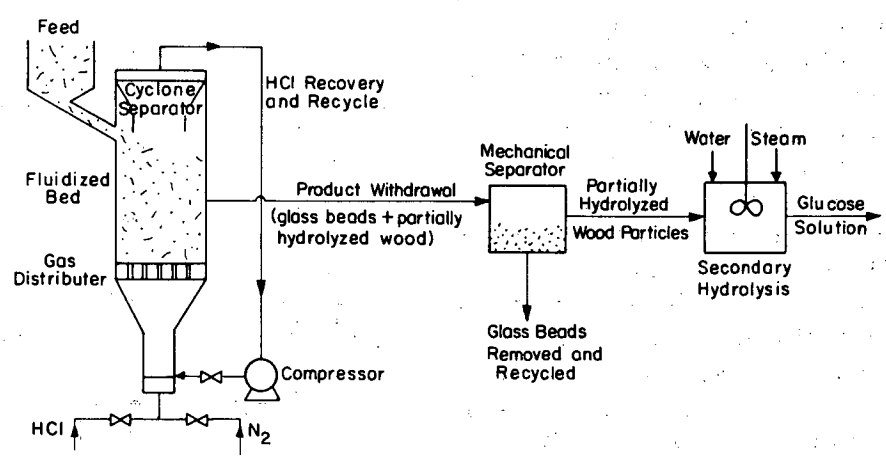


Figure 2. Flow diagram for proposed fluidized bed process. (XBL 812-5299)

per mole of lignin monomer. This resulted in a loss of 0.1453 pounds of HCl per pound of wood. The adduct was broken upon the addition of water.

A process design and economic evaluation for a plant producing 214 tons per day of glucose from ground and air-dried poplar wood (*Populus tristi*) gave an estimated glucose cost of 15.1 cents per pound. This would correspond to $2.54 per gallon of ethanol if the glucose were fermented. Key factors contributing to the cost of glucose production were unrecovered HCl, which contributed 5.70 cents per pound of glucose, and the cost of wood, which, at $25 per ton, contributed 4.17 cents per pound.

Microbiological and Enzymatic Studies

Production of Cellulase Enzyme from High-Yielding Mutants

Economic studies of enzymatic hydrolysis of biomass have indicated that enzyme production alone accounts for some 40% of the cost of glucose production from cellulosic material. To reduce the cost of enzymes, corn-steep liquor (CSL) has been investigated and found to be an adequate replacement for the more expensive proteose peptone. CSL at 0.5% w/v adequately replaces 1 g/l proteose peptone.

Two-stage continuous fermentation to increase cellulase production was also studied. This process uses two vessels; for both, the optimum pH was O and the optimum temperature was 28°C, and the incoming medium contained 20 g/l Solka Floc (finely ground, bleached white spruce). Maximum productivity was obtained at a dilution rate of 0.046 hr^{-1} in the first stage and 0.028 hr^{-1} in the second stage. This resulted in an exit stream containing 3.3 IU/ml of filter paper activity (FPA) at a productivity of 58 IU/l-hr. The first stage, viewed separately, produced 2.1 IU/ml FPA at a productivity of almost 100 IU/l-hr. The results are summarized in Fig. 3.

"Fed-batch" cultivation of the high-yielding fungus *T. reesei* Rut-C30 resulted in great improvements in cellulase productivity as well as enzyme activity. This mode of cultivation allows the use of high substrate concentration without leading to the repression effects and the agitation and aeration difficulties encountered with batch fermentation. The experiments were started as a conventional batch process with an initial Solka Floc concentration of 20 g/l. After 48 hours, Solka Floc was regularly added without exceeding a concentration of 20 g/l. In this manner, the total effective Solka Floc concentration was raised to as high as 150 g/l. Up to this limit, a proportional increase in cellulase production resulted. A maximum of 30.4 IU/ml FPA was achieved (the highest activity yet reported for this strain), with 47.6 g/l soluble protein at a high titre productivity of 206 IU/l-hr and a maximum productivity of 177 IU/l-hr. Further experiments will examine the upper limit of substrate concentration and the optimal conditions for enzyme production and activity by this very efficient cultivation procedure.

Hydrolysis Reactor Development

Enzyme Recovery in Cellulose Hydrolysis. The adsorption of cellulase enzymes on unconverted cellulosic solids represents a large loss of enzyme, and hence increased glucose production costs. Alternative means to enhance the recovery of Rut-C30 cellulase enzyme from corn-stover hydrolysis were investigated.

In one, several nitrogenous salts were introduced to the hydrolysis to maximize the fraction of enzyme remaining in solution.[4] Urea was then added to the enzyme solution at a concentration of 1 *M*, resulting in 65% retention of enzyme in the hydrolyzate, with about 35% remaining on the extracted residue, compared to the usually observed 50 to 60% retained on the unextracted residue. For subsequent fermentation of the hydrolyzate, it is necessary to concentrate the sugar solution, which results in 5-7 *M* urea levels. However, at urea concentrations greater than 0.75 *M*, metabolic activities of *Saccharomyces cerevisiae*

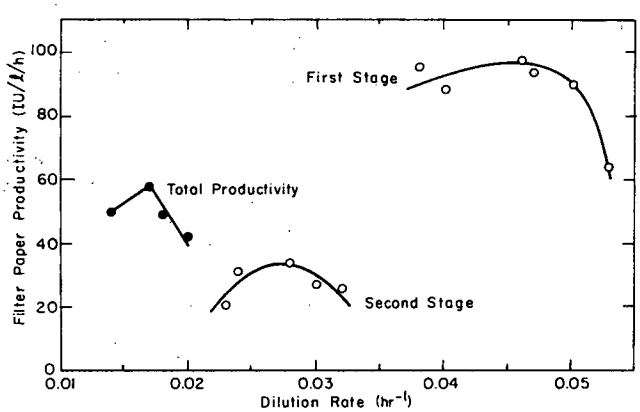


Figure 3. Two-stage continuous cultivation of *T. reesei* Rut-C30 on 20 g/l Solka Floc. (XBL 823-5436)

were greatly inhibited. Therefore, addition of urea to the hydrolysis is not feasible. No economical means of removing the urea prior to fermentation was found.

Among other alternatives investigated, countercurrent contacting of the solids results in an estimated 27% recovery of the enzyme entering the hydrolysis. A solids wash with concentrated urea solution recovers an estimated 35% of the enzyme entering the hydrolysis from the solids alone. Ultrafiltration was also evaluated. Because of losses attributed to the ultrafiltration units, the maximum enzyme recovery is estimated to be 56%. This alternative is marginally uneconomical because of excessive consumption of urea. Replacing the ultrafiltration units with precipitation of enzyme by acetone results in greater costs.

It is concluded that the most economical alternative for enzyme recovery is countercurrent contacting of the hydrolyzate with fresh solids. This is discussed further below.

Cellulase Recovery by Countercurrent Adsorption. This study evaluated countercurrent adsorption as a means of recovering enzyme from hydrolyzate.[5] Results from adsorption studies and hydrolysis experiments were used to design a system for enzymatic hydrolysis of steam-exploded corn stover that operated with two stages of countercurrent adsorption. Steam-exploded corn stover was selected because of the high conversions obtained (as much as 94%) through enzymatic hydrolysis. Enzyme concentration determinations included refinement of the assays for filter paper, crystalline, amorphous, and cellobiase activities, as all of the enzymatic assays are inaccurate when a high concentration of background sugars is present. To overcome this problem, acetone precipitation can be used to separate enzyme from sugars. Standard curves were constructed for the recovery of enzyme after acetone precipitation.

Studies to determine the effect of temperature and solids concentration on enzyme adsorption were performed. The initial enzyme-to-substrate ratio was 25 filter paper units (FPU) per gram solid. Adsorptions at 5.0 wt.% were observed at 15, 25, 35, and 45°C. In all four cases, adsorption decreased considerably within 5 to 10 minutes. At 30 to 45 minutes, 35% of the original filter paper activity remained in solution, regardless of temperature. Adsorption is greatest at low temperatures and low enzyme loadings. Enzyme is adsorbed quickly; most of the adsorption is complete within 5 minutes. Steam explosion is superior to Wiley milling followed by acid treatment in increasing the susceptibility of the substrate to enzyme attack.

Adsorption of filter-paper activity, activity towards cotton, activity towards carboxymethylcellulose, and cellobiase activity onto steam-exploded corn stover were measured and modeled by a Langmuir isotherm. The enzyme responsible for activity toward cotton is adsorbed to the greatest extent. Adsorption of cellobiase is weak.

Glucose yields as high as 94% are achieved by enzymatic hydrolysis of steam-exploded corn stover. High conversions permit release of enzyme so that it may be recovered from the liquid. The glucose yield decreases with increasing solids concentration because of product inhibition by glucose and cellobiose.

A 10 wt.% suspension of steam-exploded corn stover was hydrolyzed with an enzyme loading of 25 FPU/g at 45°C for 24 hours. Enzyme in the hydrolyzate was recovered by two stages of countercurrent adsorption, with each stage operated at 25°C for 45 minutes. The make-up enzyme requirement, measured as filter paper activity, was 35% of that required for the control experiment (batch hydrolysis without enzyme recovery). Compared to the control experiment, the release of filter paper activity and the rate of sugar production was considerably slower. This is attributed to poor recovery of cellobiase.

A preliminary economic evaluation showed that the enzyme production cost can be reduced by 61% if enzyme is recovered by countercurrent adsorption. This includes the cost of operating the countercurrent adsorption system.

Xylose Fermentation

Xylose Utilization by Bacillus Macerans. The ability of *B. macerans* to ferment pentoses to ethanol was examined.[6] The organism was grown in a continuous-flow stirred-tank fermentor. In continuous culture at steady state, ethanol and acetic acid and acetone were produced. The organism was found to have a relatively high maximum specific growth rate. This maximum was higher than previously reported for *B. macerans* organisms.

However, *B. macerans* had difficulty attaining and maintaining a steady state when grown in continuous culture. A perturbation of the conditions in the fermentor, such as a step-change to a higher dilution rate, as shown in Fig. 4, or injection of a small amount of xylose into the fermentor, would cause growth to stop. Several days were required for the fermentor to return to normal.

A possible explanation for this behavior is an interaction between the magnitude of the transmembrane pH gradient, the metabolic rate, and protonated acetic acid inhibition. At a constant external pH, a decreasing metabolic rate would cause the pH gradient to decrease; this would increase acetic acid inhibition, in turn causing the metabolic rate to decline further. This was enhanced by the strong dependence of cell yield on metabolic rate. A small decrease in metabolic rate would cause a large decrease in specific growth rate because cell yield would decrease. A satisfactory mathematical model of the growth and metabolism of *B. macerans* was constructed to test this hypothesis of an interaction between metabolic rate, pH gradient, and acetic acid inhibition.

Although *B. macerans* grows rapidly and produces ethanol from pentoses, its instability and transient behavior in continuous culture render it unsuitable for use in a commercial process.

Xylose Fermentation by Clostridium thermohydrosulfuricum. The economic feasibility of fermenting xylose to ethanol with *Clostridium thermohydrosulfuricum* was examined. Initial experiments aimed at determining basic fermentation kinetics, as shown in Fig. 5. The maximum specific growth rate and specific ethanol productivity was found to be 0.32 hr^{-1} and 0.31 g/l-hr, respectively, while the yield of ethanol from xylose was 0.33 g ethanol/g xylose. By-products of the fermentation include lactate and acetate.

These organisms are very sensitive to ethanol. Growth inhibition of 50% ws observed in the presence of 0.5 w/v% ethanol. To improve the organism's tolerance, an adapted strain, capable of growing at a rate of 0.29 hr^{-1} in 3.5 w/v% ethanol, has been developed. Unfortunately, the adapted organism produces ethanol at a reduced yield of only 0.20 g/g xylose.

Recent research has focused on increasing the

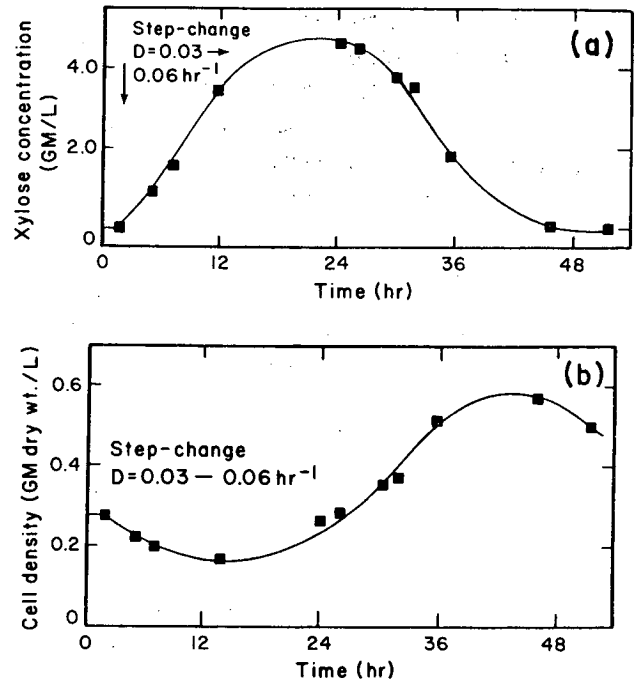


Figure 4. (a) Xylose concentration during a transient induced by a step-change in dilution rate from 0.03 to 0.06 hr^{-1}. Inlet xylose concentration was 11.6 g/l. (b) Cell density during a transient induced by a step-change in dilution rate from 0.03 to 0.06 hr^{-1}. Inlet xylose concentration was 11.6 g/l. [(a) XBL 819-1823; (b) XBL 819-1819]

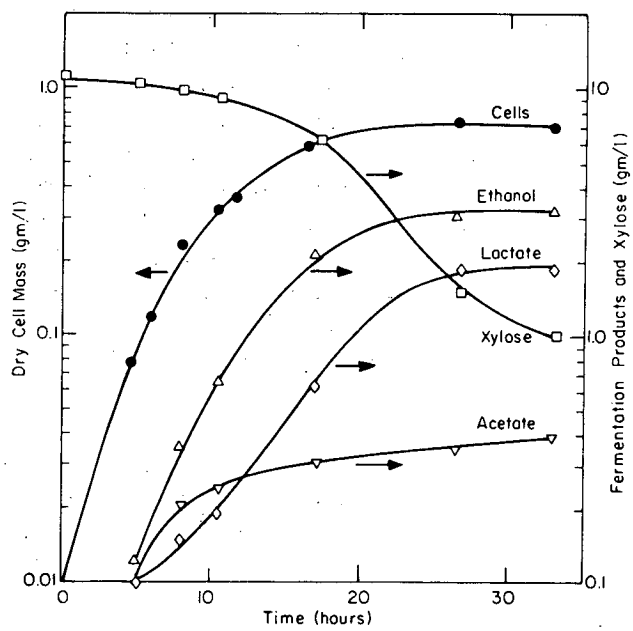


Figure 5. Fermentation profile of *Clostridium thermohydrosulfuricum.* (XBL 823-5405)

yield of ethanol produced by this ethanol-tolerant strain of *C. thermohydrosulfuricum* (strain UC-40). the effect of pH and by-product concentrations on ethanol yield has been examined. In addition, mutants producing relatively less by-product acids than UC-40 have been isolated.

C. thermohydrosulfuricum was grown at various pH's ranging from 6.0 to 7.9. The growth rate was highest (0.48 hr^{-1}) at pH 7.2. The yield of ethanol (0.22 g/g xylose fermented) was not a strong function of pH. Specific ethanol productivity had a maximum value of 0.36 hr^{-1} over a pH range of 6.0 to 6.8.

Adding acetate and lactate to the growth medium shifted the distribution of end products formed by strain UC-40. Low concentrations (1 to 3%) of acetate completely suppressed acetate formation; the yield of ethanol was increased by 20%, while the yield of lactate was unaffected. Lactate formation was inhibited by including lactate (2 to 3%) in the medium; a corresponding increase in acetate formation but no ethanol formation was observed.

Ethyl methane sulfonate was used to induce mutants with lower lactate yields than strain UC-40. Strain UC-40-L1 produced 60% less lactate and 20% more ethanol than UC-40. Unfortunately, this strain was not very stable and reverted after approximately 35 generations. Another strain (UC-40-L2), one producing 57% less lactate, has also been isolated. This isolate appears to be more stable than UC-40-L1 and is currently being characterized.

Fermentation and Separation Processes

Ethanol Distillation Technology

The DISTILL computer package for the design and evaluation of alternative ethanol/water distillation processes has been completed and used to determine the minimum ethanol/water separation cost for an efficient two-stage vacuum distillation process.

At high-feed ethanol concentrations, the distillation energy requirement for 95 wt.% "azeotropic" ethanol production is set by an azeotrope-associated pinch. This pinch limitation is reduced at low pressure. The ETOH equilibrium package, using a modified temperature-dependent UNIQUAC equilibrium model based on over 2,000 data points, allows accurate distillation design, including evaluation of reduction of the pinch limitation at low pressure. The minimum external reflux ratio to distill a concentrated feed is reduced from 3.3 at one atmosphere to 1.8 at 100 mmHg pressure. The savings at 100 mmHg can be realized only after a feed of at least 13.2 wt.% ethanol is used.

The two-stage vapor reuse method overcomes this feed limitation. Dilute beers are fed first to an atmospheric pressure stripper. The concentrated stripper product is then fed to the vacuum distillation. High energy efficiency is maintained by reusing the stripper heat, condensing the stripper vapor in the vacuum distillation reboiler to drive this second distillation step.

The cost of this process has been assessed for base-case cost assumptions of steam at $3.15/1000 pounds, cooling water at 22.6 cents/1000 gal, labor (including supervision) at $12.6/man-hour, 18-year depreciation, and a 15% after-tax return on investment. For very dilute feeds (1 wt.% ethanol), the charge for distillation is high (7.5 cents/l). At typical (6 wt.%) feed concentrations, the distillation cost is reduced (2.2 cents/l). Beyond 9 wt.% ethanol, the pinch limitation (even at reduced pressure) is controlling and the distillation cost to produce 95% wt.% product is constant (1.8 cents/l). The steam requirement for an optimized typical 6 wt.% feed case is 1.61 kg/l of product.

The sensitivity of these costs to changes in the cost of steam and cooling water and to changes in required return on investment were also studied.

Finally, the vapor-reuse methods were extended to develop a five-column distillation process with acetaldehyde and fuel-oil removal to produce anhydrous ethanol. Capital costs are increased (for the added columns), but by careful staging of distillation-column pressures, no added energy is required to produce anhydrous ethanol as compared to 95 wt.% ethanol.

Solvent Extraction for Ethanol Recovery

Solvent extraction represents a process for ethanol recovery that can allow significant energy savings compared to distillation, especially when the ethanol is to be recovered from a fairly dilute process stream. The advantage of extraction is in avoiding the vaporization of large quantities of water that occurs during distillation. The key to achieving this, however, lies either in using a solvent with a high separation factor (the ratio of ethanol to water distribution coefficients).

or in selectively removing the ethanol from the extractant stream.

Progress has been made toward the first goal with the experimental finding that high-molecular-weight aldehydes have better distribution coefficients and separation factors than any compounds tested previously. While the use of aldehydes in a commercial process is questionable because of their reactivity (including oxidation and aldol condensation), their desirable properties suggest that solvents with similar functional groups but less reactivity should be investigated. Interestingly, the effect of temperature on the ethanol distribution coefficient for aldehydes is opposite that for similar acids or alcohols. That is, the coefficient decreases with increasing temperature in the case of aldehydes, while it increases in the other cases.

The UNIFAC model for activity coefficient calculation has been applied to the ethanol-water-solvent systems, using the liquid-liquid equilibrium parameters suggested by Magnussen et al.[7] Although the results are not quantitatively correct, they are qualitatively correct in all cases tested. This holds the promise of a valuable method of screening solvents and ranking them in order of distribution coefficients and separation factors. Such an approach could significantly reduce the amount of experimental work necessary to identify good extraction solvents.

To synthesize an extraction process, a flexible computer simulation package is being prepared that incorporates economic analysis. The executive program is working, and a series of subroutines to model extraction, stripping, absorption, heat exchange, and other unit operations is being developed. The result will allow extraction optimization with regard to solvent, operating temperature, and process configuration.

PLANNED ACTIVITIES FOR FY 1983

Mutation and selection studies on *Clostridium thermohydrosulfuricum* will be continued, with the objective of finding mutants suitable for ethanol production in the flash-fermentation apparatus. Once suitable strains are found, the efficiency of this device for xylose utilization will be examined, both experimentally and economically.

REFERENCES

1. Perez, J., Wilke, C.R., and Blanch, H.W. (1981), *Enzymatic Hydrolysis of Corn Stover Process Development and Evaluation,* Lawrence Berkeley Laboratory Report LBL-14223.
2. Bazua, C.D., and Wilke, C.R. (1977), "Ethanol Effects on the Kinetics of a Continuous Fermentation with *Saccharomyces cerevisiae,*" *Biotechnol. Bioeng. Symp. 7,* p. 105.
3. Blanch, H.W., Antonopolis, R., Freitas, R., Sciamanna, A., and Wilke, C.R. (1982), "High Pressure HCl Conversion of Cellulose to Glucose," submitted to *Biotechnol. Bioeng.*
4. Dove, G.B., Wilke, C.R., and Blanch, H.W. (1982), "Process Development Studies: the Enhanced Recovery of Cellulase in Cellulose Hydrolysis," submitted to *Biotechnol. Bioeng.*
5. Orichowskyj, S., Wilke, C.R., and Blanch, H.W. (1982), *Recovery of Cellulase Enzymes by Countercurrent Adsorption,* Lawrence Berkeley Laboratory report LBL-15153.
6. Delfino, T., Blanch, H.W., and Wilke, C.R. (1981), *The Fermentation of Xylose by Bacillus macerans,* Lawrence Berkeley Laboratory Report LBL-14648.
7. Magnussen, T., Rasmussen, P., and Fredenslund, A. (1981), "UNIFAC Parameter Table for Predicting Liquid-Liquid Equilibria," *Ind. Eng. Chem. Proc. Des. Dev. 20,* p. 331.

HOMOGENEOUS CATALYTIC HYDROGENATION: REGIOSPECIFIC REDUCTIONS OF POLYNUCLEAR AROMATIC AND HETEROAROMATIC NITROGEN COMPOUNDS CATALYZED BY TRANSITION-METAL CARBONYL HYDRIDES*

R.H. Fish, A.D. Thormodsen, G.A. Cremer, T. Vermeulen, and H. Heinemann

Synthetic fuel products derived from coal or oil shale require additional hydroprocessing to minimize their nitrogen and sulfur content; the selective hydrogenation of polynuclear heteroaromatics therefore becomes critical.[1–3] To this end, it is extremely important to have a basic understanding of which polynuclear aromatic and heteroaromatic compounds are hydrogenated in these complex fossil-fuel matrices.

Recently, Pettit and his co-workers[4–6] elegantly demonstrated the use of carbon monoxide and water as an alternative reducing agent to hydrogen in the hydroformylation of olefins and the reduction of nitroarenes. These reactions were catalyzed by transition metal carbonyl compounds [$M_x(CO)_y$] and are thought to proceed via the formation of transition metal carbonyl hydrides (e.g., $H_2M_x(CO)_y$), by nucleophilic attack of water or base on coordinated carbon monoxide.[7–9] Other methods of generating transition metal carbonyl hydrides from the corresponding carbonyls have used carbon monoxide and hydrogen and hydrogen alone as reagents.[10]

We therefore thought that the rather facile generation of transition metal carbonyl hydrides under water-gas shift (CO, H_2O, base) and synthesis gas (CO, H_2, 1:1) conditions as well as strictly hydrogenation conditions (H_2 alone) made these reagents very attractive for the purpose of testing their regioselectivities in the reductions of polynuclear aromatics and polynuclear heteroaromatic nitrogen compounds. Additionally, it is well known that homogeneous catalytic reductions proceed at lower temperatures and pressures, and, in fact, give the higher regioselectivities we were seeking when compared to their heterogeneous counterparts.[11,12]

ACCOMPLISHMENTS DURING FY 1982

Figure 1 shows the polynuclear aromatic and polynuclear heteroaromatic nitrogen compounds (**1-8**) that we used as model synthetic fuel compounds.

We reacted a wide variety of transition metal carbonyl compounds with compounds **1-3** under water-gas shift (wgs) and synthesis gas (sg) conditions[13] and found that only $Fe(CO)_5$, $Mn_2(CO)_8(Bu_3P)_2$, and $Co_2CO_6(\Phi_3P)_2$ produced reduction products. For example, **1** was reduced to 9,10-dihydroanthracene (**9**) under wgs conditions with these carbonyls in rather poor yields of 8%, 13%, and 3% respectively,

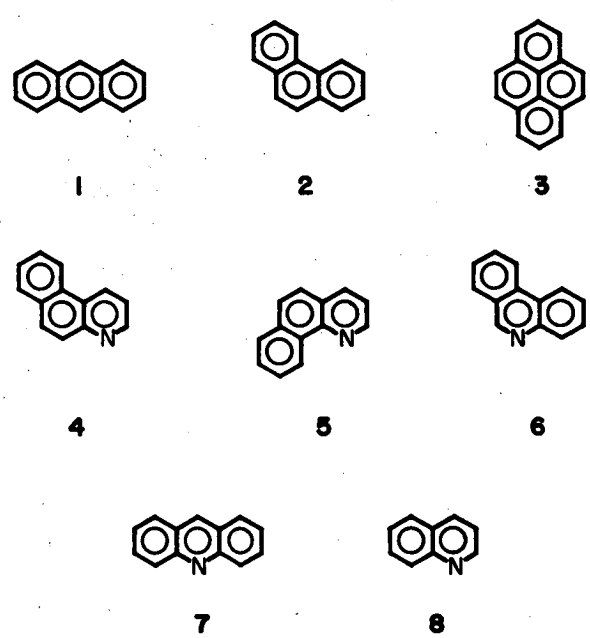


Figure 1. Model synthetic fuel compounds used in the catalytic hydrogenations with transition-metal carbonyl hydrides: **1**, anthracene; **2**, phenanthrene; **3**, pyrene; **4**, 5,6-benzoquinoline; **5**, 7,8-benzoquinoline; **6**, phenanthridine; **7**, acridine; and **8**, quinoline. (XBL 821-7773)

*This work was jointly supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division, and the Assistant Secretary of Fossil Energy, Office of Coal Research, Liquefaction Division of the U.S. Department of Energy through the Pittsburgh Energy Technology Center under Contract No. DE-AC03-76SF00098.

while substrates **2** and **3** were totally unreactive.

In view of these discoveries, we decided to learn more about this reaction, using $Mn_2(CO)_8(Bu_3P)_2$ as the catalyst. The reaction of carbon monoxide and deuterium oxide (D_2O) with **1** provided only 9,10-dideuteroanthracene (**10**),[14] and this result strongly indicates that the hydrogen comes exclusively from water.

To elucidate the stereochemistry of the anthracene reaction, we reacted an analog of **1**, 9,10-dimethylanthracene (**11**) with $Mn_2(CO)_8(Bu_3P)_2$ under wgs conditions (180°, 5 hrs, 350 psi CO, 0.2 *M* KOH in THF, substrate-catalyst ratio = 20) to provide a 30% yield of *cis* and *trans* 9,10-dihydro-9,10-dimethylanthracene (**12** and **13**), in a ratio of 53%:47%.[15] A similar result was recently reported by Sweany et al.,[16] for the reaction of **10** and $HMn(CO)_5$ and by Taylor and Orchin[17] with $HCo(CO)_4$ under sg conditions (CO, H_2 1:1, ~200°).

We also found that, under sg conditions (CO/H_2 = 1),[13] better yields of reduced polynuclear aromatic products could be obtained using $Mn_2(CO)_8(Bu_3P)_2$ as the catalyst and compounds **1–3** as substrates. Thus, reaction of **1** with $Mn_2(CO)_8(Bu_3P)_2$ provided **9** in 30% yield, while reaction with **2** gave no product and **3** produced 4,5-dihydropyrene (**14**), in a 3% yield.

From these results, it is evident that bent polynuclear aromatic compounds are extremely unreactive under either wgs or sg conditions when compared to **1**, a linear polynuclear aromatic compound.[18,19]

As previously stated, it is important to study the polynuclear heteroaromatic nitrogen compounds under various homogeneous hydrogenation conditions because they are prevalent in all coal and oil shale products. Despite this importance, few studies of their reactivity under either wgs or sg conditions or, for that matter, under strictly hydrogenation conditions, have been published. For example, Laine et al.[20] reported on the hydrogenation of the mononuclear heterocyclic compound pyridine under wgs conditions with $Rh_6(CO)_{16}$ as catalyst, and Derencsenyi and Vermeulen[19] reported that, under sg conditions, quinoline, **8**, was regioselectively reduced to 1,2,3,4-tetrahydroquinoline, using $Mn_2(CO)_8(Bu_3P)_2$ as a catalyst. Furthermore, Jardine and McQuillin[21] have reported that **8** was again reduced to 1,2,3,4-tetrahydroquinoline, when $RhCl_2Py_2(dmf)BH_4$ was used as the catalyst.

As seen in Table 1, we found a greater reactivity for the polynuclear heterocyclic nitrogen compounds, **4-8**, under either wgs or sg conditions, compared to their carbon analogs; e.g., acridine, **7**, is more reactive than anthracene, **1**. It is also important to note the high regioselectivity of compounds **4–8**—only the nitrogen ring was hydrogenated. This regioselectivity

Table 1. Reductions of polynuclear heteroaromatic nitrogen compounds **4–8**, under water-gas shift[a] (wgs) and syngas (sg) conditions[b] with transition metal carbonyls as catalysts.

Substrate	Catalyst	Sub/Cat ratio	Temp. (°C)	Time (hr)	Conditions	Products (%)[d]
4	$Mn_2(CO)_8(Bu_3P)_2$	20	200	2	sg	1,2,3,4-tetrahydro-5,6-benzo-quinoline (7)
4	$Mn_2(CO)_8(Bu_3P)_2$	20	200	5	wgs	1,2,3,4-tetrahydro-5,6-benzo-quinoline (4)
4	$Fe(CO)_4(Bu_3P)$	10	180	5	wgs	1,2,3,4, tetrahydro-5,6-benzo-quinoline (1)
4	$Co_2(CO)_6(\Phi_3P)_2$	20	200	2	sg	1,2,3,4-tetrahydro-5,6-benzo-quinoline (8)
5	$Mn_2(CO)_8(Bu_3P)_2$	20	200	2	sg	1,2,3,4-tetrahydro-7,8-benzo-quinoline (2)
5	$Mn_2(CO)_8(Bu_3P)_2$	20	200	2	wgs	No product
6	$Mn_2(CO)_8(Bu_3P)_2$	20	200	2	wgs	9,10-dihydro-phenanthridine (1)
6	$Mn_2(CO)_8(Bu_3P)_2$	20	200	2	sg	9,10-dihydro-phenanthridine (11)
6	$Co_2(CO)_6(\Phi_3P)_2$	20	200	2	sg	9,10-dihydro-phenanthridine (21)
7	$Fe(CO)_5$[c]	10	180	2	wgs	9,10-dihydro-acridine (100)
7	$Mn_2(CO)_8(Bu_3P)_2$	10	200	2	wgs	9,10-dihydro-acridine (38)
7	$Mn_2(CO)_8(Bu_3P)_2$	20	200	2	sg	9,10-dihydro-acridine (100)
7	$Co_2(CO)_6(\Phi_3P)_2$	20	200	2	sg	9,10-dihydro-acridine (100)
8	$Fe(CO)_5$	10	180	2	wgs	1,2,3,4-tetrahydro-quinoline (0)
8	$Mn_2(CO)_8(Bu_3P)_2$	20	200	5	wgs	1,2,3,4-tetrahydro-quinoline (4)
8	$Mn_2(CO)_8(Bu_3P)_2$	20	200	5	sg	1,2,3,4-tetrahydro-quinoline (33)
8	$Co_2(CO)_6(\Phi_3P)_2$	20	200	1	sg	1,2,3,4-tetrahydro-quinoline (70)

[a]Reaction run in THF (12 ml) with 0.2 *M* KOH (3 ml), 350 psi CO.

[b]350 psi H_2 and 350 psi CO in THF (15 ml).

[c]800 psi CO.

[d]Determined by capillary GC using a digital integrator (HP 5880A). Isolated by column chromatography (Florisil) and identified by GC-MS and NMR spectroscopy (250 MHz, ^1H).

might be explained by the lowered aromaticity of the nitrogen-containing ring versus that of their carbon analogs, which would provide a lower activation energy for hydrogenation.[22]

That Fe, Mn, and Co carbonyls did provide reduced product under wgs conditions, while other transition metal carbonyls did not, may indicate that the former compounds are very poor shift catalysts.[23] Moreover, Mn and Co catalysts were also able to hydrogenate the substrates studied under sg conditions, while the other transition metal carbonyls were unreactive under these conditions.

We examined the reaction parameters and found that reduced product dramatically increased when carbon monoxide was removed from the reactions catalyzed by ruthenium carbonyls.

In initial experiments, we used $Ru(Cl)_2(CO)_2(\Phi_3P)_2$ as a catalyst. Interestingly, with this catalyst, both hydrogen and base were needed to reduce compound **1**.[24] No reaction occurred in the presence of carbon monoxide or in the absence of base. The reduction of **1** was highly regiospecific and gave exclusively 1,2,3,4-tetrahydroanthracene, **15**, in 30% yield.[25] A control experiment was performed to establish that 9,10-dihydroanthracene, **9**, was not the initial product formed; this product rearranged to compound **15**. We reacted **9** under similar reaction conditions and found that it did not produce compound **15**; hence, no rearrangement occurred.

Compounds **2** and **3** were unreactive under the reaction conditions, consistent with the previous finding that bent aromatic compounds are extremely unreactive versus the linear aromatics such as **1**. The polynuclear heteroaromatic nitrogen compounds, **4–8**, were reacted under similar conditions to produce poor to moderate yields of reduced product (Table 2). However, we found that the removal of base (KOH) in the reactions of **4–6** and **8** (but not **7**) with $Ru(Cl)_2(CO)_2(\Phi_3P)_2$ as catalyst provided an increase in the yields of all reduced products (Table 2). For example, compound **5** provided no reduced product with base present, while affording a 72% yield of 1,2,3,4-tetrahydro-7,8-benzoquinoline, **16**, in the absence of base. Additionally, as with compound **1**, carbon monoxide totally inhibited reduced product formation in the reactions of **4–8** with $Ru(Cl)_2(CO)_2(\Phi_3P)_2$ as catalyst. Interestingly, compound **8**, with H_2 and base, provided a small amount (5%) of the reduced aromatic ring compound 5,6,7,8-tetrahydroquinoline, which was not produced when base was omitted.

Table 2. Reductions of compounds **1–8** with $Ru(Cl)_2(CO)_2(\Phi_3P)_2$ and $H_4Ru_4(CO)_{12}$ as catalysts.

Substrate	Catalyst	Products (%)[b]
1	$Ru(Cl)_2(CO)_2(\Phi_3P)_2$[a]	1,2,3,4-tetrahydroanthracene (30)
1	$Ru(Cl)_2(CO)_2(\Phi_3P)_2$[c]	no product
2	$Ru(Cl)_2(CO)_2(\Phi_3P)_2$[a,c]	no product
3	$Ru(Cl)_2(CO)_2(\Phi_3P)_2$[a,c]	no product
4	$Ru(Cl)_2(CO)_2(\Phi_3P)_2$[a]	1,2,3,4-tetrahydro-7,8-benzoquinoline (10)
4	$Ru(Cl)_2(CO)_2(\Phi_3P)_2$[c]	1,2,3,4-tetrahydro-7,8-benzoquinoline (92)
5	$Ru(Cl)_2(CO)_2(\Phi_3P)_2$[a]	1,2,3,4-tetrahydro-7,8-benzoquinoline (0)
5	$Ru(Cl)_2(CO)_2(\Phi_3P)_2$[c]	1,2,3,4-tetrahydro-7,8-benzoquinoline (72)
6	$Ru(Cl)_2(CO)_2(\Phi_3P)_2$[a]	9,10-dihydrophenanthridine (5)
6	$Ru(Cl)_2(CO)_2(\Phi_3P)_2$[c]	9,10-dihydrophenanthridine (15)
7	$Ru(Cl)_2(CO)_2(\Phi_3P)_2$[a]	9,10-dihydroacridine (100)
7	$Ru(Cl)_2(CO)_2(\Phi_3P)_2$[c]	9,10-dihydroacridine (74)
8	$Ru(Cl)_2(CO)_2(\Phi_3P)_2$[a]	1,2,3,4-tetrahydroquinoline (42) 5,6,7,8-tetrahydroquinoline (5)
8	$Ru(Cl)_2(CO)_2(\Phi_3P)_2$[c]	1,2,3,4-tetrahydroquinoline (100)
4	$H_4Ru_4(CO)_{12}$[d]	1,2,3,4-tetrahydro-5,6-benzoquinoline (75)
5	$H_4Ru_4(CO)_{12}$[d]	1,2,3,4-tetrahydro-5,6-benzoquinoline (8)
6	$H_4Ru_4(CO)_{12}$[d]	9,10-dihydrophenanthridine (15)
7	$H_4Ru_4(CO)_{12}$[d]	9,10-dihydroacridine (100)
8	$H_4Ru_4(CO)_{12}$[d]	1,2,3,4-tetrahydroquinoline (100)

[a]Experiments were performed in a 45 ml Parr mini-reactor containing 1 m*M* of substrate, 0.1 m*M* $Ru(Cl)_2(CO)_2(\Phi_3P)_2$ in THF (12 ml), 0.2 *M* KOH (3 ml), 180°C, 350 psi H_2 for 5 hr, **1–7**, 2 hr, **8**.

[b]Analyzed by gas chromatography on a 12 m × 0.1 mm i.d. fused silica capillary column (OV101) using an HP-5880A instrument with flame ionization and digital integration. The percent product conversion was obtained by integration of product and any starting material remaining and normalizing to 100%. Products were isolated by column chromatography (Florisil) and identified by GC-MS and NMR spectroscopy (^1H, 250 mHz).

[c]180°C, THF (12 ml), 0.1 m*M* $Ru(Cl)_2(CO)_2(\Phi_3P)_2$, 1 m*M* substrate, 350 psi H_2 for 2 hr.

[d]Experiments were performed in a 45 ml Parr mini-reactor containing 1 m*M* of substrate, 0.1 m*M* $H_4Ru_4(CO)_{12}$ (10:1 substrate-to-catalyst ratio) in 15 ml of cyclohexane with 350 psi H_2 for 2 hr at 150°C.

In concurrent experiments, we discovered that tetrahydridotetraruthenium dodecacarbonyl, $H_4Ru_4(CO)_{12}$, was also an excellent catalyst for the hydrogenation of compounds **4–8** but was inactive for the reductions of compounds **1–3** under the conditions studied.[26,27] It was not, however, the initial

catalyst used; rather, we employed the catalytic activity of triruthenium dodecacarbonyl, $Ru_3(CO)_{12}$. We found that, under our reaction conditions, $H_4Ru_4(CO)_{12}$ readily formed (IR and MS analysis) by reaction of $Ru_3(CO)_{12}$ with hydrogen gas (Eq. 1)[27]:

$$4Ru_3(CO)_{12} + 6H_2 \rightarrow 3H_4Ru_4(CO)_{12} + 12CO \quad (1)$$

Under the latter reaction conditions, reduction of **4–8** was evident; however, catalytic activity increased dramatically if $H_4Ru_4(CO)_{12}$ was formed prior to substrate addition. In this process, CO was flushed from the system. Evidently, even a small partial pressure of CO [~10 psi CO was generated in the formation of $H_4Ru_4(CO)_{12}$ from $Ru_3(CO)_{12}$] was sufficient to inhibit substrate coordination to ruthenium and greatly reduced product yield. For example, $Ru_3(CO)_{12}$ provided a 7% yield of 1,2,3,4-tetrahydro,-5,6-benzoquinoline (**17**) from **4**, while $H_4Ru_4(CO)_{12}$ produced the same product in 75% yield.

Tetrahydridotetraruthenium dodecacarbonyl has been previously described as a hydrogenation catalyst for olefins, carboxylic acids and ketones,[28,29] but, to our knowledge, never for polynuclear heteroaromatic nitrogen compounds.[30] As with $Ru(Cl)_2(CO)_2(\Phi_3P)_2$, the results of these catalytic hydrogenations with $H_4Ru_4(CO)_{12}$ indicate high regioselectivity for the nitrogen heterocyclic ring.

PLANNED ACTIVITIES FOR FY 1983

This study has provided evidence for the individual reactivity of a number of model synthetic fuel compounds under homogeneous catalytic hydrogenation conditions. However, their relative reactivities need to be ascertained, especially in mixtures of these compounds and in the presence of other polynuclear heterocyclics (e.g., sulfur and oxygen heterocycles). Also, work on the many mechanistic details, as well as expansion to the reactivities of polynuclear heterocyclic compounds of oxygen and sulfur, and the activity of heterogenized forms of the reported catalysts, is being pursued.[31]

Finally, our results point to the possible usefulness of these homogeneous catalysts and others in future synthetic fuel processes concerned with ultimately removing nitrogen from the nitrogen-containing ring in polynuclear heterocyclic nitrogen compounds.[32] The reported catalysts may also find some important uses in synthetic organic chemistry.[33]

REFERENCES

1. Whitehurst, D.D., Ed. (1980), *Coal Liquefaction Fundamentals,* ACS Symposium Series 139, American Chemical Society, Washington, D.C.
2. Larsen, J.W., Ed. (1978), *Organic Chemistry of Coal,* ACS Symposium Series 7, American Chemical Society, Washington, D.C.
3. Yen, T.F., and Chillingarian, G.V., Eds. (1976), *Development of Petroleum Science,* Vol. 5, "Oil Shale," Elsevier Scientific Publishing Co., Amsterdam.
4. Kang, H.C., et al. (1977), "Reductions with Carbon Monoxide and Water in Place of Hydrogen. 1. Hydroformylation Reaction and Water Gas Shift Reaction," *J. Amer. Soc. 99,* p. 8923 and references therein.
5. Cann, K., et al. (1978), "Catalytic Reductions Using Carbon Monoxide and Water in Place of Hydrogen. 2. Reduction of Aromatic Nitro Compounds to Amines," *J. Amer. Chem. Soc.* 100, p. 3969.
6. Cole, T., et al. (1980), "Hydrogeneous Catalyst for Utilization of Synthesis Gas as a Reducing Agent," *J. Amer. Chem. Soc. 102,* p. 6182.
7. Grice, N., Kao, S.C., and Pettit, R. (1979), "Chemical Properties of Metallocarboxylic Acids of Transition Metals," *J. Amer. Chem. Soc. 101,* p. 1627.
8. Darensbourg, D.J., Baldwin, B.J., and Froelich, J.A. (1980), "Phase-Transfer-Catalyzed Nucleophilic Reactions of Hydroxide Ions at Metal-Bound Carbon Monoxide Centers," *J. Amer. Chem. Soc. 102,* p. 4688.
9. Ford, P.C. (1981), "The Water-Gas Shift Reaction: Homogeneous Catalysis by Ruthenium and Other Metal Carbonyls," *Accts. Chem. Res. 14,* p. 31.
10. Kaesz, H.D., and Saillant, R.B. (1972), "Hydride Complexes of the Transition Metals," *Chem. Rev. 72,* p. 231, and references therein.
11. James, B.J. (1973), *Homogeneous Hydrogenation,* John Wiley and Sons Inc., New York (1973).

12. Parshall, G.W. (1980), "Organometallic Chemistry in Homogeneous Catalysis," *Science 2098*, p. 1221.
13. Fish, R.H., Thormodsen, A.D., and Cremer, G.A. (1982), "Homogeneous Catalytic Hydrogenations, 2: Regiospecific Reductions of Polynuclear Aromatic and Polynuclear Heteroaromatic Nitrogen Compounds Catalyzed by Transition-Metal Carbonyl Hydrides," *J. Amer. Chem. Soc. 104*, p. 5234. Lawrence Berkeley Laboratory Reports LBL-13734 and LBL-13735.
14. GC-EI mass spectral analysis showed *m/e* 182 (100%), consistent with two deuterium atoms being incorporated into compound **1** (*m/e* 178).
15. The *cis* and *trans* isomers of 9,10-dihydro-9,10-dimethylanthracene (**12, 13**) could be cleanly separated on a 12 m × 0.1 mm i.d., fused silica capillary column (OV 101) using a HP 5880A instrument with flame ionization detection (temperature programming 60°–200°C, 10°/min).
16. Sweany, R., Butler, S.C., and Halpern, J. (1981), "The Hydrogenation of 9,10-Dimethylanthracene by Hydridopentacarbonyl Management (I.). Evidence for a Free Mechanism," *J. Org. Chem. 213*, p. 487.
17. Taylor, P.D. and Orchin, M.J. (1972), "Hydrogenation of 9,10-Dimethylanthracene with Cobalthydride Carbonyl," *J. Org. Chem. 37*, p. 3913.
18. Friedman, S., et al. (1959), "Selective Hydrogenation of Polynuclear Aromatic Hydrocarbons," *J. Org. Chem. 24*, p. 1287.
19. Derencsenyi, T.T., and Vermeulen, T. (1979), *Kinetics and Mechanism of Metal-Carbonyl-Catalyzed Hydrogenation of Aromatic Hydrocarbon Models for Coal Constituents* (Ph.D. dissertation of T.T.D.), Lawrence Berkeley Laboratory Report LBL-9777; also (1980), *Chem. Abs. 93*, no. 188929.
20. Laine, R.M., Thomas, D.W., and Cary, L.W. (1979), "Catalytic Reactions of Pyridine with Carbon Monoxide and Water. Reduction of Carbon Monoxide to Hydrocarbon. Applications of the Water-Gas Shift Reaction," *J. Org. Chem. 44*, p. 4964.
21. Jardine, I. and McQuillin, F.J. (1970), *Chem. Comm.*, 626.
22. Dewar, M.J.S. (1969), *The Molecular Orbital Theory of Organic Chemistry*, McGraw-Hill, New York.
23. For example, we found that $Mn_2(CO)_8(Bu_3P)_2$ did not produce CO_2 and H_2 to any significant extent in the absence of substrates **1–8** under wgs conditions (350 psi CO, 0.2 *M* KOH, 200° for 5 hr gave 10 psi H_2). Selected gas analysis under wgs conditions gave a qualitative order of wgs activity as follows: $Rh_6(CO)_{16} > Ru_3(CO)_{12} > Cr(CO)_6 > Mo(CO)_6 > W(CO)_6 > Fe(CO)_5 > Mn_2(CO)_{12} > Co_2(CO)_8$.
24. $Ru(Cl)_2(CO)_2(\Phi_3P)_2$ has been described as a homogeneous hydrogenation catalyst (H_2) for aliphatic and aromatic aldehydes [Strohmeier, W. and Weigelt, L. (1978), *J. Organometal. Chem. 145*, 189]; however, no references to its use as a homogeneous catalyst for polynuclear aromatic or heteroaromatic compounds have been found.
25. A similar regioselectivity was obtained with **1** and a ruthenium anion hydride under strictly H_2 conditions. See Grey, R.A., Pez, P.G., and Wallo, A. (1980), "Selective Homogeneous Catalytic Hydrogenation of Polynuclear Aromatics," *J. Amer. Chem. Soc. 102*, p. 5948, and references therein.
26. Piacenti, F., Bianchi, M., Frediani, P., and Benedetti, E. (1971), "Preparation and Reactivity of Some Ruthenium Carbonyl Hydrides," *Inorgan. Chem. 10*, p. 2759.
27. Knox, S.A.R., Keopke, J.W., Andrews, M.A., and Kaesz, H.D. (1975), "Synthesis of Hydrido- and Deuterio-Carbonyl Cluster Complexes of Ruthenium, Iron-Ruthenium, and Osmium from Metal Carbonyls and Hydrogen at Atmospheric Pressure," *J. Amer. Chem. Soc. 97*, p. 3943.
28. Valle, M., Osella, D., and Vaglio, D. (1976), *Inorg. Chem. Acta. 20*, p. 213, and references therein.
29. Bianchi, M., et al. (1980), "Homogeneous Catalytic Hydrogenation of Free Carboxylic Acids in the Presence of Cluster Ruthenium Carbonyl Hydrides," *J. Organometal. Chem. 188*, p. 109.
30. Infrared analysis of the yellow-colored reaction solutions of compounds **4–8** clearly shows $H_4Ru_4(CO)_{12}$ still present after reaction. More

important, no "heterogeneous" component was found after reaction at 150°C for the $H_4Ru_4(CO)_{12}$ catalyzed hydrogenations. The infrared analysis does not unequivocally demonstrate that $H_4Ru_4(CO)_{12}$ is the actual active catalyst, as pointed out by a referee, and we are presently running these reactions in a spectroclave (high-pressure RI cell) to clarify this point.

31. A preliminary account was presented at the 182nd National American Chemical Society Meeting, August 23-28, 1981, New York (Abstract Inorg. 49), and at the Pacific Conference on Chemistry and Spectroscopy, Anaheim, CA, October 19-21, 1981 (Abstract 188).
32. Laine, R.M., Thomas, D.W., and Cary, L.W. (1982), "Modeling Heterogeneous Catalysts with Homogeneous Catalysts. 2. Modeling Catalytic Hydrodenitrogenation," *J. Amer. Chem. Soc. 104*, p. 1763.

MOLECULAR CHARACTERIZATION AND FINGERPRINTING OF VANADYL PORPHYRIN AND NON-PORPHYRIN COMPOUNDS FOUND IN VARIOUS HEAVY CRUDE PETROLEUMS AND THEIR ASPHALTENES*

R.H. Fish, J.J. Komlenic, B. Wines, and T. Vermeulen

As reserves of light crude oil throughout the world decrease, and as the nation switches to a more diversified and self-sufficient energy base, the processing of heavy crude petroleums and residuals will become increasingly important. In the past, primarily because of uneconomical catalyst poisoning effects associated with naturally occurring trace metal compounds in these oils, processing of such heavy crude feedstocks has been limited.[1-8] Although the concentrations of these trace metals—primarily vanadium and, to a lesser extent, nickel—are small, usually at the parts per million level, their harmful effects—both to the processing catalyst and, potentially, to the environment—are severe.

To design processes capable of efficiently removing vanadium and nickel from heavy crude oils before processing, it is essential to characterize or speciate the vanadium- and nickel-bearing compounds present. Such knowledge will be valuable in several ways. The information will help us to:

(1) design selective separation, removal, and recovery processes[9,10];
(2) explore for and process suitable heavy crude-oil feedstocks;
(3) identify oils in future pollution abatement efforts; and
(4) derive important geochemical information about the origin and biogenesis of heavy crude petroleum deposits.[11]

ACCOMPLISHMENTS DURING FY 1982

Speciation Using HPLC–GFAA

The automatic coupling of a high-performance liquid chromatograph to a graphite furnace atomic absorption spectrometer (HPLC–GFAA) is a promising means of speciating unidentified vanadyl compounds in heavy crude oils. This coupling of instruments provides continuous, on-line, element-specific detection of HPLC effluent peaks and combines the versatility, speed, and efficiency of HPLC with the selectivity and sensitivity of GFAA detection. This coupled system has been described elsewhere.[12-13]

Model Vanadyl Porphyrin and Non-Porphyrin Compounds

Speciation using the HPLC–GFAA technique requires a large collection of model compounds in order to compare and characterize the elution behavior of unidentified components.[14,15]

Figure 1 shows VOEtio, VODPEP, and VORhodo porphyrin compounds that have been identified in heavy crude oils, as well as model vanadyl porphyrins and non-porphyrins used in this study. Porphyrin compounds consist of a 16-member ring containing

*This work was supported by the Assistant Secretary for Fossil Energy and the Division of Oil, Gas and Shale Technology, and the Bartlesville Energy Technology Center of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

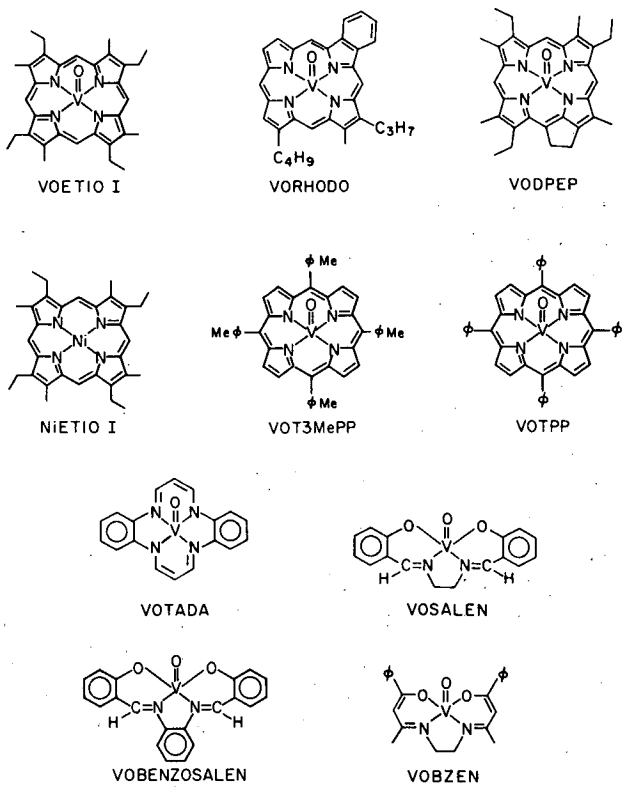


Figure 1. Model vanadyl porphyrin and non-porphyrin compounds. (XBL 8211-3357)

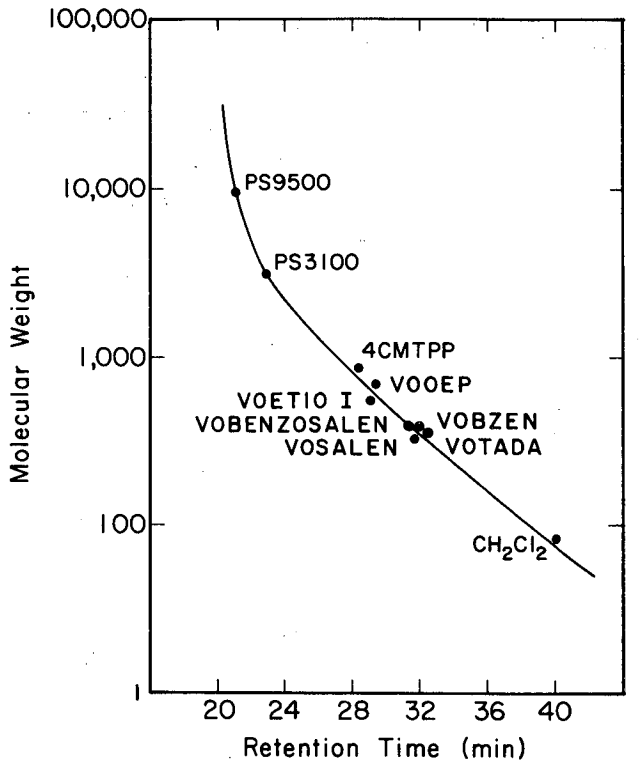


Figure 2. Log plot of molecular weight versus retention time for the 50/100 Å column combination. (XBL 826-10469)

four nitrogen donor atoms located in four conjugated pyrole groups. When a vanadyl ion is incorporated into this structure, these systems are extremely stable. VOT3MePP and VOTPP represent synthetic (not occurring in nature) vanadyl porphyrins that, because of the added conjugation of the peripherally attached phenyl rings, are stable in strong acid solutions.

Vanadyl non-porphyrins constitute a much broader class of compounds, with ring sizes varying from 12 to 16 members and with nitrogen, oxygen, and sulfur, in a variety of combinations, constituting the donating atoms. Although they give characteristic absorbances in the UV region of the spectrum, absorbance in the visible region is possible, depending on the extent of ring conjugation. Unlike vanadyl porphyrins, most vanadyl non-porphyrins decompose readily in dilute acid solutions. VOBenzosalen, VOSalen, VOTADA, and VOBZEN represent vanadyl non-porphyrin compounds that have yet to be identified in heavy crude petroleums.

The SEC calibration plot for the 50/100 Å column combination, which gives a linear working range of 100 to 3000 daltons, is shown in Fig. 2. Vanadyl porphyrin and non-porphyrin compounds have again been used as calibration standards, to minimize error when assigning molecular weights to components in the petroleum samples. Polystyrene standards of 3100 and 9500 daltons have been used to calibrate the high molecular weight ranges, since no vanadyl compounds at these ranges were available.

The 50/100 Å SEC–HPLC–GFAA data for the separation of several of the standards is shown in Fig. 3 (a). The polystyrene standards were monitored at 254 nm, the vanadyl porphyrins and the metal-free porphyrin at 400 nm, and the vanadyl non-porphyrin compounds at 320 nm. The lower portion of Fig. 3 (a) shows the GFAA vanadium histograms. The added 100 Å column provides increased resolution of molecules with molecular weights greater than 900 daltons, allowing for accurate determination from 100 to slightly greater than 2000 daltons. All quantitative calculations in this study have therefore been based on the 50/100 Å column combination.

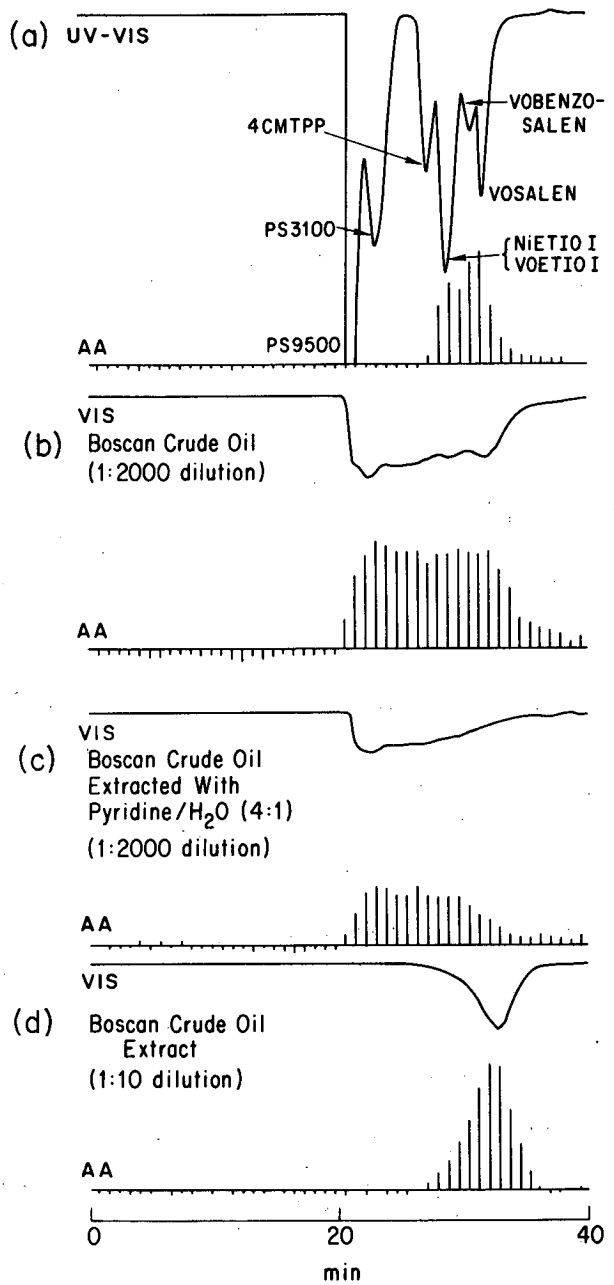


Figure 3. Combined 50/100 Å column SEC–HPLC–GFAA data for (a) standards, (b) Boscan crude oil, (c) crude oil after extraction, and (d) crude oil extract.

(XBL 826-10466)

The results shown in Fig. 2 were used to classify vanadyl compounds in the heavy crude oils by assigning them to one of four molecular-weight categories. In the first two categories, compounds with molecular weights of less than 400 daltons were classified as low-molecular-weight vanadyl non-porphyrins, and those between 400 and 900 daltons as vanadyl porphyrins, according to the definitions of these compound classes. With molecular weights above 900 daltons, vanadyl porphyrins cannot be present because of the increased ring conjugation that would be necessary. Instead, compounds with molecular weights between 900 and 2000 daltons were classified as high-molecular-weight vanadyl compounds, and, above 2000 daltons, as very high molecular weight vanadyl compounds. These latter two categories could include both low-molecular-weight vanadyl porphyrins and non-porphyrins intercalated into the asphaltenes, and high-molecular-weight vanadyl porphyrin and non-porphyrin compounds existing as asphaltenes.

Although vanadyl porphyrin compounds are not normally associated with molecular weights greater than 900 daltons, complexation to the asphaltene fraction of the oil could drastically increase their apparent molecular weight and change their physical and chemical properties. Likewise, low-molecular-weight vanadyl non-porphyrins could be incorporated into the asphaltene fraction of the oil by H–H interaction or hydrogen bonding, drastically altering their stability and other spectroscopic properties.

Figures 3 (b), (c), and (d) show the 50/100 Å column combination data for Boscan crude oil, the oil after extraction, and the extract, respectively. The upper portion of Fig. 3 (b) shows the visible absorbance, measured at 408 nm, while the lower portion gives the vanadium histogrammic output. The histogrammic peaks show vanadium in Boscan crude eluting at retention times from 20 to 40 minutes, corresponding to molecular weights ranging from more than 10,000 to 100 daltons. Interestingly, the HPLC–GFAA output shows that Boscan crude contains nearly equivalent percentages of vanadyl compounds in all four molecular-weight categories.

Figure 3 (c) shows vanadyl compounds being removed from the entire molecular-weight range of the crude oil. However, as evidenced in Fig. 3 (d), only vanadyl compounds with retention times greater than 28 minutes and centered at 32 minutes, corresponding to a molecular weight of 350 daltons, exist in the extract. Thus, although vanadyl compounds have been extracted from molecular weights greater than 900 daltons, only low-molecular-weight (less than 400 daltons) vanadyl porphyrin and non-

porphyrin compounds are present in the extract.

On the basis of the accuracy of the calibration data in Fig. 2, most of the vanadyl compounds in the extract can be classified as vanadyl non-porphyrins. The absence of high-molecular-weight vanadyl compounds from the extracts indicates that pyridine did not remove them from the oil. This raises important questions regarding the chemical nature of the non-extractable vanadyl compounds remaining in the asphaltenes.

Comparisons of the four oils, based on the SEC–HPLC–GFAA fingerprints from selective solvent extraction experiments, reveal several important features. Although the vanadium concentration varies widely, each oil contains a nearly similar percentage of all four molecular-weight categories. Geochemically, this is important, because it suggests that a similar mechanism of incorporation and competition for ligand sites occurs for the four oils. Also, vanadyl compounds remaining after extraction are evenly distributed between the two higher molecular-weight classes. This suggests that these heavier vanadyl compounds are similarly complexed. Of the three oils studied, only Prudhoe Bay crude shows any high-molecular-weight vanadyl compounds present in the extracts; this may be accounted for by a difference in the biogenesis and maturation of this relatively ancient petroleum.

Molecular-weight data for the four oils, based on the 50/100 Å SEC column combination, are summarized in Table 1. This table shows the vanadium concentrations (ppm) and percentage distributions for

Table 1. Molecular-weight distributions of vanadyl compounds present in heavy crude oils, oils after extraction, and the extracts, as determined by 50/100 Å SEC-HPLC-GFAA analysis.

Source	Molecular Weight	>2000	<2000 >900	<900 >400	<400	>2000	<2000 >900	<900 >400	<400
		Boscan				Cerro Negro			
Heavy crude oil	V (ppm)	307.[a]	229.	257.	315.	175.	123.	114.	148.
	V(%)	27.9[b]	20.0	23.4	28.7	31.3	21.9	20.4	26.4
Oil after extraction	V (ppm)	176.	128.	127.	109.	106.	93.0	55.7	25.2
	V (%)	32.6	23.7	23.6	20.1	37.9	33.2	19.9	9.0
Removed	V(ppm)	131.	92.	130.	206.	69.0	30.0	58.3	123.
	V (%)	42.3	41.8	50.7	65.4	39.4	24.4	51.1	83.0
Extract	V (ppm)	—	6.0	136.0	418.	—	—	74.0	206.
	V (%)	—	1.1	24.3	74.6	—	—	26.4	73.6
		Wilmington				Prudhoe Bay			
Heavy crude oil	V (ppm)	13.8	11.1	9.3	14.3	5.8	5.3	4.3	3.3
	V (%)	28.5	22.9	19.1	29.5	31.1	28.6	22.9	17.4
Oil after extraction	V (ppm)	2.6	1.8	1.1	0.9	3.2	2.8	2.1	1.1
	V (%)	40.2	28.3	16.8	14.7	34.6	30.6	22.9	11.9
Removed	V (ppm)	11.2	9.3	8.2	13.4	2.6	2.5	2.2	2.2
	V (%)	81.1	83.8	88.2	93.7	44.8	47.2	51.1	66.7
Extract	V (ppm)	0.3	0.8	7.5	33.5	0.5	0.5	3.1	5.4
	V (%)	0.8	1.9	17.8	79.5	5.0	5.0	32.9	57.1

[a]Concentration of metal present at molecular weights greater than 2000 daltons.

[b]Percentage of total metal present at molecular weights greater than 2000 daltons.

the whole crudes, the oils after extraction, and the extracts in terms of the four molecular weight categories. The vanadium percentages were calculated using the 50/100 Å SEC calibration data from Fig. 2 and the digitally recorded histogrammic outputs. From Fig. 2, the retention times for eluting species in each molecular-weight category were ascertained. The histogrammic vanadium outputs in each category were then summed and divided by the total histogrammic output for each oil, as summed over all four molecular-weight categories.

The vanadium concentrations (in ppm) were then calculated by multiplying each percentage by the total amount of vanadium present in the heavy crude oils and in the oils after five extractions. The vanadium concentrations for the extracts were calculated from the amount of vanadium removed by extraction from each oil. Values for vanadium removal were calculated by subtracting vanadium concentrations after extraction from those concentrations before extraction for each molecular-weight category; the corresponding percentages were calculated by dividing the vanadium concentration for each molecular-weight category by the total vanadium extracted from each crude oil.

Although the total amount of vanadium in Boscan, Cerro Negro, and Wilmington crude oils varies substantially, the percentages of vanadyl compounds present in each molecular-weight category are very similar. As Table 1 indicates, they have nearly equal percentages of vanadyl compounds in the heaviest and lightest classes (greater than 2000 and less than 400 daltons) and also contain nearly equivalent percentages of vanadyl compounds in the intermediate classes. These three oils have approximately 10% less vanadium in the two intermediate molecular-weight fractions than in both the heaviest and lightest fractions. Prudhoe Bay crude, however, has increasing percentages of vanadyl compounds as molecular weight increases over all four fractions.

As Table 1 shows for the crude oils after extraction, the percentages of vanadyl compounds with molecular weights greater than 2000 daltons increased for all four oils. The increases ranged from 11% for Prudhoe Bay oil to 41% for Wilmington oil, for an average increase of 22%. The percentages of vanadyl compounds between 900 and 2000 daltons also increased, from 7% for Prudhoe Bay to 52% for Cerro Negro, for an average increase of 25%. The percentages of vanadyl compounds with molecular weights between 400 and 900 daltons decreased by 2 and 12% for Cerro Negro and Wilmington oils, but remained equal for Prudhoe Bay and increased by 1% for Boscan. The percentages of vanadyl compounds of less than 400 daltons decreased for all four oils, from 30% for Boscan to 66% for Cerro Negro, an average decrease of 44%.

Table 1 also shows the weight percentages of vanadyl compounds removed from the four molecular-weight categories for each oil. While the oils show a trend toward increased removal at decreased molecular weights (especially for less than 400 daltons), Wilmington crude oil shows significantly more vanadium removal over all four fractions.

That extraction of vanadyl compounds from the low-molecular-weight categories was greater than that from the high-weight categories is not surprising. Vanadyl porphyrin and non-porphyrin compounds in the low-molecular-weight, malthene fraction of the crude oils occur freely suspended and are therefore more likely to form ligational complexes. Vanadyl compounds in the high-molecular-weight, asphaltene fraction can be strongly complexed to the asphaltenes, making removal more difficult and sometimes impossible.

Finally, Table 1 shows the amounts and percentages of vanadyls in the four weight categories for each crude-oil extract. These data indicate that most of the vanadyl compounds in each extract exist at molecular weights of less than 400 daltons. Cerro Negro extract contains no vanadyl compounds above 900 daltons. Of the other extracts, only Prudhoe Bay has significant amounts of vanadyl compounds at molecular weights greater than 900 daltons.

This finding is important because it reveals that, although vanadyl porphyrin compounds are present in the extracts, they account for only 18 to 33% of the total vanadium present. The majority of the vanadyl compounds in the extracts are low-molecular-weight vanadyl non-porphyrin compounds. Demetallation of the pyridine extracts conceivably prohibits identification of these compounds because of their instability in dilute acid solutions.

This lack of high-molecular-weight vanadyl compounds in three of the four extracts suggests that, if distinct species are in fact present, removal of these highly conjugated molecules with coordinating solvents will be difficult.

SEC–HPLC–GFAA Analysis of Heavy Crude Asphaltenes

The asphaltenes in the heavy crude oils contain a significant percentage of the vanadium, and thus examination of their content for vanadyl porphyrin and non-porphyrin compounds by HPLC–SEC–GFAA analysis would be critical. Additionally, extraction of the asphaltenes with a pyridine/H_2O solution would be helpful in learning more about non-porphyrin vanadyl compounds complexed to the macromolecular structure of the asphaltenic fraction.

During this year, work has continued with the asphaltenes of Boscan, Cerro Negro, Wilmington, and Prudhoe Bay heavy crude oils. Separation is achieved by agitating samples in 10 volumes of pentane at about 300 motions per minute for 24 hours. Separations have also been made using heptane as the solvent, but these samples have not yet been analyzed. The asphaltenes are separated from the pentane solubles with a 0.45 micron Millipore filter, washed with pentane, and stored under nitrogen. X-ray fluorescence analysis for vanadium has been performed and compared with earlier results for whole crude oils (Table 2). A significant percentage of the vanadium in the oils is contained in the asphaltenes. The percentage of vanadium in the asphaltenes is not directly proportional to the amount of asphaltenes present in an oil; and although the asphaltenes represent less than 3% of the weight of a crude, they still account for almost half of the vanadium present.

Samples of the asphaltenes are redissolved in methylene chloride and analyzed by HPLC–SEC–GFAA using 50Å and 100Å SEC columns in series with element-specific vanadium detection at 318.4 nm. The visible detector was set at 408 nm to detect the soret bands of vanadyl porphyrins. The extraction and analysis were repeated three times for each oil. Figure 4 shows a typical SEC result. The asphaltenes were separated into the four molecular-

Table 2. Concentrations of vanadium in heavy crude oils and asphaltenes.

Sample	ppm V in crude oil	ppm V in asphaltene	Wt.% of asphaltene in crude	Wt.% of total V in asphaltene
Boscan	1100	4310	25	98
Cerro Negro	560	1680	20	60
Wilmington	49	422	6.2	53
Prudhoe Bay	19	280	2.9	43

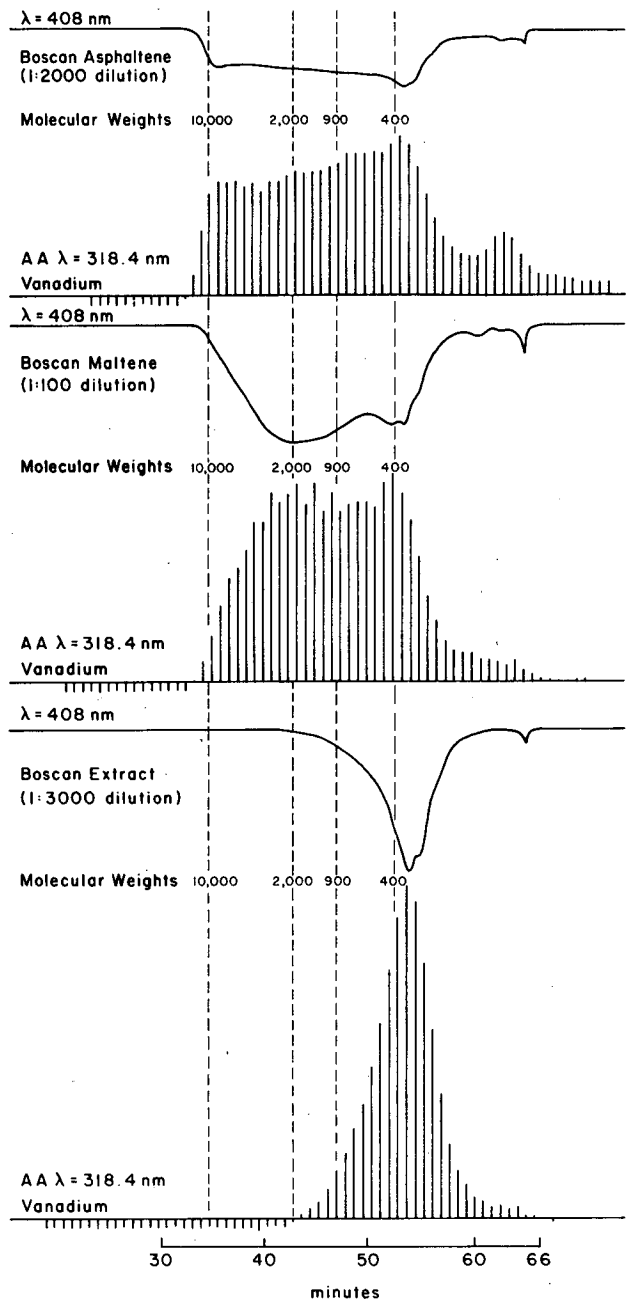


Figure 4. Combined 50/100/1000 Å column SEC–HPLC–GFAA analysis of Boscan asphaltene, malthene, and asphaltene extracts. (XBL 8210-3112)

weight fractions used before: greater than 2000, between 2000 and 900, between 900 and 400, and less than 400. The third fraction is assumed to be rich in vanadyl porphyrins. It can be shown that the percentage of vanadium in the 900-to-400 fraction is much lower for the asphaltenes. This does not mean that fewer porphyrins are in the asphaltenes, but rather that the asphaltenic porphyrins are incorporated into larger complexes, because there is intense visible absorption in the highest molecular-weight fraction.

The pentane-soluble, malthene fractions of the oils were vacuum-distilled to remove the pentane and then dissolved in methylene chloride for HPLC–SEC–GFAA analysis. Figure 4 shows a typical vanadium distribution for the malthene of Boscan heavy crude oil. By comparing the asphaltenes and malthenes with their whole oils, it can be observed that, in general, the asphaltenes are richer in the high-molecular-weight vanadium compounds, while the malthenes are richer in the two middle fractions. The heavier vanadium concentrations in the very highest and very lowest fractions of the asphaltenes conform well with the concept of asphaltenes as large molecules with smaller molecules encapsulated within them. It is also interesting to note that Boscan crude, which has the highest asphaltenic vanadium concentration of the four oils studied, has an asphaltenic vanadium distribution very similar to the vanadium distribution of the whole crude oil.

The four oils can also be divided into two groups: high-asphaltene oils, including Boscan and Cerro Negro, and low-asphaltene oils, including Wilmington and Prudhoe Bay. The high-asphaltene oils have similar molecular-weight distributions of vanadium in their asphaltenes and whole oils and have similar percentages of vanadium in the highest and lowest molecular-weight ranges of the asphaltenes. The low-asphaltene oils have more extreme variations in vanadium distribution between the asphaltenes and the whole oils, and their vanadium concentrations are significantly greater in the heaviest range than in the lightest. This feature is especially pronounced in the lowest-asphaltene oil, Prudhoe Bay, which has 57% of its vanadium in the greater-than-2000 range and only 17% in the less-than-400 range.

We have also attempted to isolate vanadyl porphyrins from the asphaltenes. Following a procedure similar to that used by other researchers, the asphaltenes were dissolved in xylene and extracted with a pyridine-water solution. The extracts have a strong absorbance at 408 nm, typical for vanadyl porphyrins. Of the four crude oils, only Boscan and Cerro Negro gave extracts with sufficiently large vanadium concentrations to make GFAA analysis possible. Analysis using the HPLC–SEC–GFAA combination showed that a substantial portion of the vanadium present in these two extracts had a molecular weight too small for porphyrins (Table 3). Further analysis with a second HPLC system equipped with an amino-cyano column and a rapid scanning UV–VIS detector has established the presence of several vanadyl non-porphyrin compounds in the pyridine-water extract. Future work will characterize these compounds.

Table 3. Vanadium distribution in pyridine-water extracts of asphaltenes (percent of total V in four classes of molecular weights).

Sample	Molecular Weight			
	>2000	<2000 >900	<900 >400	<400
Boscan Extract	4	18	39	39
Cerro Negro Extract 4	20	36	40	—
Boscan Filtrate	54	24	12	10

PLANNED ACTIVITIES FOR 1983

We will continue to work on the speciation of vanadyl non-porphyrin compounds in heavy crude petroleums and their asphaltenes; we expect the resulting knowledge may lead to rational removal methods and contribute to understanding catalyst poisoning phenomena.

REFERENCES

1. Silbernagel, B.G., (1979), *J. Catalysis 56*, p. 315.
2. Silbernagel, B.G., Riley, K.L. (1980), in *Catalyst Deactivation*, B. Delmon and G.F. Froment, Eds., Elsevier Scientific Publishing Co., p. 313.
3. Sie, S.T. (1980), in *Catalyst Deactivation*, B. Delmon and G.F. Froment, Eds., Elsevier Scientific Publishing Co., p. 545.

4. Rahbe, G., Pachano, J., Krasuk, J.H., and Rodriquez, O. (1978), *J. Japan Petrol. Inst. 21*, p. 2.
5. Hung, C., and Wei, J. (1980), *Ind. Eng. Chem. Process Des. Dev. 19*, p. 250.
6. Hung, C., and Wei, J. (1980), *Ind. Eng. Chem. Process Des. Dev. 19*, p. 257.
7. Morales, A., and Galiasso, R. (1982), *Fuel 61*, p. 13.
8. Fish, R., and Tannous, R.S., (1982), *Organometallics 1*, p. 1238.
9. Bottino, Finocchiaro, P., Libertini, E., Reale, A., and Recca, A. (1980), *Inorg. Nucl. Chem. Letters 16*, p. 417.
10. Hodgson, G.W. (1973), *Ann. N.Y. Acad. Sci. 206, p. 417.*
11. Hodgson, G.W., (1973), *Ann. N.Y. Acad. Sci. 206, p. 670.*
12. Andrae, M.O., Klumpp, D. (1979), *Environ. Sci. Technol. 13*, p. 738.
13. Brinckman, F.E., Bellama, J.M., Eds. (1978), *Organometals and Organometalloids: Occurrence and Fate in the Environment,* ACS Symposium Series 82, American Chemical Society, Washington, D.C.
14. Fish, R.H., Jewett, K.L., and Brinckman, F.E. (1982), *Environ. Sci., and Tech. 16*, p. 174, and references therein.
15. Brinckman, F.E., and Fish, R.H., Eds. (1981), *Environmental Speciation and Monitoring Needs for Trace Metal-Containing Substances from Energy-Related Processes,* National Bureau of Standards Special Publication 618.

SYNTHESIS, STRUCTURAL ELUCIDATION, AND STEREOCHEMISTRY OF FIVE-COORDINATE ORGANOARSENIC CATECHOLATES*

R.H. Fish and R.S. Tannous

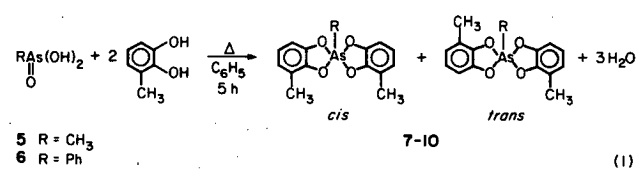
Recently, we have been investigating the speciation or molecular characterization of organoarsenic compounds thought to be present in oil shale kerogen and the products of its pyrolysis, including the retort waters.[1,2] These studies led to the identification, for the first time, of methyl and phenylarsonic acids in these precursors and products.

We have since initiated studies to find innovative methods of removing these compounds and other organometallics from fossil fuel products. In this regard, we have been experimenting with a method that utilizes substituted catechols as potential ligands that could be placed in a polymeric matrix for the future removal of organoarsenic compounds from the above mentioned products.

Surprisingly, we found very few references on the reactions of catechols with alkyl or arylarsonic acids[3-8] and none on similar reactions with substituted catechols.[9]

ACCOMPLISHMENTS DURING FY 1982

Chart 1 shows the catechols, **1–4**, that we used in the reactions with methyl and phenylarsonic acid, **5** and **6**. Compound **1** reacts with either **5** or **6** to provide a mixture of *cis* and *trans* five-coordinate organoarsenic catecholates **7–10** (Eq. 1).



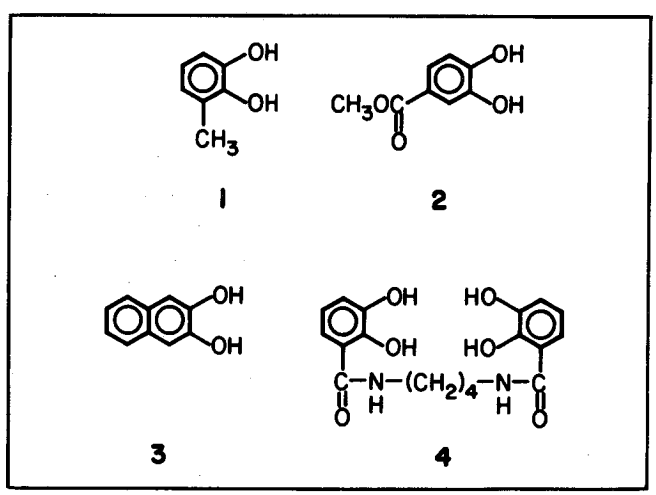


Chart 1. Catechols used in the synthesis of five-coordinate organoarsenic catecholates. (XBL 823-8458)

*This work was supported by the Assistant Secretary for Fossil Energy and the Division of Oil, Gas and Shale Technology, and the Bartlesville Energy Technology Center of the U.S. Department of Energy under contract No. DE-AC03-76SF00098.

Compounds **7–10** were characterized by a combination of nuclear magnetic resonance spectroscopy (NMR), mass spectrometry (MS), infrared spectroscopy (IR), and elemental analysis.[10] The 250 MHz ^1H NMR spectrum provided definitive evidence that compound **1** reacted with either **5** or **6** to give a mixture of *cis* and *trans* isomers (**7, 8** R = CH_3 and **9, 10** R = Ph). Thus, compounds **7** and **8** showed two methyl resonances (catecholate ring) at 2.21 and 2.19 ppm (benzene-d_6, TMS) and two methyl resonances for groups bonded to arsenic at 1.33 and 1.32 ppm in the ratio of 53:47.

The corresponding *cis* and *trans* compounds, **9** and **10**, where R = Ph, had methyl resonances at 2.26 and 2.12 ppm (benzene-d_6, TMS) in the ratio of 90:10. The complexity of the phenyl region at 250 MHz did not allow the catecholate protons and phenylarsenic protons to be separated, and thus the ^1H NMR spectrum was obtained at 400 MHz. The 400 MHz ^1H NMR spectrum of **9, 10** (benzene-d_6, TMS) showed resonances at 7.81 (doublet, J = 8.3 Hz); 6.83 (multiplet) and 6.74 ppm (overlapping triplets J = 8.3 Hz) for the phenylarsenic protons in the ratio of 2:1:2. The catecholate protons were found at 6.56 (doublet of doublets, J_{ortho} = 7.8 Hz, J_{meta} = 1.4 Hz); 6.65 (overlapping triplets, J = 7.8 Hz), 6.93 (triplet, J = 7.8 Hz) and the methyl groups at 2.24 ppm (singlet) in the ratio of 2:2:2:6. The complexity of the phenyl region, where protons on the phenyl group attached to arsenic appeared to be all non-equivalent, provided tentative evidence for the *cis* isomer, **9**, rather than the *trans* isomer, **10**, as the major product in this reaction.

In order to unequivocally ascertain the stereochemistry of the major isomer, as **9** (*cis*) or **10** (*trans*), we obtained a single-crystal x-ray analysis.[11] Figure 1 shows an ORTEP drawing of the major isomer, **9,** with the methyl groups clearly *cis* to each other and the geometry around the arsenic essentially rectangular-pyramidal (95%), while the axial phenyl group is twisted so that it lies in the same plane as oxygen 2 and oxygen 3. The angle between the carbons 1 through 6 on the phenyl group attached to arsenic and the oxygen-arsenic-oxygen plane is 4.7°. (See Table 1 for other pertinent bond angles and lengths.[12–14]) Recently, Day et al.[15] reported on the crystal structure of a product from the reaction of phenylarsenic acid and catechol.[6] This five-coordinate organoarsenic catecholate was also found to have a rectangular pyramidal geometry around arsenic.[15] Our study represents the first stereochemical assignment to be made on a five-coordinate organoarsenic catecholate and has implications for the mechanism of formation of these compounds.

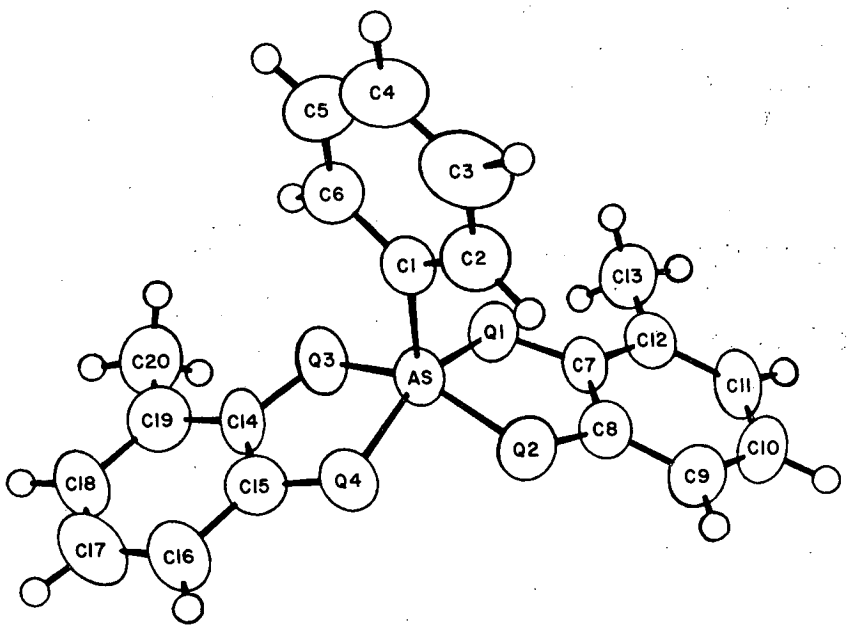


Figure 1. ORTEP diagram of *cis* $(3\text{-}CH_3\text{-}C_6H_3O_2)_2\ AsC_6H_5$, compound **9**, showing 50% probability ellipsoids. (XBL 823-8156A)

Table 1. Selected bond lengths and angles for *cis* $(3\text{-}CH_3\text{-}C_6H_3O_2)_2AsC_6H_5$, **9**.[a]

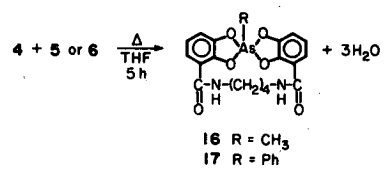
Atoms	Bond Length	Atoms	Angle, Deg.
$As\text{-}O_1$	1.806 (1)	$O_1\text{-}As\text{-}O_2$	87.93 (7)
$As\text{-}O_2$	1.799 (2)	$O_1\text{-}As\text{-}O_3$	85.43 (7)
$As\text{-}O_3$	1.784 (2)	$O_1\text{-}As\text{-}O_4$	150.84 (9)
$As\text{-}O_4$	1.825 (2)	$O_2\text{-}As\text{-}O_3$	149.85 (9)
$As\text{-}C_1$	1.899 (2)	$O_2\text{-}As\text{-}O_4$	82.71 (8)
$C_7\text{-}O_1$	1.365 (3)	$O_3\text{-}As\text{-}O_4$	88.95 (9)
$C_8\text{-}O_2$	1.370 (3)	$O_1\text{-}As\text{-}C_1$	105.5 (8)
$C_{14}\text{-}O_3$	1.413 (3)	$O_2\text{-}As\text{-}C_1$	104.99 (9)
$C_{15}\text{-}O_4$	1.345 (3)	$O_3\text{-}As\text{-}C_1$	105.12 (9)
$C_{12}\text{-}C_{13}$	1.474 (4)	$O_4\text{-}As\text{-}C_1$	103.59 (9)
$C_{19}\text{-}C_{20}$	1.410 (4)	$As\text{-}O_1\text{-}C_7$	111.12 (13)

[a]Estimated standard deviations in parentheses.

Compound **2** reacted with **5** to provide a compound, **11**, with a single methylarsenic resonance at 1.92 ppm (^1H, 250 MHz, DMSO-d_6, TMS) and a single methoxyl resonance at 3.78 ppm; this is indicative of one isomer, which we presume to have *cis* stereochemistry as in **9**. Compound **2** also reacts with **6** to provide a mixture of compounds, **12** and **13**, with two methoxyl signals (^1H, 250 MHz, DMSO-d_6, TMS) at 3.76 and 3.74 ppm in the ratio of 95:5. Again, as with **11**, we presume *cis* stereochemistry for the major isomer.

Compound **3**, a benzo-substituted catechol, reacted with **5** and with **6** to give the five-coordinate organoarsenic compounds **14** and **15** respectively. While no stereochemistry is involved in the formation of either **14** or **15**, it is important to note that substitution on the naphthyl ring is certainly possible for future attachment of this type of compound to a polymeric backbone. The pertinent ^1H NMR data (250 MHz, DMSO-d_6, TMS) provided an upfield shift, as with the NMR spectra of compounds **7–13**, for the catechol ring protons of **14** and **15** when compared to **3**. Thus, **14** had the catechol protons (singlet) at 7.09 ppm, **15** at 7.10 ppm, and **3** at 7.12 ppm, which indicates the influence of arsenic atoms on the shift of protons on catechol rings to higher fields. A similar NMR result was obtained by McArdle et al.[16] for some gallium and rhodium catecholate complexes.

Our final ligand of interest, **4**,[17] was important to study, since it represented a model for a recently reported polymer of potential use for our future applications.[18] We chose **4** (4-LICAM) after making Dreiding models that clearly showed the central cavity capable of accommodating an arsenic atom (~3.58 to 3.63 Å, Fig. 1). Reaction of **4**, with either **5** or **6** provided the intramolecular five-coordinate organoarsenic derivatives **16** and **17** (Eq. 2).



The 250 MHz ^1H NMR and 70 eV MS (solid probe) data were consistent with the structures assigned. Notably, the mass spectra provided the parent ion and an ion resulting from a loss of the catechol group with a carbonyl attached. This was followed by a fragmentation of the $\text{-}CH_2CH_2\text{-}NH$ groupings. For example, with **17**, the MS ions of interest were: *m/e* 508 ($M^{+\cdot}$); 373 ($M\text{-}C_7H_{13}N_2O_3$); 331 ($M\text{-}C_9H_8NO_3$); and 287 ($M\text{-}C_{11}H_{13}N_2O_3$).

A typical procedure for the preparation of a five-coordinate organoarsenic catecholate derivative is that for **9**, as follows.

In a 50 ml flask, equipped with condenser, drying tube, and Dean-Stark trap for water removal, was placed 1.29 g (10.42 m*M*) of phenylarsonic acid and 1.05 g (5.21 mM) 3-methylcatechol (freshly sublimed) in 30 ml of benzene. The reaction mixture was refluxed for 5 h. The benzene was removed on a rotary evaporator and the compound recrystallized from carbon tetrachloride/methanol and dried under vacuum to give 1.88 g (91% yield) of **9** (melting point, 134-135°C). Calculated for $C_{20}H_{17}O_4As$: C, 60.6; H, 4.3. Found: C, 60.39; H, 4.46; electron impact mass spectrometry (70 eV, solid probe), *m/e* 396 ($M^{+\cdot}$), 274, 197, 151, 106.[19,20]

We have used this procedure to derivatize both methyl and phenylarsonic acid, **5** and **6**, that had been isolated from a Green River oil shale kerogen by

extraction with methanol. Since **7** and **9** can be chromatographed on a 30 m fused silica capillary column (OV101), the use of GC-MS will enhance the utility of these organoarsonic acid derivatives for other applications.

PLANNED ACTIVITIES FOR 1983

In future experiments, we hope to place several of our catechol derivatives in polymeric backbones to see if they retain their reactivity with organoarsonic acids.

REFERENCES

1. Fish, R.H., Brinckman, F.E., and Jewett, K.L. (1982), *Environ. Sci. Technol. 16*, p. 174.
2. Weiss, C.S., Brinckman, F.E., and Fish, R.H. (1981), in *Proceedings on Environmental Speciation of Trace Metal-Containing Compounds in Energy-Related Processes*, May 18–20, Gaithersburg, Maryland. National Bureau of Standards Special Publication 618, p. 197.
3. Salmi, E.J., Merivuori, K., and Laaksonen, E. (1946), *Kemistilehti Suomen 19B*, 102 (Chem. Abs., *41*, 5440a).
4. Bacher, J.H., and Van Oosten, R.P. (1940), *Rec. Trav. Chem. 59*, p. 41.
5. Englund, B. (1926), *Chem. Ber. 59*, p. 2669.
6. Sau, A.C. and Holmes, R.R. (1980), *J. Organometal. Chem. 217*, p. 157.
7. Wieber, M., Eichhorn, B., and Gotz, J. (1973), *Chem. Ber. 106*, p. 2738.
8. Maroni, P., et al. (1976), *Tetrahedron Letters*, 1193.
9. Fish, R.H., and Weitl, F.L., (1981), in *Proceedings of the Tenth International Conference on Organometallic Chemistry, Toronto, Canada, August 9–14, 1981*, Abstract 1D12, p. 62.
10. All new compounds we report had elemental analyses (C, H, N) within ±0.5% of theory. The EIMS, IR, and NMR spectra for all compounds supported their structures.
11. A full account of the structural parameters for **9** will be given in a future paper.
12. Goldwhite, H. and, Teller, R.G. (1978), *J. Amer. Chem. Soc. 100*, p. 5357.
13. Wunderlich, H. (1978), *Acta Cryst. B 34*, p. 1000.)
14. Holmes, R.R. and Deiters, J. (1977), *J. Am. Chem. Soc. 99*, p. 3318.
15. Day, R.O. et al. (1982), *J. Am. Chem. Soc. 104*, p. 2127.
16. McArdle, J.V., Sofen, S.R., Cooper, S.R., and Raymond, K.N. (1978), *Inorg. Chem. 17*, p. 3075.
17. The series of LICAM derivatives of increasing methylene chains, **2-6**, were prepared according to the procedures of Dr. F.L. Weitl; see e.g., Weitl, F.L., and Raymond, K.N. (1980), *J. Amer. Chem. Soc. 102*, p. 2289.
18. Dawson, M.I., Chan, R.L.-S., Cloudsdale, I.S., and Harris, W.R. (1981), *Tetrahedron Letters 22*, p. 2739.
19. Fish, R.H., Tannous, R.S., Weiss, C.S., and Brinckman, F.E. (1983), *J. Chem. Soc. Chem. Commun.* (in press).
20. Fish, R.H., and Tannous, R.S. (1982), *Organometallics 1*, p. 1238.

ORGANOMETALLIC GEOCHEMISTRY: ISOLATION AND IDENTIFICATION OF ORGANOARSENIC COMPOUNDS FROM GREEN RIVER FORMATION OIL SHALE*

R.H. Fish, R.S. Tannous, W. Walker, C.S. Weiss,† and F.E. Brinckman†

The molecular characterization of naturally occurring organometallic compounds in fossil fuel precursors is becoming a significant area of research because of the importance of these compounds in emerging synthetic fuel processes and their impact on the environment.[1]

Recently, using a high-performance liquid chromatograph coupled to a graphite-furnace atomic absorption spectrometer as an element-selective detector

*This work was supported by the Assistant Secretary for Fossil Energy and the Division of Oil, Gas and Shale Technology, and the Bartlesville Energy Technology Center of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. A portion of the NBS study was supported by the NBS Office of Standard Reference Materials. C.S.W. was a National Research Council–National Bureau of Standards Postdoctoral Research Associate (1980–1982).

†Chemical and Biodegradation Processes Group, Center for Materials Science, National Bureau of Standards, Washington, DC 20234.

(HPLC-GFAA), we identified methyl- and phenylarsonic acids as well as arsenate in oil-shale retort waters.[2] We also have analyzed the oils produced by shale pyrolysis and have found that the same organoarsonic acids occur, but in association with iron-containing macromolecules with molecular weights in the range of 2000 to 4000 daltons.[3,4]

In order to discern whether these compounds were natural products in the precursor of the shale oil and the retort waters or were formed during pyrolysis, we examined a sample of Green River Formation oil shale. Oil shale from the Green River Formation is a fine-grained sedimentary rock that contains appreciable quantities of organic material. It consists of three fractions—kerogen, bitumen, and an inert substance. Kerogen and bitumen, which constitutes the organic material, are regarded as biogeochemical fossil products, emanating largely from lipid fractions of ancient algae and forming the ubiquitous oil-source matrix in shales.[5]

ACCOMPLISHMENTS DURING FY 1982

The Green River Formation oil shale sample (10 g) was crushed and Soxhlet-extracted with 500 ml of methanol for 48 hours. This effectively removed about 20% of its total arsenic. [The Green River oil shale sample from Anvil Points, Colorado (NBS Standard Reference Material) was found to contain approximately 20 ppm of total arsenic.] Following evaporation (25 ml) and filtration, we speciated the extract by HPLC, using a Dionex anion exchange column with 0.2 *M* ammonium carbonate in water/methanol (85:15) as the eluting solvent. The arsenic compounds were detected via automatic GFAA analysis at 197.3 nm.[1,2]

Figure 1 gives the arsenic-specific chromatogram of the compounds we identified as methylarsonic acid, phenylarsonic acid, and arsenate, based on retention times of the authentic arsenic compounds.[2] One or more unknown neutral organoarsenic compounds also eluted with the solvent front.

We recently studied the reactions of methyl- and phenylarsonic acids with substituted catechols and established that they provide five-coordinate organoarsenic catecholates.[6] Since many of these organoarsenic catecholates can be gas-chromatographed on fused silica capillary columns and characterized by electron impact mass spectros-

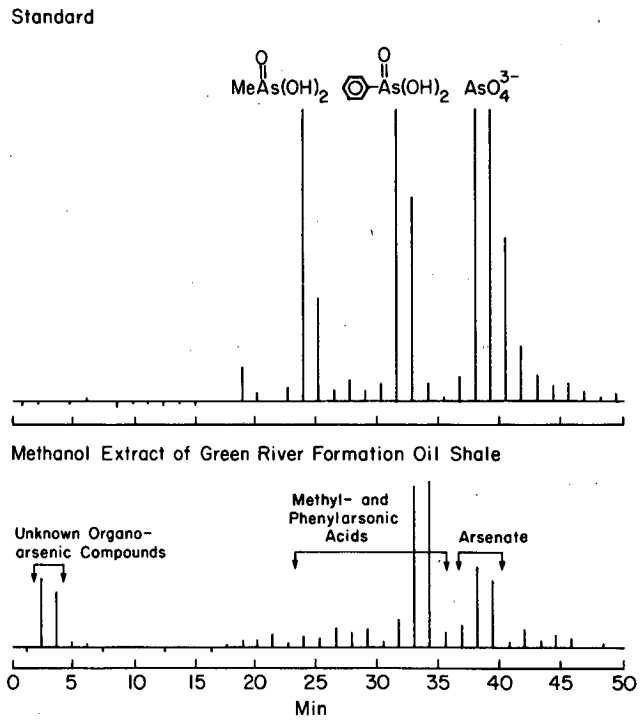


Figure 1. HPLC-GFAA analysis of Green River Formation oil shale extracted with refluxing methanol. AA detection of arsenic was at 193.7 nm. For HPLC, a Dionex anion-exchange column with 0.2 *M* $(NH_4)_2CO_3$ in aqueous methanol as the eluting solvent was used. Bracketed areas were isolated by preparative HPLC. (XBL 8210-3116)

copy (GC–EIMS), we decided to apply this technique to unequivocally identify the methyl- and phenylarsonic acids in the oil shale extract.

The methanol extract was purified by preparative HPLC (the area from 22 to 35 min was collected, see Fig. 1), lyophilized, and dissolved in benzene. To this solution was added excess 3-methylcatechol, and the reaction mixture was refluxed for 5 h and worked up to remove the excess 3-methylcatechol. A concentrated sample was subjected to GC-EIMS analysis to provide spectra and scan numbers (retention times) identical to the known samples of the 3-methylcatecholates of both methyl- and phenylarsonic acids.

Figure 2(A) shows the reconstructed ion chromatogram of the two standards, 3-methylcatecholates of methyl- and phenylarsonic acids; the single-ion chromatograms show pertinent fragments of interest at *m/e* 197 and 212 for the methylarsonic acid derivative [Fig. 2(B),(C)] and *m/e* 197 and 274 for

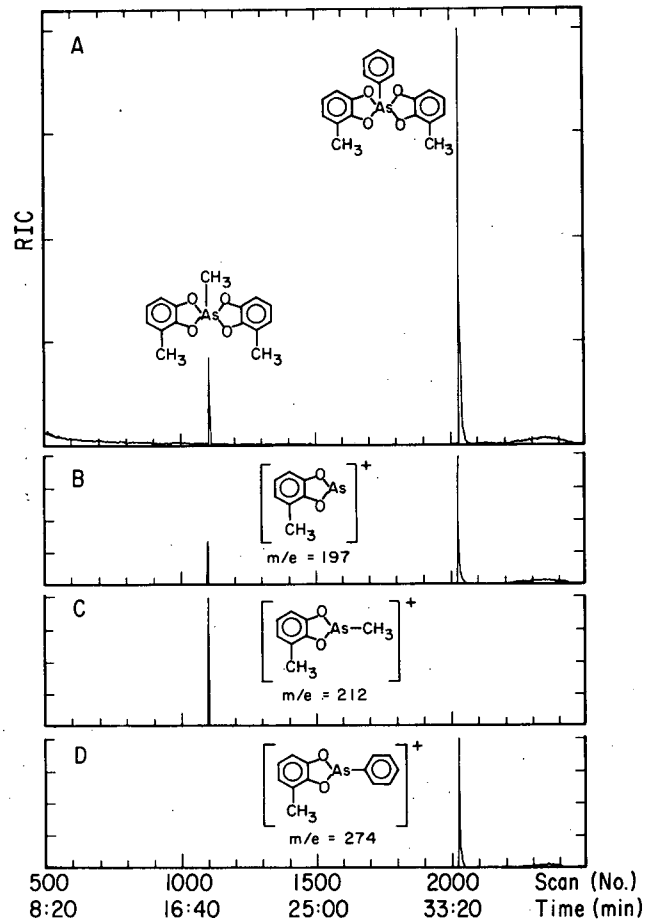


Figure 2. GC-EIMS analysis of the 3-methylcatecholates of methyl- and phenylarsonic acids. (A) Reconstructed ion chromatogram of known methyl- and phenylarsonic acid derivatives of 3-methylcatechol. (B) Selected ion chromatogram showing *m/e* 197 for each derivative. (C) Selected ion chromatogram for methylarsonic acid-3-methylcatecholate at *m/e* 212. (D) Selected ion chromatogram for phenylarsonic acid-3-methylcatecholate at *m/e* 274. (XBL 828-10938A)

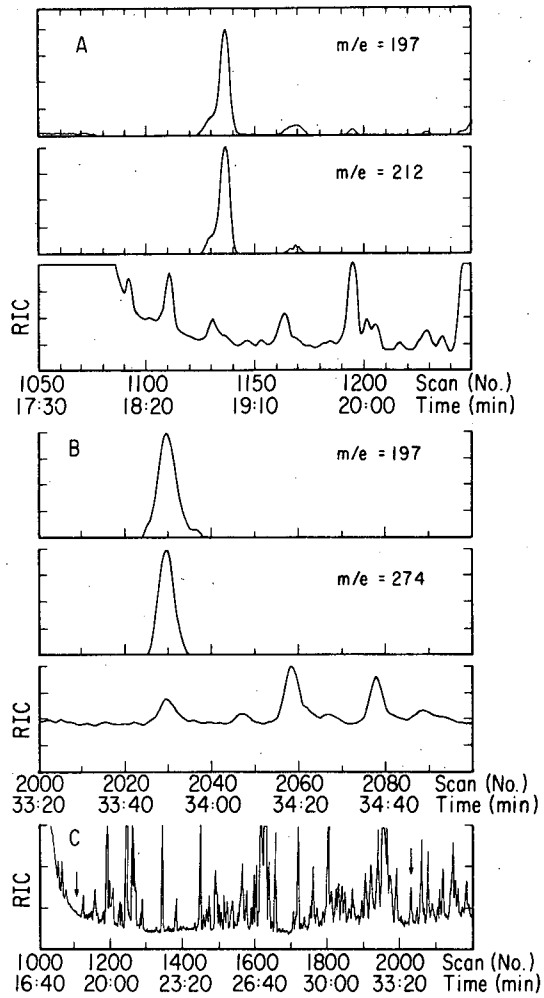


Figure 3. GC-EIMS analysis of the derivatized, HPLC-purified methanol extract. (A) Ion chromatograms near scan 1137 for *m/e* 197 and *m/e* 212, confirming identification of 3-methylcatecholate of methylarsonic acid in (C). (B) Ion chromatograms near scan 2030 for *m/e* 197 and *m/e* 274, confirming identification of 3-methylcatecholate of phenylarsonic acid in (C). (C) Reconstructed ion chromatogram of HPLC-purified methanol extract; arrow on left designates methylarsonic acid-3-methyl catecholate, and arrow on right designates phenylarsonic acid-3-methyl catecholate. (XBL 828-10939A)

the phenylarsonic acid derivative [Fig. 2(B),(D)]. Figure 3(C) shows the region we purified by HPLC containing the organoarsonic acids, which were derivatized, and the expanded sections of this chromatogram containing the organoarsenic catecholates with the important ions, *m/e* 197, 212, and 274, clearly evident for the 3-methylcatecholates of methylarsonic [Fig. 3(A)] and phenylarsonic [Fig. 3(B)] acids. Additionally, the inorganic anion, arsenate (AsO_4^{3-}), was verified in a similar fashion (preparative HPLC of the region from 35.5 to 41 min) by preparation of the *tris* (trimethylsilyl-) derivative of the ammonium salt of arsenate and analyzing the purified extract by GC-EIMS for ions at *m/e* 207, 343, and 358.[7] The organoarsenic compound or compounds that elute with the solvent front (Fig. 1) have not yet been identified, and work is in progress to determine the structure.[7]

PLANNED ACTIVITIES FOR FY 1983

We believe these identifications of the organoarsonic acids to be the first such molecular characterizations of trace organometallic compounds to be reported for any fossil fuel precursors and that they initiate a new field, organometallic geochemistry, that has heretofore been totally unexplored.

Our findings imply that these organoarsonic acids are natural products and hence have a biogeochemical origin in the oil shale fossilization process. It is also interesting to note that no examples of biophenylation have been reported, whereas biomethylation of arsenic compounds is well-known.[8] How the phenylarsonic acid forms will have to be answered by examining oil shale precursors such as freshwater algal mats and other biogeochemical samples. We plan to proceed with this aspect in FY 1983.

Finally, the fact that these organoarsonic acids are released upon oil shale pyrolysis has important implications for synthetic fuel processes in which the role of organometallic compounds in poisoning process catalysts and in contributing to environmental problems is paramount.[9]

REFERENCES

1. Brinckman, F.E. and Fish, R.H., Eds. (1981), *Environmental Speciation and Monitoring Needs for Trace Metal-Containing Substances from Energy-Related Processes,* NBS Special Publication 618, National Bureau of Standards, Washington, D.C.
2. Fish, R.H., Jewett, K.L., and Brinckman, F.E. (1982), *Environ. Sci. and Tech. 16,* p. 174, and references therein.
3. Brinckman, F.E., Weiss, C.S., and Fish, R.H. (1983), in *Chemical and Geochemical Aspects of Fossil Energy Extraction,* T.F. Yen, Ed., Ann Arbor Science, Ann Arbor, MI, chap. 13, p. 197.
4. Weiss, C.S., Parks, E.J., and Brinckman, F.E., (1982), in *Arsenic: Industrial, Biomedical, and Environmental Perspectives,* W.H. Lederer and R.J. Fensterheim, Eds., Van Rostrand-Reinhold Co., New York.
5. Yen, T.F., and Chilingarian, G.V., Eds. (1976), *Developments in Petroleum Science,* vol. 5, Elsevier, Amsterdam.
6. Fish, R.H. and Tannous, R.S. (1982), *Organometallics 1,* p. 1238.
7. Butts, W.C., and Rainey, W.T., Jr., (1979), *Anal. Chem. 43,* p. 538.
8. McBride, B.C., Merilees, H., Cullen, W.R., and Pickett, W. (1968), in *Organometals and Organometalloids: Occurrence and Fate in the Environment,* F.E. Brinckman and J.M. Bellama, Eds., ACS Symposium Series 82, American Chemical Society, Washington, D.C., p. 94.
9. Fish, R.H., Tannous, R.S., Walker, W., Weiss, C.S., and Brinckman, F.E. (1983), *J. Chem. Soc. Chem. Comm.* (in press). Lawrence Berkeley Laboratory report LBL-15060.

PROCESSING OF CONDENSATE WATERS FROM COAL GASIFICATION*

C.J. King, J. MacGlashan, D. Mohr, P. Mackenzie, R. Thompson, and J. Bixby

Large volumes of condensate water are formed when effluents from coal-gasification reactors are cooled. These waters contain large concentrations of dissolved acid gases and ammonia, as well as substantial amounts of dissolved polar organics, notably phenols and related compounds. For water economy and environmental protection, it is desirable to recycle these waters to the gasification process. The principle objective of this project is to develop workable, reliable, and economical physicochemical processing methods that will enable such condensate waters to be recycled. Particular attention is being given to solvent-extraction and energy-efficient stripping processes, and to combinations of these.

Work to date has focused upon four areas:

(1) analyses of individual components contributing to the measured Chemical Oxygen Demand (COD);

(2) extraction with both conventional and novel solvents to allow more complete reduction of COD and/or lower energy consumption;

(3) interpretation of rates of stripping of ammonia and acid gases from condensate waters; and

(4) innovative combinations of extraction and stripping that have the potential to reduce substantially the energy required to remove ammonia and isolate it as a salable product.

Results through 1981 are described in the Annual Reports for FY 1979 through 1981.

*This work was supported by the Assistant Secretary for the Environment, Office of Environmental Compliance and Overview, Division of Environmental and Safety Engineering, Environmental Control Technology Branch of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

ACCOMPLISHMENTS DURING FY 1982

Analyses of Condensate Waters

In the preceding year (FY 1981), three condensate-water samples were obtained from the slagging fixed-bed gasifier at the Grand Forks Energy Technology Center (GFETC) and analyzed (see FY 1981 Annual Report). During FY 1982, a fourth sample (RA-120) was obtained, also from GFETC. This sample was analyzed by a reversed-phase, gradient-elution, high-performance liquid chromatography (HPLC) technique. This technique can detect very polar, hydrophilic compounds that are not recovered by the methylene chloride extraction step in many gas-chromatography/mass-spectrometry (GC/MS) analytical procedures. Qualitative identification of individual HPLC fractions was accomplished by GC/MS and co-chromatography tests with known compounds. The procedures for condensate-water sampling and for qualitative and quantitative analysis have been described previously.[1]

Table 1 shows the results of chemical analyses of the four condensate-water samples received so far from GFETC. The compounds are divided into three categories—monohydric phenols and their derivatives (nos. 1–5), dihydric phenols (nos. 6–9), and hydantoin compounds (nos. 10–12). The hydantoin compounds are very polar and have low distribution coefficients (K_D) into common solvents. The structure of dimethyl hydantoin is shown in the FY 1981 Annual Report.[2]

The concentrations of compounds 1–9 in the RA-120 sample did not change significantly from the initial measurement to a sample age of 65 days. The concentration of dimethyl hydantoin measured in RA-120 increased with time from 70 ppm at 0.7 days to 165 ppm and 110 days, with intermediate values of 110 ppm and 150 ppm at 10 and 30 days, respectively. These observations are similar to the time-dependent behavior of the samples discussed in the FY 1981 report.

The most important differences between the samples are the high concentration of dihydric phenols (components 6–9) in the first two samples (RA-78 and RA-97), and the high concentration of dimethyl

Table 1. HPLC analyses of GFETC gasifier condensate waters (all concentrations expressed in ppm, w/w).

Date of sample:	6/20/80	6/10/81	9/30/81	4/20/82
GFETC run no:	RA-78	RA-97	RA-106	RA-120
Sample age at analysis (days):	200	40	1.7	0.7
Components:				
1. Phenol	5028	7405	3528	4370
2. Cresols	3238	4267	2422	2565
3. C_2 Monohydric phenols	456	473	434	400
4. o-Methoxy phenol	259	448	165	260
5. p-Hydroxy acetophenone	48	33	3	ND
6. Pyrocatechol	973	848	38	2
7. 4-Methyl catechol	613	497	21	ND
8. Resorcinol	62	28	2	ND
9. Hydroquinone	33	25	1	ND
10. 5,5-Dimethyl hydantoin ($C_5H_8O_2N_2$)	1755	294	293	70
11. 5-Methyl hydantoic acid ($C_4H_6O_2N_2$)	99	128	ND	35
12. 5-Methyl hydantoin ($C_4H_6O_2N_2$)	136	41	ND	10
Measured COD	35,810	46,650	23,510	24,740
Fractions of measured COD accounted for by:				
Components 1–5	0.621	0.661	0.685	0.797
Components 6–9	0.092	0.059	0.005	0.0001
Components 10–12	0.112	0.014	0.019	0.004
All identified components	0.825	0.734	0.709	0.801

ND = not detected

hydantoin in RA-97. These differences may be due to changes in the operation of the coal-gasification process.

As reported in Table 1, the identified compounds account for 71 to 83% of the measured COD in these condensate-water samples.

Extraction of Condensate Waters

Additional information about the chemical nature of the organic compounds in these samples can be obtained by various solvent-extraction procedures. This information can also be used to evaluate the performance of industrial solvent-extraction processes.

Methylisobutyl ketone (MIBK) is an attractive solvent for an industrial condensate-water treatment process because it gives high equilibrium distribution coefficients compared to other conventional solvents, and because it can be regenerated easily by distillation. Two sequential batch extractions with MIBK at a solvent-to-water volume ratio of 1:1 in each stage removed 92.5% of the COD from the RA-120 sample at a sample age of 0.7 days. This degree of COD removal could be accomplished in a countercurrent extraction process with an economically feasible solvent-to-water ratio.

Two other solvents were studied—tributyl phosphate (TBP) and 25 wt% trioctyl phosphine oxide (TOPO) dissolved in MIBK. TBP is a stronger Lewis base than MIBK, and TOPO is a stronger Lewis base than TBP. Batch extractions with a solvent-to-water volume ratio of 1:1 removed the following fractions of the COD from the RA-120 sample at a sample age of 11 days: MIBK, 0.881; TOPO/MIBK, 0.915; TBP, 0.920. Each solvent removed nearly all of the compounds 1–9 in Table 1. The COD that remains after extraction is therefore due to compounds that have not yet been identified. These remaining organic compounds are very polar and hydrophilic. Since the stronger Lewis-base solvents remove more of them, some of them may be Lewis acids. Ultrafiltration experiments using a membrane with a nominal molecular-weight cut-off of 1000 showed that none of the solutes remaining after MIBK extraction were retained by the membrane.

The portion of the COD removed from the RA-120 sample by a single extraction with MIBK decreased from 88.5% at a sample age of 0.7 days to 86.4% at a sample age of 190 days. The portion of the COD removed by two sequential MIBK extractions decreased from 92.5% to 88.4% over the same interval. This indicates that chemical reactions occurred during storage. It also demonstrates the importance of testing proposed treatment processes with fresh condensate-water samples.

Repeated extractions with MIBK from the RA-120 sample at 190 days showed that about 10% of the COD had a vanishingly small K_D into this solvent. Residual dissolved MIBK was removed from the raffinate water after extraction by nitrogen stripping under conditions shown to leave no appreciable

amount of the solvent in the water. This stripping was to prevent dissolved MIBK from contributing to the COD analysis.

A technique for measuring organic nitrogen has recently been applied to the RA-120 sample. In this procedure, NaOH was added to the condensate water, and most of the ammonia was stripped out of the solution with 4 moles N_2 per mole H_2O at 25°C. The difference between Kjeldahl nitrogen and ammonia nitrogen was then interpreted to be nitrogen contained in organic compounds. At an age of 190 days, the RA-120 sample contained about 250 mg N/l of organic nitrogen. After repeated extractions with MIBK, about 150 mg N/l remained in solution. This organic nitrogen has a very small K_D into MIBK and was not removed by MIBK or methylene chloride at high pH. Therefore much of the poorly extracted COD may be due to very polar, nitrogen-containing compounds.

Extraction of Phenols with Trioctyl Phosphine Oxide (TOPO)

Measurements of equilibrium distribution coefficients (K_D) for extraction of phenol, resorcinol, and pyrogallol from water into solvent mixtures of TOPO and diisobutyl ketone (DIBK) have been completed. The results and their interpretation in terms of complexation equilibria are presented elsewhere.[3]

We have found that regeneration of TOPO solutions by back-extraction into strong aqueous bases is complicated by emulsification. Also, the variation of K_D with temperature[3] appears to be insufficient for a regeneration process based upon back-extraction into water at higher temperature. Regeneration by distillation is more likely to be cost-effective. Since DIBK has a lower boiling point than phenol, a higher ketone, isobutyl helptyl ketone (IBHK), was tested as a diluent for TOPO. Although the normal boiling point of phenol (181°C) is less than that of IBHK (218°C), it was found that complexation of phenol with TOPO substantially reduces the volatility of phenol under distillative regeneration conditions. For a solvent composed of 25% w/w TOPO in IBHK, measured values of the relative volatility of phenol to IBHK were only 0.85 and 1.11 at TOPO/phenol molar ratios of 1.0 and 0.5, respectively. Diluents with still higher boiling points appear to be required if phenol is to be regenerated from TOPO by distillation.

Combined Stripping and Extraction for Removal and Isolation of Ammonia

As explained in the FY 1981 report, it may be possible to reduce the steam requirements for stripping ammonia and acid gases (carbon dioxide and hydrogen sulfide) from water by carrying out stripping and solvent extraction simultaneously. The energy used for this combined process plus that for solvent regeneration may be less than that for stripping alone. The process would also isolate the ammonia from the acid gases.

Before FY 1982, we had determined that (1) ammonia rather than the acid gas should be extracted, (2) a liquid ion exchanger is needed to achieve a high degree of ammonia removal, (3) the rate of acid gas removal by stripping in the presence of such a solvent is substantially faster than by stripping in the absence of a solvent, and (4) certain liquid ion exchangers can be regenerated by stripping at a temperature greater than that of the original combined stripping and extraction.

Several difficulties arise with liquid ion exchangers, however. Since they are ionic, they tend to be surface-active and to have a fairly high solubility in an aqueous phase, particularly in the salt form. This can result in poor phase separation and excessive extractant losses. In addition, they can degrade thermally at elevated temperatures, which would lead to additional costs for replenishing the extractant.

Work carried out in FY 1982 addressed the problems of extractant purity, alternative liquid ion exchangers, degree of ammonia extraction, phase separation, extractant losses, and regenerability.

Previously, the principal extractant studied had been di-2-ethylhexyl phosphoric acid (D2EHPA). The commercial product contains about 2% mono-2-ethylhexyl phosphoric acid, which is water soluble. In a continuous process, this impurity would wash out of the organic phase fairly quickly. To obtain meaningful results for the degree of extraction, extractant losses, etc., the commercial D2EHPA was purified by a copper-salt precipitation method[4] for measurements that began in FY 1982.

Other extractants examined were dinonylnaphthalene sulfonic acid (DNNSA) and octylphenyl phosphoric acid (OPAP). DNNSA had been shown previously to degrade irreversibly when attempts were made to regenerate it. OPAP comes as a mixture of

mono- and di-acids, so it was washed before use to remove the di-acid. It gave results comparable to D2EHPA for ammonia extractability and phase separation, but, being a stronger acid, it is much more soluble in the aqueous phase than D2EHPA. Thus D2EHPA is still the most promising extractant examined thus far.

Since D2EHPA is a viscous liquid, it is dissolved in an organic diluent before use. The nature of this diluent can affect the degree of extraction, phase separation, extractant losses, and regenerability.

The degree of ammonia extraction by D2EHPA is greater in an inert diluent, such as an aliphatic hydrocarbon, than in an aromatic, such as toluene. This is probably due to the interaction of the π electrons of the aromatic with D2EHPA, which reduces the availability of D2EHPA for ammonia extraction. Under identical conditions, using Norpar 12 (King Industries) (C_{11} to C_{13} paraffins) as diluent, 96% of the ammonia is extracted from an aqueous solution, while only 94% is extracted when the diluent is toluene.

Using a mixed diluent of toluene plus a modifier with D2EHPA allows us to take advantage of the chemical nature of a modifier that might be too viscous to use alone, but much depends on the acidity or basicity of the modifier. If the modifier is a stronger base than ammonia, such as a secondary or tertiary amine, ammonia extraction is markedly decreased. TOPO, a weaker base, which therefore does not compete as successfully for the D2EHPA as the amines do, has only a slightly detrimental effect on extraction.

Use of 1,1,2,2-tetrachloroethane, which has acidic protons, as a modifier with D2EHPA and toluene does not affect the degree of extraction much. Adding carboxylic acids, especially straight-chain ones such as 1-decanoic acid, as modifiers with D2EHPA and toluene greatly enhances the extraction of ammonia, although the carboxylic acids themselves do not extract ammonia significantly.

Sterically unhindered alcohols and phenols added as modifiers also exhibit this enhancement. For instance, under otherwise identical conditions, a diluent composed of 12.2% (by volume) 1-octanol in toluene results in 96.2% extraction of ammonia by D2EHPA, while a diluent composed of 12.2% (vol) 2-ethyl-1-hexanol in toluene yields only 93.6% extraction. Likewise, a diluent composed of 18.8% (vol) nonylphenol in toluene used with D2EHPA extracts 98.9% of the ammonia, while 18.8% (vol) 4-sec-butyl-2-(α-methylbenzyl) phenol in toluene as a diluent with D2EHPA extracts only 93.7%. These results are to be compared with 94% for toluene alone as the diluent.

To illustrate this point about alcohols further, the following percents of ammonia extracted were found for D2EHPA mixed with a diluent of toluene plus increasing amounts of 1-decanol: Zero percent decanol, 94% extracted; 1.8% (vol) decanol, 95.4% extracted; 12% (vol) decanol, 96.3% extracted; 50% decanol, 97% extracted; and 100% decanol, 98.5% extracted. Commercially available isodecyl alcohol behaves similarly to 1-decanol. The -OH group may be solvating the ammonia-D2EHPA complex in the organic phase and therefore lowering its activity.

Another problem in this system, poor phase separation, manifests itself as a white emulsion at the interface. We therefore attempted to reduce the surfactant nature of the organic phase. Since the ammonium salt of D2EHPA is highly surface-active, operating under conditions of low conversion of the D2EHPA to the salt form improved the phase separation. Modifiers that interact with the ammonium salt of D2EHPA also can decrease its interfacial activity. Hence, adding the unhindered carboxylic acids, alcohols, and phenols as modifiers to a toluene diluent greatly improves phase separation, especially at high modifier concentrations. Of particular interest are the excellent separations attained with a diluent composed of only 1.8% (vol) 1-decanoic acid in toluene and with another diluent containing 50% (vol) isodecyl alcohol in a commercial aromatic diluent (Chevron Solvent 25), both at an aqueous-to-organic phase ratio of 0.185.

Extractant losses from the organic phase to the aqueous phase are also affected by the nature of the organic diluent. These losses were quantified as follows: A solution of D2EHPA at 0.2 *M* in a given diluent was contacted with an aqueous solution containing 0.58 *M* ammonia, at an aqueous-to-organic phase ratio of 0.185. The concentration of phosphorus-containing compounds in the resulting aqueous phase was measured by a standard decomposition and precipitation method.[5]

Replacing an aliphatic diluent with an aromatic reduces extractant losses by about 50%, because the aromatic can better solvate the D2EHPA and its ammonium salt. By using modifiers in toluene that reduce the extraction of ammonia, less of the

ammonium salt of D2EHPA was formed, and the extractant loss was also reduced. Presumably, this is because the ammonium salt of D2EHPA is more soluble in water than is D2EHPA itself.

Sterically unhindered carboxylic acids, alcohols, and phenols added as modifiers to toluene also significantly reduce extractant losses to the aqueous phase. The strong interaction between the -OH group on these compounds and the ammonia-D2EHPA complex is probably responsible. For instance, using 50% isodecyl alcohol in the aromatic diluent, Chevron Solvent 25 reduces the extractant losses by 90% from those measured using an aliphatic diluent (Norpar 12). Under practical operating conditions, the extractant losses can thereby be reduced to less than $1.90/1000 gallons of water treated.

These results point to 50% isodecyl alcohol in an aromatic solvent as a good choice of diluent for D2EHPA, at least with respect to phase separation and extractant losses. So far, only one attempt has been made to regenerate such a solvent system. It was easily regenerated at 160°C, but some evidence of thermal decomposition was noted. Regeneration, therefore, will probably have to be carried out at a lower temperature. This may require a diluent that gives a lower extraction efficiency for ammonia, since the ammonia will then not be as tightly held and will therefore be more readily liberated from the solvent. A trade-off may exist between costs for extractant losses and steam requirements for regeneration.

PLANNED ACTIVITIES FOR FY 1983

Analyses of condensate waters will continue, with the objective of identifying the remaining unknown components contributing to the COD. The initial focus will be on organic nitrogen compounds and amphoteric ionizing compounds. Solvent-extraction measurements will be continued to provide chemical information on the condensate-water constituents, and to provide effective solvent-extraction processes for removal of the compounds that have been identified.

Higher-boiling diluents for TOPO will be sought, most likely from among commercially available ketones, aromatics, alcohols, and naphthalenes, with aliphatic solvents being added to the diluent when needed to alter density or viscosity. Equilibrium data for the extraction of phenol will be obtained for mixtures of TOPO with diluents which appear promising from the standpoint of solvent-regeneration properties.

In the experiments directed toward simultaneous extraction of ammonia and stripping of acid gases, regeneration rates will be measured for mixtures of TOPO with diluents composed of aromatics and -OH-containing compounds, with the aim of identifying the most attractive diluent mixture on the bases of regenerability, low extractant losses through solubility or poor settling, and low thermal degradation. Equilibrium data will be quantified for the more attractive extractant/diluent combinations, and tests will be made with samples of real condensate waters.

REFERENCES

1. Mohr, D.H., Jr., and King, C.J. (1981), "Identification and Removal of the Organic Compounds in Coal-Conversion Condensate Waters," presented at the Workshop on Processing of Wastewaters from Synthetic Fuels Processes, U.S. Department of Energy, Germantown, Maryland, June 24–25, 1981. Lawrence Berkeley Laboratory report LBL-13584 Revised.
2. King, C.J., et al. (1982), "Processing of Condensate Waters from Coal Conversion," in *Energy and Environment Division Annual Report, FY 1981*, p. 1-35.
3. MacGlashan, J.D., and King, C.J. (1982), *Extraction of Phenols From Water*, Lawrence Berkeley Laboratory report LBL-13963.
4. McDowell, W.J., Perdue, P.T., and Case, G.N. (1976), "Purification of di(2-ethylhexyl)phosphoric Acid," *J. Inorg. Nucl. Chem. 38*, p. 2127–29.
5. Pregl, F., and Grant, J. (1951). *Quantitative Organic Microanalysis*, The Blakiston Company, Philadelphia, Pennsylvania, p. 140–146.

TECHNOLOGY BASE RESEARCH PROJECT FOR ELECTROCHEMICAL ENERGY STORAGE*

E.J. Cairns and F.R. McLarnon

The Lawrence Berkeley Laboratory (LBL) is lead center for management of the Technology Base Research (TBR) Project. During FY 1982, this project consolidated the research activities of several smaller programs in the electrochemical branch of DOE's Energy Storage Division. The general aim of the TBR Project is to provide an applied research base supporting the development of batteries and electrochemical systems that exhibit superior performance and acceptable life-cycle costs. The intended applications include electric vehicles and stationary energy storage and conversion. A major goal is to identify electrochemical technologies having the greatest potential to satisfy performance and economic requirements and transfer them to DOE's Exploratory Technology Development and Testing project and/or private industry for further development and scale-up.

The TBR Project includes four major elements: electrochemical systems, supporting research, electrochemical processes, and fuel cell research. (Fuel cell research is managed by the Los Alamos National Laboratory.) The generic research topics included in each of these elements are listed in Table 1.

The LBL scientists who participate in the program are E.J. Cairns and F.R. McLarnon of the Energy and Environment Division, and L.C. DeJonghe, J.W. Evans, R.H. Muller, J.S. Newman, P.N. Ross, and C.W. Tobias of the Materials and Molecular Research Division.

*This work was supported by the Assistant Secretary for Conservation and Renewable Energy, Office of Energy Systems Research, Energy Storage Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

Table 1. Topics covered by the Technology Base Research Project for electrochemical energy storage.

I. ELECTROCHEMICAL SYSTEMS
- New Rechargeable Electrochemical Cells
- Metal/Air Cells

II. SUPPORTING RESEARCH

A. Engineering-Science Research
- Electrode Morphological Studies, Chemical/Structural Analysis
- Transport Phenomena, Electrocatalysis, Electrode Kinetics, and Cell Thermodynamics
- Modeling of Electrochemical Cells and Battery Systems
- Advanced Physiochemical Methods for Electrochemical Research

B. Materials Research
- Ceramic, Molten-Salt, Glass, and Polymeric Electrolytes
- Novel Electrode Structures
- New Fabrication Techniques for Components
- Battery Separators

III. ELECTROCHEMICAL PROCESSES
- Corrosion Problems in Electrochemical Storage Devices
- Characterization of Multi-Phase[a] Electrochemical Systems
- Electroorganic Synthesis
- Thermally-Regenerative Cells

IV. FUEL CELL RESEARCH
- New Components for Fuel Cells
- New Electrolytes
- Electrocatalysis

[a]Gas-solid-liquid.

ACCOMPLISHMENTS DURING FY 1982

LBL monitored 40 subcontracts during FY 1982 and conducted a vigorous in-house research program. The in-house work, "Electrochemical Energy Storage," is summarized in the next article and in the *Materials and Molecular Research Division 1982 Annual Report* (LBL-15150). Progress in the subcontracted work, divided according to the four major elements of Table 1, can be briefly described as follows:

Electrochemical Systems Research

(1) A multicell phototype Al/air system was successfully tested at Lawrence Livermore National Laboratory.

(2) A new project to investigate the use of sulfolane-based organic electrolytes in ambient-temperature rechargeable lithium batteries was initiated at EIC Laboratories, Inc.

Supporting Research

(1) SRI International has nearly completed a program to measure the electrochemical kinetic parameters of rechargeable alkaline Zn, Fe, and NiOOH electrodes.

(2) A new effort to adapt a "transformation toughening" procedure to the manufacture of ceramic electrolytes was initiated at Rockwell International, Inc. Tetragonal ZrO_2 is incorporated into beta alumina (β''-Al_2O_3) electrolytes in high-temperature Na/S cells.

(3) Several less-promising research and development projects have been phased out of the TBR Project:

(a) Three projects (conducted by SRI International, EIC Laboratories, and Giner, Inc.), focusing on photoelectrochemical storage cells, identified significant material corrosion problems and/or very low current densities.

(b) NASICON ($Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$, $0 < x < 3$) was shown by LBL and Ceramatec, Inc. to be unstable in molten sodium at 300°C; this material is therefore unsuitable for use in Na/S cells.

(c) An attempt by the University of Southampton (England) to employ Raman spectroscopy to identify reaction products at metal/electrolyte interfaces suffered from very low signal-to-noise ratios.

(d) Measurements of composition profiles in LiAl/LiCl-KC1/FeS cells at Oak Ridge National Laboratory lacked sufficient accuracy to confirm or refute proposed mathematical models.

(e) The Energy Research Corporation had previously shown that adding certain oxides to ZnO material employed in Zn/KOH/NiOH cells could reduce the solubility and increase the conductivity of the ZnO, which could thereby lead to improvements in cell performance and lifetime. However, subsequent work showed that these additions lowered the electrochemical activity of the ZnO.

(f) A study of transition-metal-coated porous titanium electrodes for redox batteries by the University of Akron failed to identify cost-effective catalyst/substrate combinations.

Electrochemical Processes

(1) A four-year joint project conducted by Diamond Shamrock Corporation and Case Western Reserve University was successfully completed. A primary objective was the development of a high-performance oxygen electrode for chlorine/caustic cells, thus reducing cell operating voltage 1.0 V below that in conventional cells. Diamond Shamrock Corporation has now commercialized this technology.

(2) A new effort to explore the use of transition-metal macrocyclic compounds as catalysts for air electrodes was initiated at Case Western Reserve University.

(3) All research and development activities related

to electrolytic technology have been phased out of the TBR Project, including the following topics:

(a) Transport processes in membranes employed in chlorine/caustic cells.
(b) Transport phenomena and electrolyte impurity effects in magnesium reduction cells.
(c) Mathematical modeling of processes in aluminum reduction cells.
(d) Use of biomass materials to reduce cell voltages in electrolysis and electrowinning cells.

Fuel Cells

Los Alamos National laboratory has prepared a plan for a "Fuel Cells for Transportation" Program. This document identifies and evaluates several candidate fuel cell technologies potentially suitable for use in vehicles.

PLANNED ACTIVITIES FOR FY 1983

Major new initiatives include the following:

(1) A prime contractor for research and development of Al/air cells will be selected.
(2) Fuel cell research projects focusing on new electrocatalysts and solid polymer electrolytes will be initiated.
(3) Industrial participation in lithium-alloy/metal-disulfide research and development activities will be solicited.
(4) Research to identify new separators for alkaline zinc cells will be initiated.
(5) Additional studies of polymeric and/or liquid electrolytes for ambient-temperature rechargeable lithium batteries will begin.
(6) Carbon corrosion phenomena in air electrodes will be examined, as will corrosion problems in high-temperature cells employing sulfur electrodes.
(7) Work on thermally regenerative electrochemical systems will be initiated.

BATTERY ELECTRODE STUDIES*†

E.J. Cairns, F.R. McLarnon, J.H. Flatt, M. Isaacson, M.H. Katz, P. Lessner, K.G. Miller, and T.J. Nichols

The purpose of this research is to study the behavior of electrodes used in secondary batteries and to investigate practical means for improving their performance and lifetime. Systems of current interest include ambient-temperature rechargeable cells with zinc electrodes [Zn/NiOOH, Zn/AgO, Zn/Cl_2, Zn/Br_2, Zn/air, and $Zn/Fe(CN)_6^{-3}$] and rechargeable molten-salt cells (Li-Al/FeS, Li-Al/FeS_2, Li-Si/FeS, Li-Si/FeS_2, and Na/β''-Al_2O_3/NaCl-$AlCl_3$-SCl_4). The approach used in this investigation is to study life- and performance-limiting phenomena under realistic cell operating conditions.

ACCOMPLISHMENTS DURING FY 1982

Investigations have centered on the zinc electrode, which exhibits satisfactory performance in rechargeable alkaline cells (Zn/NiOOH, Zn/air, $Zn/Fe(CN)_6^{-3}$, Zn/AgO) but has an inadequate cycle life. Its short lifetime and continual loss of capacity are closely related to a phenomenon known as shape change, the redistribution of active material over the face of the electrode as the cell is cycled.

Computer Control of Electrochemical Experiments with Application to Zinc/Nickel Oxide Cells

(by M.H. Katz, E.J. Cairns, and F.R. McLarnon)

A computer-controlled test system has been designed and constructed to allow the simultaneous and continuous cycling of 16 or more electrochemical cells. The system offers resolution and stability

*This work was supported by the Assistant Secretary for Conservation and Renewable Energy, Office of Energy Systems Research, Energy Storage Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

†This project is part of a larger effort, "Electrochemical Energy Storage," described in the *Materials and Molecular Research Division 1982 Annual Report* (LBL-15150).

within 0.025% of full scale, and response times are typically 1 millisecond. A wide variety of charge and discharge regimes, including pulsed charge and power discharge profiles, are implemented through various computer algorithms. The software configuration allows two programs to execute concurrently in the computer memory and to communicate with each other through a set of codified messages. This arrangement permits flexible interaction with all experiments and provides on-line data reduction and display.

The test system has been employed to investigate the effects of constant-current and various pulsed-current charging modes on the cycle life and capacity retention of Zn/NiOOH cells cycled at 100% depth-of-discharge. Test results included cell voltages, potentials of the NiOOH and Zn electrodes versus Hg/HgO reference electrodes, coulombs, watt-hours, average voltages, and associated efficiencies. Postmortem tests included Zn electrode x-ray studies.

A pulse profile of 30 ms-on/90 ms–off, with a 15 mA/cm^2 peak current density, improved the operating conditions of the cells by minimizing the overpotentials on the Zn and NiOOH electrodes. In contrast to all other charge profiles tested, it eliminated cell shorting (for at least 100 cycles) and slowed the loss of ZnO reserve, thereby preventing a rapid decline in cell capacity.

Active Materials Redistribution Rates: Effect of Alkaline Electrolytes Having Reduced Zinc Oxide Solubility

(by J.T. Nichols, E.J. Cairns, and F.R. McLarnon)

A series of electrolytes formulated with low hydroxide-ion concentration has been tested in 1.35 Ah tri-electrode Zn/NiOOH cells to assess their ability to reduce zinc redistribution rates. A 3.5 *M* OH^- electrolyte and a 3.5 *M* OH^-–3.4 *M* F^- electrolyte were tested along with a borate electrolyte. The electrolytes were chosen to exhibit ZnO solubility approximately one-fourth that of the standard 30% KOH–1% LiOH electrolyte. A 6-hour charge rate and a 2½-hour discharge rate were employed for the 62-by-70 mm zinc oxide, Teflon-bonded electrodes to which 2% PbO was added to reduce hydrogen evolution rates. Zinc redistribution rates were found to be lower for electrolytes with reduced ZnO solubility, and zinc penetration of the separator was non-existent, even when overpotentials approached 130 mV when charging the Zn electrode in the borate electrolyte and 290 mV in the fluoride electrolyte. The 3.5 *M* OH^- electrolyte demonstrated reduced zinc penetration, and the cells with standard electrolyte shorted from zinc penetration through the face of the separator. The high overpotentials were found to exist when substantial amounts of ZnO remained in the electrode. Less than 2% inactive zinc was found in the zinc electrodes cycled in the fluoride and borate electrolytes, and a similar low amount was present in electrodes cycled in the 3.5 *M* and 7.4 *M* OH^- electrolytes.

Mathematical Modeling

(by K. Miller, E.J. Cairns, and F.R. McLarnon)

The zinc electrode in Zn/NiOOH cells exhibits failure upon cycling, and the purpose of this work is to develop a comprehensive model that describes this behavior. Suggested causes of failure include passivation by a zinc oxide film[1,2] and shape change, the redistribution of zinc across the face of the electrode due to the high solubility of zinc-bearing species.[3-5] Models have already been written to describe the variation of current density and species concentrations in directions parallel to[4] and perpendicular to[1] the electrode surface. The present work combines both features to provide a two-dimensional, time-dependent model. The equations for the model are being developed, and an existing model[6] is being coupled with more rigorous chemical analyses to determine mechanisms of electrode failure.

Other activities include experiments to determine parameters needed for modeling efforts. Microscopy will also be performed on cycled zinc electrodes to determine the character of the zinc deposit on the current collector.

Effect of Mixed Electrolytes on the Performance and Cycle Life of Zn/NiOOH Cells

(by M. Isaacson, E.J. Cairns, and F.R. McLarnon)

The high solubility of the zincate ion in Zn/NiOOH battery electrolytes contributes to its limited cycle life.[3,4] The solubility of the zincate ion may be decreased by adding a less polar solvent, such as an alcohol, to the electrolyte while maintaining a high KOH concentration. These additions may improve the

cycle life of Zn/NiOOH cells.

ZnO solubilities were measured in KOH-water-methanol and KOH-water-ethanol electrolytes to determine the extent of the Zn species solubility suppression. The data for 30% KOH-water-methanol electrolyte showed:

(1) The solubility was a maximum for 30% KOH–70% water.
(2) The solubility decreased by 75% for a 30% KOH–40% water–30% methanol electrolyte.
(3) The solubility decreased by 90% for a 30% KOH–20% water–50% methanol electrolyte.

Cell cycling to determine the effect of the alcohol additions on cycle life and cell performance are planned.

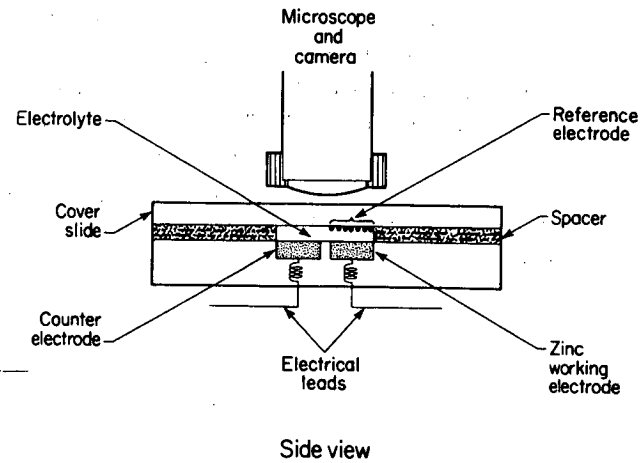


Figure 1. Electrochemical cell for studying the behavior of a model zinc electrode pore in alkaline electrolyte.
(XBL 831-27)

Study of Model Zinc Electrode Pores

(by J. H. Flatt, E.J. Cairns, and F.R. McLarnon)

An electrochemical cell has been developed to study the behavior of a model zinc electrode pore in alkaline electrolyte. The cell design (Fig. 1) permits in-situ microscopic observation of the electrode surface, and multiple zinc reference microelectrodes provide simultaneous measurements of local electrochemical potentials. The reference microelectrodes are fabricated by using semiconductor processing techniques, including vacuum metal deposition and photolithography. The effect of varying pore diameters, electrolyte formulations, and electrode-area/electrolyte-volume ratios on zinc electrode discharge behavior will be studied. Experiments are in progress.

Engineering Analysis of Photoelectrochemical Cells

(by P. Lessner, E. J. Cairns, and F. R. McLarnon)

Photoelectrochemical cells offer a convenient and efficient method to convert solar energy to electrical energy. We are modeling systems that include a photoelectrode, a catalytically active (in the dark) counterelectrode, and a redox couple.

Current work aims to identify catalytically active counterelectrodes for various redox couples, in particular the S^{2-}/S_x^{2-}/NaOH system because of its ability to stabilize several photoelectrodes. Literature references[7] and our preliminary work show that insoluble sulfur may foul these electrodes when operated in the anodic direction.

Future work will include an assessment of desirable qualities of electrolytes and an analysis of the effect of cell geometry and optical variables on photoelectrochemical cell performance.

PLANNED ACTIVITIES FOR 1983

Planned efforts for each on-going project are described in the previous sections. New projects include the study of phase equilibria in molten lithium polysulfide electrolytes, the examination of novel electrolytes for use in Li/S cells, the study of corrosion-resistant current collector materials for use in sulfur electrodes, and an assessment of superacid electrolytes for fuel cells.

REFERENCES

1. Sunu, W.T., and Bennion, D.N. (1980), "Transient and Failure Analysis of the Porous Zinc Electrode. I. Theoretical," *J. Electrochem. Soc. 127*, p. 2007.
2. Sunu, W.G. and Bennion, D.N. (1980), "Transient and Failure Analysis of the Porous Zinc Electrode. II. Experimental," *J. Electrochem. Soc. 127*, p. 2017.
3. McBreen, J. (1972), "Zinc Electrode Shape Change in Secondary Cells," *J. Electrochem. Soc. 119*, p. 1620.

4. Choi, K.W., Bennion, D.N., and Newman, J. (1976), "Engineering Analysis of Shape Change in Zinc Secondary Electrodes. I. Theoretical," *J. Electrochem. Soc. 123,* p. 1616.
5. Choi, K.W., et al. (1976), "Engineering Analysis of Shape Change in Zinc Secondary Electrodes. II. Experimental," *J. Electrochem. Soc. 123,* p. 1628.
6. Sunu, W.G. (1980), *Transient and Failure Analyses of Porous Zinc Electrodes,* Ph.D. dissertation, School of Engineering, University of California, Los Angeles.
7. Hodes, G., et al. (1980), "Electrocatalytic Electrodes for Polysulfide Redox System," *J. Electrochem. Soc. 127,* p. 544.

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720