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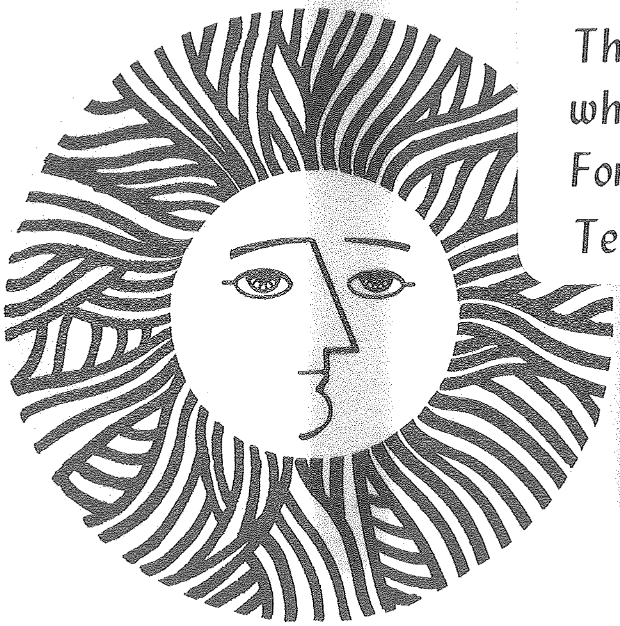
Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

ENERGY & ENVIRONMENT DIVISION

CHEMICAL PROCESS RESEARCH AND DEVELOPMENT PROGRAM

Chapter from the Energy and Environment Division
Annual Report 1980

March 1981



Prepared for the U.S. Department of Energy under Contract W-7405-ENG-48

DISCLAIMER

CHEMICAL PROCESS RESEARCH AND DEVELOPMENT PROGRAM
FY 1980

Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

Prepared for the U.S. Department of Energy under Contract W-7405-ENG-48

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INTRODUCTION

C. Judson King

The Chemical Process Research and Development Program deals with three principal application areas of chemistry: (1) production of synthetic fuels, (2) processing of effluent or recycled water and gas streams and/or feedstocks to achieve environmental compatibility, and (3) electrochemical energy storage. These projects have in common the use of principles of transport, thermodynamics, kinetics, separations and physical chemistry to improve fundamental mechanistic understanding and thereby to develop improved processing approaches.

Two of the larger projects pertain to different processes for the conversion of biomass--such as agricultural wastes, wood chips, newsprint--into fuels. The first of these projects consists of a study of enzymatic reactions that lead successively to sugars and then to ethanol. This product could be used as a fuel itself or could be blended with gasoline to make "gasohol." An important research target has been development of higher-capacity processing approaches that would significantly lower production costs. Another important research area has been the coupling of vacuum fermentation with vacuum distillation; this promises to bring about a major reduction in energy consumption. Still other studies are directed toward fundamental questions underlying these and related processing approaches.

The second biomass project concerns production of a fuel oil and a chemical feedstock by thermal, reductive conversion of biomass. Lawrence Berkeley Laboratory (LBL) has provided technical consultation and guidance to a Process Development Unit (PDU) of the Department of Energy (DOE) located at Albany, Oreg. A smaller, more flexible Process Engineering Unit (PEU) has been constructed in Berkeley, Calif. Recent research has dealt with means of pretreating biomass prior to liquefaction to improve properties such as pumpability in three ways: (1) by improving the means and understanding of homogenous catalysis for this process, (2) by solvolysis in acidified organic solvents, and (3) by chemical characterization of the product.

Another project relating to synthetic fuels deals with selective hydrogenation of coal using strong Lewis acid catalysts to achieve substantial conversion of coal to liquid at temperatures below those required for pyrolysis. This approach may require less severe process conditions, and it retains a large amount of coal's molecular structure and fuel value. At the same time, this project gives important insight into the mechanisms of homogeneous catalysis and solvation relating to coal liquefaction.

For environmental reasons, sulfur must somehow be removed from coal-burning systems, rather than being allowed to enter the atmosphere as SO_2 or SO_3. One approach is to remove sulfur from coal before coal combustion or further processing. A project is investigating oxidative acid-leaching as an improved means of sulfur removal. A by-product of this study is additional insight into the nature of sulfur bonding in coals.

A second approach for sulfur removal is flue-gas desulfurization. Under investigation are fundamental chemistry and transport mechanisms underlying reagent additive effects in flue-gas desulfurization processes based on scrubbing. This project is also working toward the development of a novel processing technique that will enable simultaneous removal of SO_2 and NO_x from flue gases.

Processes for coal conversion and manufacture of most other synthetic fuels generate large quantities of condensate water which have been in direct contact with the reacting mixture. These waters commonly have large loadings of ammonia, acid gases, and soluble organics. We are investigating novel separation methods that will allow the recycling of these condensate waters within fuels-conversion processes. Two areas of principal concern are (1) development of novel solvents that will enable a high degree of organics removal through extraction, and (2) combined stripping and extraction techniques that will substantially reduce the energy consumption for ammonia removal.

In the area of electrochemical energy storage, the division is involved in field management of the Applied Battery and Electrochemical Research Program supported by the Energy Storage Systems Division (STOR) of DOE. In addition, fundamental research is being carried out on mechanisms of redeposition and rearrangement of active material on battery electrodes during recharging processes. These studies are expected to lead to improved methods of reducing capacity loss during recharging, thereby eventually leading to longer service lifetimes for important battery systems that might be used for electric automobiles and large-scale energy storage.

PROCESS DEVELOPMENT STUDIES ON THE BIOCONVERSION OF CELLULOSES*

H. W. Blanch, C. R. Wilke, G. Dove, J. Perez, and A. F. Sciamanna

INTRODUCTION

The Department of Energy program has concentrated on the hydrolysis of cellulose and hemicellulose to sugars and on their subsequent fermentation to ethanol for use as a liquid fuel. A range of candidate cellulosic materials, mainly in the form of agricultural residues, forest-produced residues and whole tree biomass, have been analyzed and assessed for yields of sugar and ethanol under various processing conditions. Processing concepts under study include chemical (acid) pretreatment of these cellulosic materials to remove lignin and hemicellulose; enzymatic and chemical hydrolysis to produce hexose sugars; and production of ethanol by fermentation. Fundamental problems related to the development of optimal processing conditions have been studied under the auspices of the Basic Energy Sciences Division (BESD). More applied aspects and pilot plant studies are sponsored by the Solar Energy Research Institute (SERI).

Important basic problems include the kinetics of enzymatic hydrolysis of cellulose, the physical and chemical nature of the raw materials, production and recovery of the enzymes involved, and the development of new organisms for direct conversion of cellulose to ethanol.

Major developmental studies under the auspices of the Solar Energy Program include development of chemical treatment processes, studies on optimal cellulase production, enzymatic hydrolysis of hemicellulose and subsequent fermentation of the pentose sugars to ethanol, and optimization of a continuous-removal process for the ethanol fermentation using low pressure distillation. In all these studies, the economic impact of each process change is evaluated.

ACCOMPLISHMENTS DURING FY 1980

Support of SERI PDU Facilities of Gulf Oil Chemical Company

Currently the SERI program at LBL has undertaken various support functions for the Gulf Jayhawk Pilot Plant, Pittsburg, Kansas. These have included training of Gulf Laboratory personnel in analytical techniques, planning and monitoring of various pilot plant studies, and in interpretation of results. Studies to date have focused primarily on enzymatic hydrolysis of corn stover and the subsequent fermentation of the resulting sugars to ethanol. Additional work performed in conjunction with Gulf has been the analysis of corn stover from Nebraska, cotton gin trash from Mississippi, and Canadian aspen that was steam exploded by Iotech. These substrates were also enzymatically hydrolyzed at bench scale to establish the benchmark for the Process Demonstration unit (PDU).

The Fall 1979 corn stover crop grown in Nebraska was milled to approximately 0.5 to 2 mm particles, and was enzymatically hydrolyzed with cellulase enzyme derived from the Rutgers C-30 strain of *Trichoderma reesei*. There was obtained an approximate 40% conversion of the available carbohydrate to sugars. This result is much lower than observed for stover grown in Indiana and California in the Fall 1976, 1977, and 1978, respectively. With an acid pretreatment[1] followed by enzymatic hydrolysis, only a 55% carbohydrate conversion was obtained. It is unknown why the expected conversion of at least 80% was not obtained. The analysis[2] of this substrate, shown in Table 1, did not have an unusual composition. In fact, it is a little higher in carbohydrate content compared to those mentioned previously. The grower stated that no unusual herbicide, fungicide, bactericide was applied before, during, or after the growth cycle. Essentially the same results were obtained at the SERI/Gulf PDU for enzymatic hydrolysis of much larger batches (~110 lb) of this residue. Several tons of this Nebraska corn stover were used in the demonstration plant studies with no marked improvement in the conversion of the available carbohydrate.

While awaiting delivery of steam-explosive decompressed wood from Iotech Co. of Canada, work was started on cotton gin trash that was on hand at the Gulf Jayhawk plant. A sample of about 5 kg of 1975 harvest, Gulf cotton gin trash, grown in Indianola, Mississippi, was supplied to us. This was analyzed, and the results are shown in Table 2. This cotton gin trash is considerably higher in carbohydrate content compared to what is generated in California.[1] On enzymatic hydrolysis, a carbohydrate conversion of only 19% was obtained--nearly equal to what was obtained with the residue from California. Even though the residue from Mississippi contains about 2.5 times more carbohydrate, apparently the cellular carbohydrate is tightly bound or completely sheathed with lignin, thus preventing enzyme accessibility. Since this residue appears to be an unlikely candidate for economic conversion of the carbohydrate to fuel alcohol, no further studies were performed here.

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* This work was supported by the Office of Energy Research in Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. W-7405-ENG-48 and by the Solar Energy Research Institute.

Table 1. Corn Stover[*] *Zeamays-L.* (Prairie Valley-76S) from Polk County, Nebr., Fall crop 1979; assay.[†]

Constituents of Sample	Percentage Composition
Carbohydrates (total)	61.6
glucan	40.7
mannan	0.36
galactan	1.2
xylan	18.0
arabinan	1.36
Sugar and/or equivalent (total)	69.9
glucose	45.2
mannose and/or fructose	0.4
galactose	1.3
xylose	20.4
arabinose	1.5
sucrose	1.1
Other constituents	
lignin	14.8
ash[‡]	5.1
azeotropic benzene/alcohol extractives	6.1
other acid insolubles (organic)	4.2
protein	4.4

[*] 1 in. tub milled particles, courtesy of Charles Wosel and Mark Holscher, Gulf Oil Chemicals Co., Pittsburgh, Kans. 66762.

[†] 2 mm Wiley-milled particles 0.25-0.35 mm fraction, 100% dry.

[‡] 0.457 of the ash is acid insoluble; 0.543 of the ash is acid soluble.

A 100-lb batch hydrolysis done at Gulf resulted in essentially the same results.

Future work will be the analysis and hydrolysis of several types of recently received exploded wood. Results from preliminary enzymatic hydrolysis on one exploded wood sample shows a better than 90% carbohydrate conversion. This wood, exploded by Iotech, Canada, is presently being used in preliminary studies at Gulf for enzyme production as well as hydrolysis.

Enzymatic Hydrolysis of Agricultural Residues

The development of mutant strains of *T. reesei* has enhanced the potential for developing economically attractive processes that enzymatically hydrolyze biomass to produce glucose. During the past year, experiments were conducted to evaluate the hydrolysis of corn stover utilizing cellulase from *T. reesei*: Rutger's C-30, a new mutant strain. The strain is of interest because it is hyperproducing, catabolite repression-resistant, and capable of yielding significantly β-glucosidase activity.

Table 2. Cotton gin trash *Gossypium Hirsutum-L.* from Indianola, Miss., 1975 harvest[*]; assay.[†]

Constituents of Sample	Percentage Composition
Carbohydrates (total)	68.3
glucan	48.9
other hexosan[‡]	2.0
xylan	16.9
arabinan	0.5
Sugar equivalent	76.5
glucose	54.4
other hexose	2.2
xylose	19.3
arabinose	0.6
Other constituents	
lignin	20.7
ash	4.8
other acid insolubles	2.8
azeotropic benzene/alcohol extractives	4.2

[*] 0.032 in. Hammer-milled particles, courtesy of Charles Wosel, Gulf Oil Chemicals, Pittsburgh, Kansas 66762.

[†] 2 mm Wiley-milled particles, unsieved fraction, 100% dry.

[‡] includes mannan (mannose) and galactan (galactose).

Batch hydrolysis were conducted for a period of 24 to 48 h employing substrate concentrations ranging from 5 to 25 wt% and enzyme activities ranging from 2.6 to 9 International units (IU)/ml. Experiments were carried out in 600 ml Wide Mouth beakers containing 200 ml or substrate-enzyme mixture. The contents were stirred at approximately 150 rpm and were maintained at a constant temperature of 45°C and pH of 5.

Prior to hydrolysis, corn stover was milled to 2 mm and treated with sulfuric acid to hydrolyze hemicellulose. Following pretreatment,[2] the corn stover was neutralized and air dried. Treated corn stover typically contained 57-70% glucose equivalent by weight.

In experiments with substrate concentrations exceeding 10 wt%, stepwise addition of substrate was employed. After an initial solids loading of 5-10%, the reaction was allowed to proceed for 1/2 h at which point an increment of corn stover was added. Subsequent substrate increments enable 25% total substrate concentrations to be achieved in 2.5 h.

Hydrolysis conducted under the conditions described produce sugar streams ranging from 15-90 g/ℓ, containing 80-85% glucose. Figure 1 presents typical hydrolysis curves. Product concentrations increase both with increasing substrate

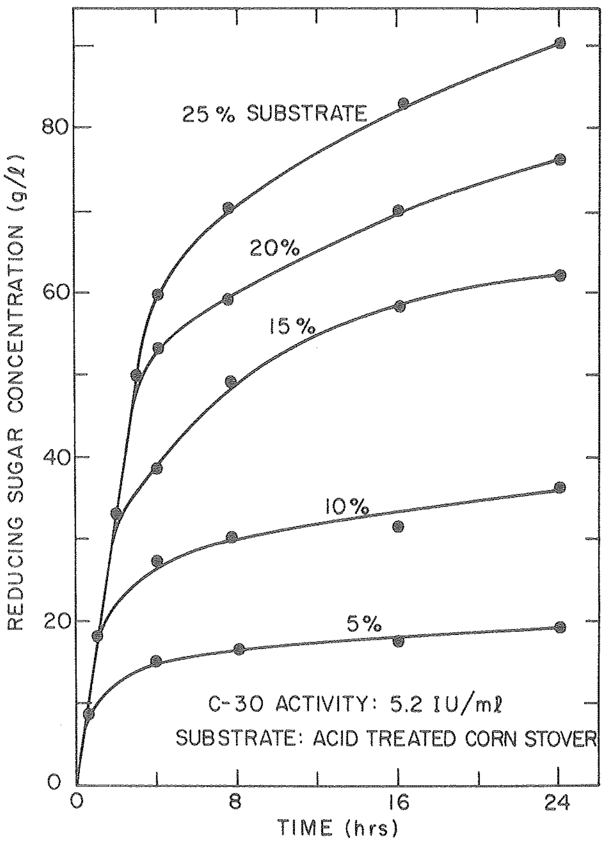

Fig. 1. Hydrolysis reducing sugar concentration versus time at various substrate loadings. (XBL 808-5703)

concentration and time. The initial linear increase in sugar concentration is apparently due to the loading technique employed.

Glucose yields typically decrease with increasing substrate concentration for a given enzyme activity. Figure 2 projects typical yield data. To date, the highest glucose yield observed was 61% corresponding to 5% substrate and enzyme activities of 5 IU/ml or greater. In general, it was observed that increasing the enzyme activity at constant substrate concentration produced an increase of yield until a threshold was reached. Beyond this point, no further increase in yield was experienced. Further work is being carried out to characterize this observation.

Enzyme activity remaining in solution during hydrolysis was measured. Dissolved cellulase activity drops rapidly during the first few hours of hydrolysis and then levels to a slightly decreasing value. Figure 3 shows a typical curve of enzyme activity remaining in solution after 24 h of hydrolysis. Activity after 24 h is usually 85-30% of original, decreasing with increasing solids suspension. Activity after 24 h decreases with decreasing initial activity, but this loss is much less pronounced than concentration-related losses. Measurement of activity profiles of cellulase components during hydrolysis indicate that

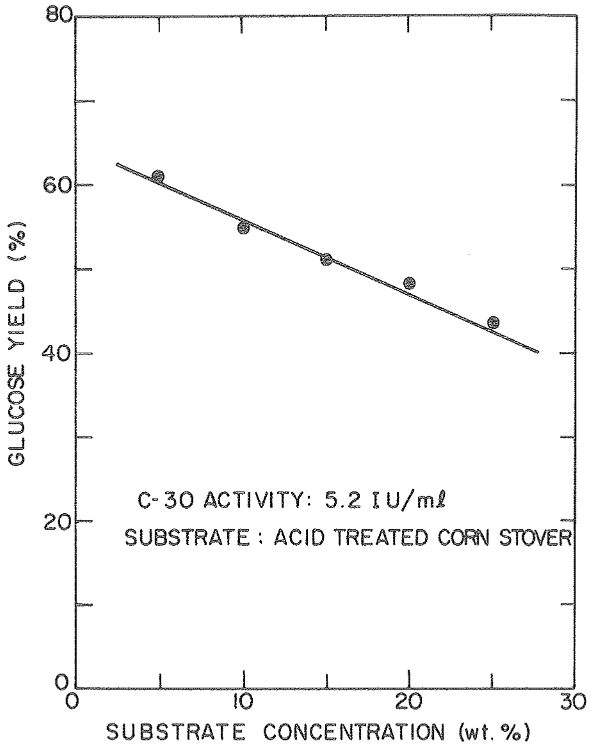

Fig. 2. Glucose yield at 24 hours versus substrate concentration. (XBL 808-5705)

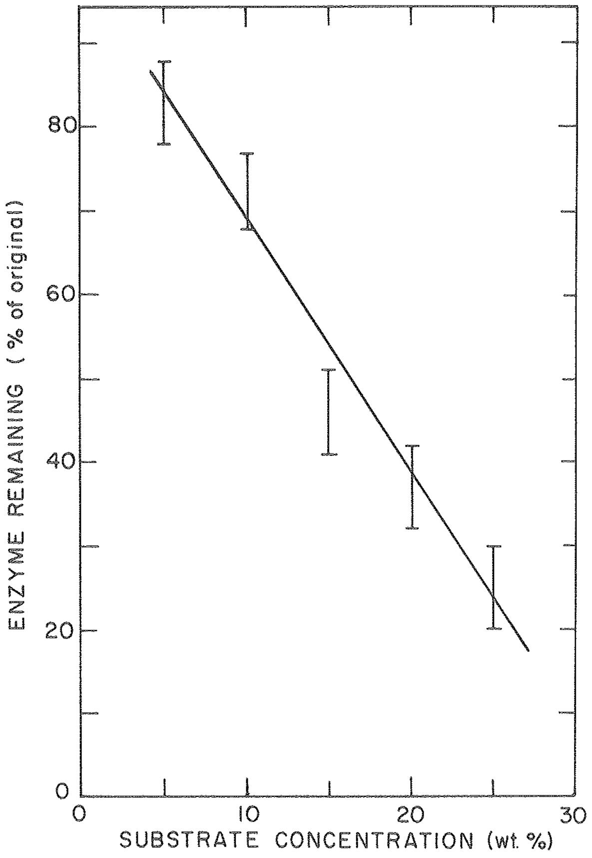

Fig. 3. Enzyme activity at 24 hours versus substrate concentration. (XBL 808-5706)

endo- and exo-glucanases parallel the behavior of the overall enzyme activity while β-glucosidase remains in solution to an appreciably greater extent.

Experiments are currently underway to investigate hydrolysis employing enzyme activities in the range of 0.5 to 2 IU ml. The incentive for this was provided by preliminary economic evaluations discussed in a later section. Preparations are being made to study enzymatic hydrolysis of steam-exploded corn stover.

Enzyme Recovery

A major economic obstacle in the conversion of cellulose to ethanol involves the loss of cellulolytic enzymes. The loss occurs primarily during the hydrolysis of cellulose to a sugar solution. The enzyme probably adsorbs onto the cellulosic residue, removing it from solution. Several approaches to cellulase recovery were analyzed: (1) isolation or immobilization of the enzyme; (2) modification of the enzyme to reduce its adsorption characteristics; and (3) modification of the substrate.

The third approach has been explored in some detail. A chemical may coat the entire substrate surface to prevent permanent adsorption, yet allow hydrolysis to occur. To observe their effects, the following salts were introduced into the hydrolysis: ammonium sulfate, ammonium oxalate, ammonium chloride, glycine and urea. Salt concentrations ranged from 6.0 M to saturated solutions. Preliminary conclusions suggest that the salts may be precipitating the enzyme reversibly ("salting out"). However, glycine may destroy the enzyme even at low concentrations.

Urea at 1 M concentration in the hydrolysis offers the most promising alternative, producing a recovery of 64%. Unfortunately, no economical method exists to remove the urea from an aqueous solution. Therefore, it must be recycled and work is being performed on exploring the feasibility of designing a cellulose to ethanol conversion scheme that employs a closed loop with total recycle of the urea. Urea is introduced into the hydrolysis, but must pass through the fermentation, distillation, and auxillary unit operations.

The effects of urea on the sugar fermentation in batch and continuous culture are being studied. A brief summary of results are given in Table 3.

Table 3. Effect of urea on enzyme growth rate and enzyme productivity.

Urea Concentration (M)	Maximum Growth Rate (h^{-1})	Ethanol Productivity* (g/ℓ-h)
0.000	0.450	4.7
0.125	0.375	4.6
0.250	0.341	4.7
0.500	0.171	-

*at a dilution rate of 0.25 h^{-1}.

The maximum growth rate and cell yield are adversely affected by urea. However, the ethanol productivity and conversion ratio of ethanol produced to glucose consumed do not decrease substantially over the range of urea concentrations explored thus far.

The efficiency of the distillation operation may be enhanced in the presence of urea. Acting as an azeotropic agent, urea distorts the ethanol-water equilibrium line and reduces the required number of separation stages. This advantage becomes significant at the pinch point at the top of the column.

A computer-generated equilibrium curve for ethanol and water only is being compiled now by other researchers in our group. This data may be very useful in predicting behavior of the urea system once some initial data are obtained with urea. This work may require six to sixteen months to complete, depending on the similarities of the two systems and the consistency of literature sources.

Process conditions in the hydrolysis have been changed dramatically in recent months. The substrate and enzyme concentrations have been increased by more than a factor of five, thereby increasing the exit sugar concentration. The effects of urea on enzyme recovery and sugar production at these conditions must be explored. The concentration of urea must be optimized over a range of combinations of substrate and enzyme to establish design parameters.

Process Economics

Preliminary economic evaluation of the Berkeley process (Figure 4) modified to include cellulase production from T. reesei Rut C-30 has been completed. Some hydrolysis results described earlier were utilized to estimate the cost of manufacturing glucose from corn stover at a rate of 214 tons per day of product.

From the limited data evaluated, a manufacturing cost of approximately 12¢/lb glucose was obtained. This constitutes 30% reduction over the cost of glucose obtained with processes of utilizing T. reesei strain QM-9414. Figures 5 and 6 give typical breakdowns of production cost by operation and by manufacturing component. For the cases presented, it can be seen that enzyme production is the dominant processing step and that, typically, capital-related factors predominate. Therefore, any subsequent improvements in cellulase production or increases in substrate yield brought about by improvements in substrate pretreatment are likely to make the largest cost reduction.

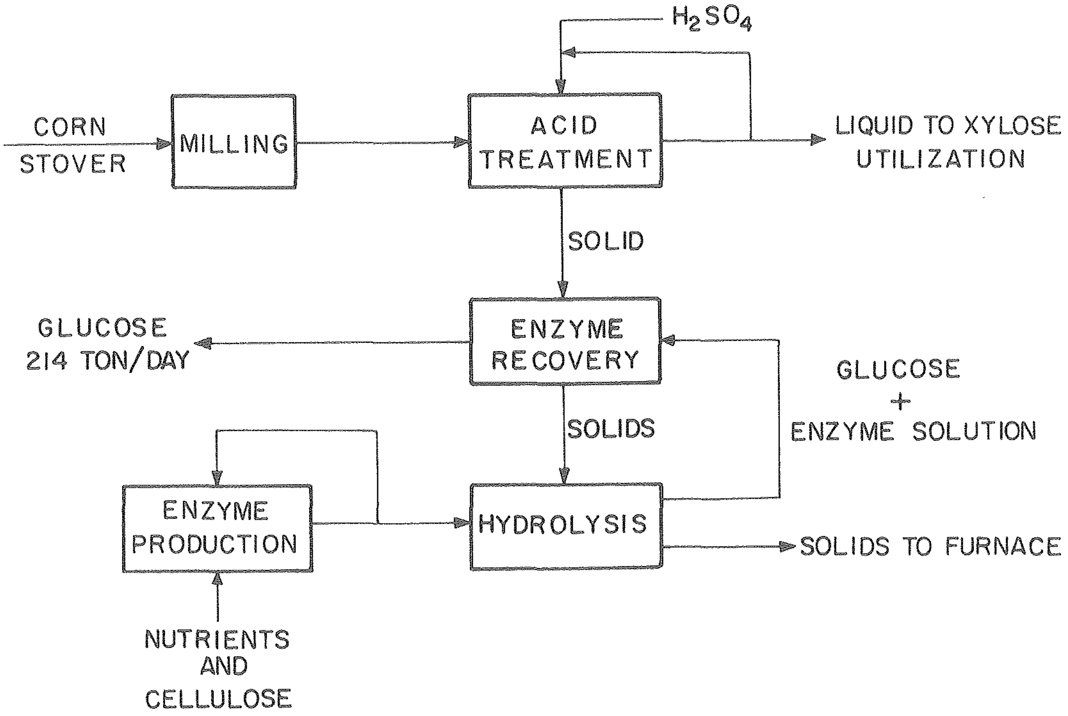

Fig. 4. Enzymatic hydrolysis process: block flow diagram. (XBL 808-5701)

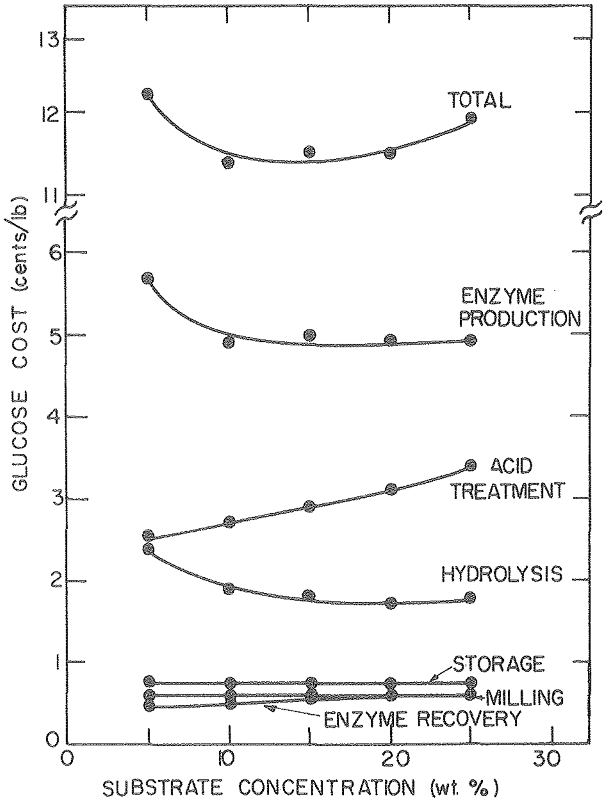

Fig. 5. Production cost by operation versus substrate concentration. (XBL 808-5710)

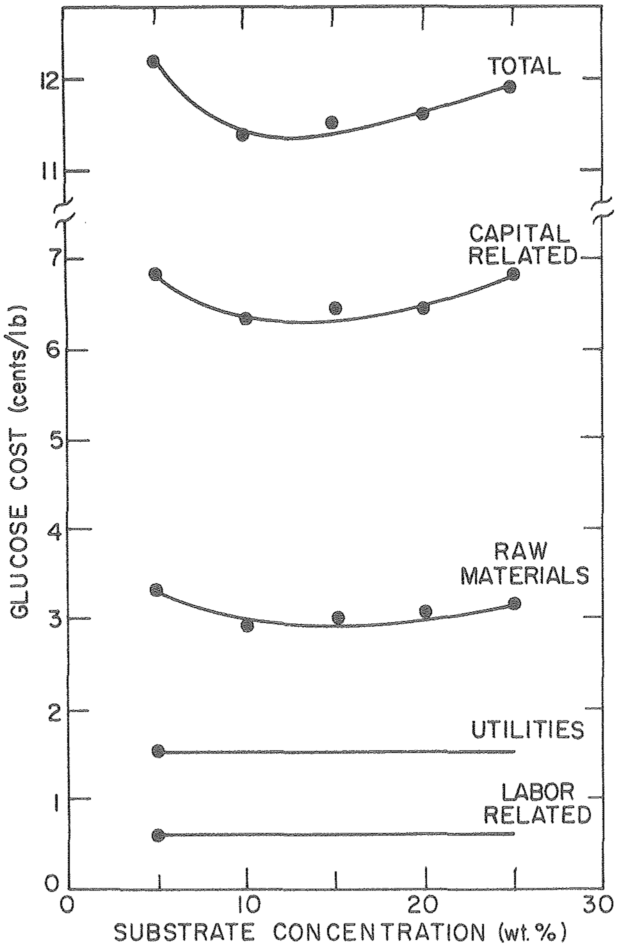

Fig. 6. Production cost by manufacturing component versus substrate concentration. (XBL 808-5709)

PLANNED ACTIVITIES FOR FY 1981

Some continued experimental work in connection with the SERI/GULF PDU is contemplated. If the program funding continues, then the predominant emphasis will be in directing modifications to the PDU for enzyme production from residues rather than from the considerably more expensive, manufactured cellulosic substrates.

Preparations are being made to study enzymatic hydrolysis of steam-explosive decompressed corn stover as a pretreatment rather than acid pretreatment.

In the fields of enzyme recovery, high concentrations of urea in the fermentor (up to 2.0 *M*) will be explored.

A computer program is being written to help evaluate the economics of the process with greater precision. When completed, the program will enable evaluation of the full range of hydrolysis data generated, and a closer approximation to the optimal processing conditions will be obtained. By evaluating process alternatives, the program should provide information useful in planning further experiments.

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ENZYMATIC CONVERSION OF WOOD AND AGRICULTURAL RESIDUES TO SUGARS*

C. R. Wilke, H. W. Blanch, K. Tangnu, D. Wiley,
B. Long, S. Rosenberg, J.-P. Riba, and L. Sindalar

INTRODUCTION

This research effort encompasses three areas: cellulase production and kinetics, hemicellulose utilization, and organism development. The work's overall goal is the hydrolysis of cellulose and hemicellulose and the fermentation of the resulting sugars to ethanol and other useful neutral products.

In our process, cellulose is hydrolyzed using cellulase enzymes produced by the mold *Trichoderma reesei*. Two of the project aims are the optimization of enzyme production and purification of components of the cellulase complex. By knowing which member or members of the complex are restricting overall conversion, supplementation schemes can be devised.

Hemicelluloses can represent as much as a third of the total carbohydrate content of lignocellulosic materials. The major component of the hemicellulose polymer is the pentosan called xylan. The bacterium *Bacillus macerans*, which ferments xylose to ethanol and acetone, is being studied in order to maximize the production of these volatile neutral products and to minimize the production of unwanted products, mainly acetic acid.

Finally, we are developing new microorganisms for the direct fermentation of cellulose to ethanol without the preliminary separate enzymatic hydrolysis step.

ACCOMPLISHMENTS DURING FY 1980

Cellulase Production and Kinetics Research

Composition of Cellulase

A scheme for separating the components of the cellulase complex of enzymes obtained from batch cultures of *T. reesei*, Rutger's C-30 strain (Rut C-30), has been scaled up to obtain purified endoglucanase (EC 3.2.1.21), cellobiohydrolase (EC 3.2.1.91), and β-glucosidase (EC 3.2.1.4). While the latter is not a cellulase in that it acts on a soluble substrate, i.e. cellobiose, rather than insoluble cellulose and cello-oligomers, it is a necessary component of the complex of enzymes involved in the ultimate degradation of cellulose to glucose.

The scheme, which is shown in Figure 1, results in the preparation of these enzymes in gram amounts rather than the milligram quantities previously obtained from an analytic separation, and will be sufficient for a kinetic study of the separate activities. Description of the reactions catalyzed by the separate enzymes is essential to the development of a general mechanism for the overall rates of cellulose hydrolysis in the production of glucose from agricultural wastes, which is the impetus for this work.

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*This work was supported by the Office of Energy Research in Basic Energy Science, Chemical Sciences Division of the U.S. Department of Energy under Contract No. W-7405-ENG-48 and by the Solar Energy Research Institute.

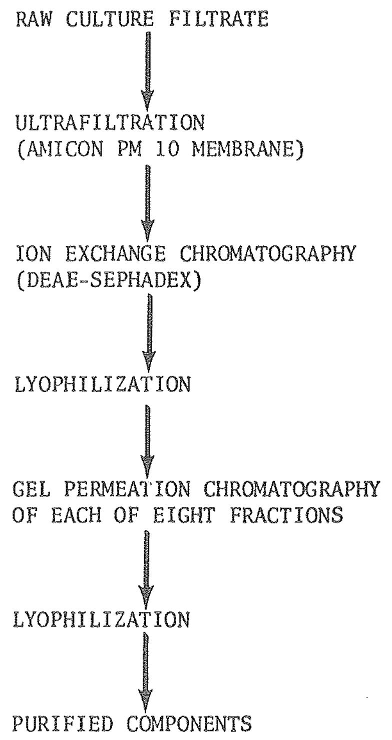

Fig. 1. Scheme for the preparation separation of cellulase components.

In the first step of the separation scheme, an ultrafiltration cell removes salts and other nonessential, low-molecular weight species, including a chromophore, from the raw culture filtrate. This enhances the separation obtained by elution with a salt gradient in the subsequent ion-exchange step. The latter results in the preparation of eight fractions, which are further purified by gel permeation chromatography after lyophilization and resuspension. Homogeneity is examined by sodium dodecyl sulfate-polyacrylamide gel electrophoresis, which indicates the requirement for an additional separation by cationic exchange for the first proteins eluted.

The preparation scheme results in the isolation of three major components: the principal cellobiohydrolase, endoglucanase, and β-glucosidase, which are listed in order of their prevalence in the cellulase complex, as well as minor components, showing each of these types of activities. Xylanase activity is presumed to be an auxillary activity of a principal component, and protease is assumed to be either irreversibly bound during the anion exchange, as expected of an acid protease, or present in such trace quantities as to be otherwise removed prior to the final purification steps.

The described separation scheme will be instrumental in the development of a kinetic model to be used in optimizing the hydrolysis of cellulosic materials.

Cellulase Production by Trichoderma Reesei

T. reesei QM-9414 and Rut C-30 were grown in batch and in a two-stage, single-stream continuous culture to produce cellulase, using cellulose as a carbon source.

Three cellulose concentrations (10, 25, and 50 g/ℓ) were tested to determine the maximum levels of cellulase activity obtainable in submerged culture. Temperature-pH profiling was tried in order to increase the cell mass to maximum levels, thereby enhancing fermentation at higher substrate concentrations.

For maximum production of cellulase by T. reesei QM-9414, the pH was allowed to decrease to 4 for the first day and to 2.8 for the second day. At the end of the second day, the pH was raised to 3.3 and controlled not to go below 3.3, while temperature was controlled at 28°C. With 50 g/ℓ and 25 g/ℓ substrate concentrations, filter paper activity of 6.1 and 4.3 International Units (IU)/ml, respectively, were obtained. There was not a substantial gain in filter paper activity with the increase in substrate concentration.

For production of cellulase and β-glucosidase by T. reesei Rut C-30, a pH of 5 and a temperature of 25°C were optimum. A higher temperature (31°C) for the initial fermentation time period (18 h) could substantially increase the β-glucosidase activity in the system. A pH of 6 can produce as much β-glucosidase in three days as can be obtained in eight days at a pH of four or five. With the help of environmental control, it is possible to produce enzyme mixtures with different ratios of FPA, C_1, C_x and β-glucosidase. Filter paper activities of 14.4 and 7.3 IU/ml were obtained using 50 g/ℓ and 25 g/ℓ of substrate, respectively.

Tween-80 concentration of 0.1% and 0.02% were optimized for T. reesei Qm-9414 and Rut C-30, respectively.

Two-stage continuous culture studies were carried out growing QM-9414 and Rut C-30 on a cellulose-containing medium in 14-liter stirred fermentors. Response to step changes in Tween-80 level, substrate concentration, dilution rate, pH and temperature was followed and steady-state values obtained.

For QM-9414 the first and second stages were operated in the pH range of 3.75-4.25 and 5.0, respectively. Decreasing the Tween-80 concentration by half (0.1%) increased the filter paper activity by 60% in the first stage of the fermentation. Increasing inlet substrate concentration from 1.75 to 2.5% did not increase the filter paper activity. Optimum dilution rates of 0.02 and 0.27 h^{-1} were found in the first and second stages, respectively. A fermentation temperature of 28°C optimized both stages.

For Rut C-30, the first and second stages were operated at a pH of 5.0. Tween-80 concentration of 0.02% and temperature 25°C were optimum for maximum cellulase production. Dilution rates of 0.02 and 0.04 h^{-1} optimized both the stages.

In the future, it would be advantageous to run two-stage fermentations with a cell recycle system.

Utilization of Hemicellulose Research

In our current bioconversion process, treatment of the cellulosic biomass substrate with hot, dilute sulfuric acid hydrolyzes the hemicellulose polymers yielding a solution rich in pentose sugars, the major component of which is D-xylose. Since as much as a third of the total carbohydrate of biomass may be in the form of hemicellulose, we have been examining methods for maximizing the fermentative conversion of D-xylose to ethanol. The organism we have been studying to effect this conversion is the bacterium *Bacillus macerans*. The major fermentation produced by this organism growing with D-xylose are ethanol, acetone, and acetic acid.

The current respective yields of ethanol, acetic acid, and acetone are 27, 23, and 1.5 g/g of xylose fermented. Theoretical considerations suggest that a balanced fermentation can occur without the production of acetic acid. Whether this can be achieved in practice will depend on the regulation of the enzymes of the biochemical pathways concerned. There is evidence from other systems that the concentrations of certain end products can affect the spectrum of fermentation products produced and their final concentrations. To investigate the regulation of fermentation pathways in *B. macerans*, it was first necessary to understand how various product concentrations would affect the organism's growth rate. These relations have been determined, and the results are shown in Figure 2. The maximum specific growth rate (μ_{max}) is approximately 0.2 h^{-1}, corresponding to a doubling time of about 3.5 h.

Organism Development Research

The goal of this research is the development of a biological process for the single-step conversion of cellulose to ethanol. To this end, we have tested a number of likely candidate microorganisms for ability to both degrade cellulose and to ferment glucose quantitatively to ethanol and CO_2.

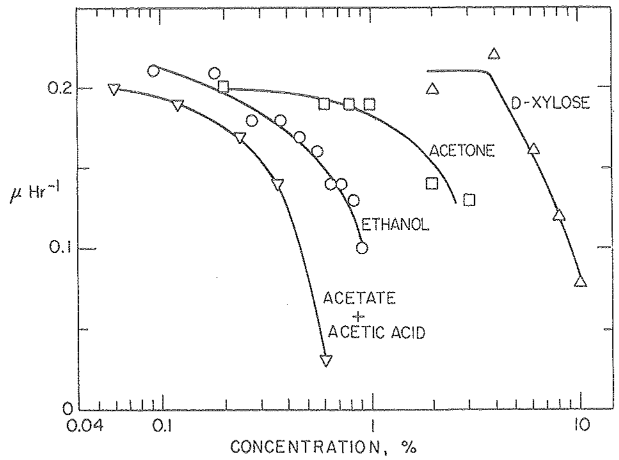

Fig. 2. Effect of substrate and fermentation product concentration of the growth rate of *Bacillus macerans*. (XBL 8011-13332)

Of 60 strains examined, 12 appeared able both to ferment glucose to ethanol and CO_2 and degrade cellulose. Of these 12, 6 showed especially good cellulose hydrolysis aerobically, and these were chosen for further detailed study. Cultures were grown with crystalline cellulose, ball-milled, crystalline cellulose, and phosphoric-acid swollen cellulose. Crystalline cellulose is most resistant to degradation, while swollen cellulose is least resistant. Strain A-106 grew faster on all three forms of cellulose and on this basis was selected for further study.

Physiological and nutritional studies reveal several important characteristics of this organism:

(1) Growth would occur on cellulose aerobically but not anaerobically.

(2) The organism would grow on glucose both aerobically and anaerobically, but anaerobic growth (fermentation) required the presence of a complex nutritional supplement, such as yeast extract, while aerobic growth could occur in an unsupplemented mineral medium.

(3) Fermentation of glucose can occur after net growth ceases.

(4) Approximately theoretical yields of ethanol (ca. 45%) are produced from glucose by this organism.

(5) Cellulose can be fermented if some oxygen is included in the culture initially. This lowers the yield of ethanol but allows the process to proceed.

During this period, we also developed a practical, small-scale culturing system that allows us to test the effects of many variables simultaneously rather than sequentially, as had been the case with our previous large-scale apparatus. This has greatly speeded up the pace of research.

PLANNED ACTIVITIES FOR FY 1981

Utilization of Hemicellulose Research

Now that we know what the growth inhibitory concentrations of the major products (and the substrate) are, we will repeat these experiments with various product concentrations and measure the concentrations of the various products produced. The resulting observations will allow us to model the regulation of the various fermentation pathways and potentially to skew the fermentation toward the production of neutral products.

Organism Development Research

Research for 1981 will be concentrated in two areas:

(1) Definition of the minimal nutrient requirements for complete fermentation of glucose. Fermentation of glucose may not be complete even in the presence of nutrients such as yeast extract unless at least a small amount of air (oxygen) is present. We need to determine what required nutrients are missing in order to eliminate the oxygen requirements and maximize ethanol productivity.

(2) Demonstration of cellulase production under anaerobic conditions. This is our major problem area. Currently cellulases are expressed aerobically but not anaerobically. We will conduct mutation-selection experiments in order to select mutant strains which produce high, unregulated levels of cellulase enzymes.

ETHANOL PRODUCTION AND RECOVERY FROM BIOMASS SUGARS*

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INTRODUCTION

Ethanol is the logical intermediate product in the utilization of biomass for energy and chemical needs. Produced by fermentation of biomass sugars, ethanol can be used directly as a liquid fuel, or it can serve as a chemical feedstock of great flexibility. These uses help to reduce this country's dependence on imported petroleum only if the overall conversion uses much less energy than is recovered in the product. Hence the goal of this research is to improve ethanol production and recovery from biomass so that it can make as great a contribution as possible to reducing our imported petroleum requirements.

Research toward this objective is proceeding in four separate but inter-related projects. In the Flash Fermentation for Rapid Ethanol Production project, a process for continuous production and purification of ethanol from fermentation is being tested on a pilot-plant scale. The Alternative Ethanol Recovery work is developing other techniques for ethanol recovery which will consume less energy than traditional distillation. In the project on Novel Fermentor Development, the use of a hollow-fiber fermentor to achieve higher productivities than those of conventional fermentors is being investigated. The remaining project, Nutritional Requirements for Yeast Fermentation, is aimed at precise identification of the metabolic needs of the ethanol-producing yeast to allow specification of medium components for maximum ethanol productivity at minimum cost.

ACCOMPLISHMENTS DURING FY 1980

Flash Fermentation for Rapid Ethanol Production

A 5-liter volume flash-fermentation pilot plant has been assembled (Fig. 1).

The fermentative ethanol production rate is ordinarily limited by ethanol inhibition. Flash fermentation eliminates this problem by continually removing alcohol as it is produced. Fermentation beer is drawn by vacuum into an auxiliary isothermal vacuum flash vessel where it boils. Ethanol and water vapors are taken as flash vessel overhead products, condensed in a condenser train and collected in a dry ice-cooled collection vessel. The ratio of ethanol to water in this final product is fixed by the temperature and pressure of flash vessel operation. Ethanol-depleted beer is pumped back to the fermentor from the flash vessel. Fermentor ethanol concentration is thus maintained at a low level. A concentrated sugar feed (such as molasses) can rapidly be fermented to produce concentrated (ca. 30 wt%) ethanol vapor product.

In a shakedown run of the flashferm apparatus, a volumetric productivity of 36 g/ℓ-h was achieved in converting 350 g/ℓ glucose feed to 19.3 wt% ethanol product. This is more than ten times the volumetric productivity in simple batch fermentation, which yields a far more dilute product.

Alternative Ethanol Recovery Processes

The major emphasis in the work on alternatives to distillation as an ethanol recovery process has been in the area of solvent extraction. An extraction process could be very energy conserving and economical given a solvent which is highly selective for ethanol and easily regenerated. However, most solvents that are selective for ethanol in a dilute aqueous solution have a very low distribution coefficient (the ratio of weight or mole fraction of ethanol in the solvent phase to that in the aqueous phase).[1] Thus, studies have been done on ways of enhancing the distribution coefficient of selective solvents.

In one such method, an agent is added to the solvent to lower the activity of ethanol in the solvent phase. An example of this approach is the use of trioctyl phosphine oxide (TOPO) in organic solvents. Data from studies of this extractant system applied to acetic acid recovery

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*This work was supported by the Office of Energy Research in Basic Energy Science, Chemical Sciences Division of the U.S. Department of Energy under Contract No. W-7405-ENG-48 and by the Solar Energy Research Institute.

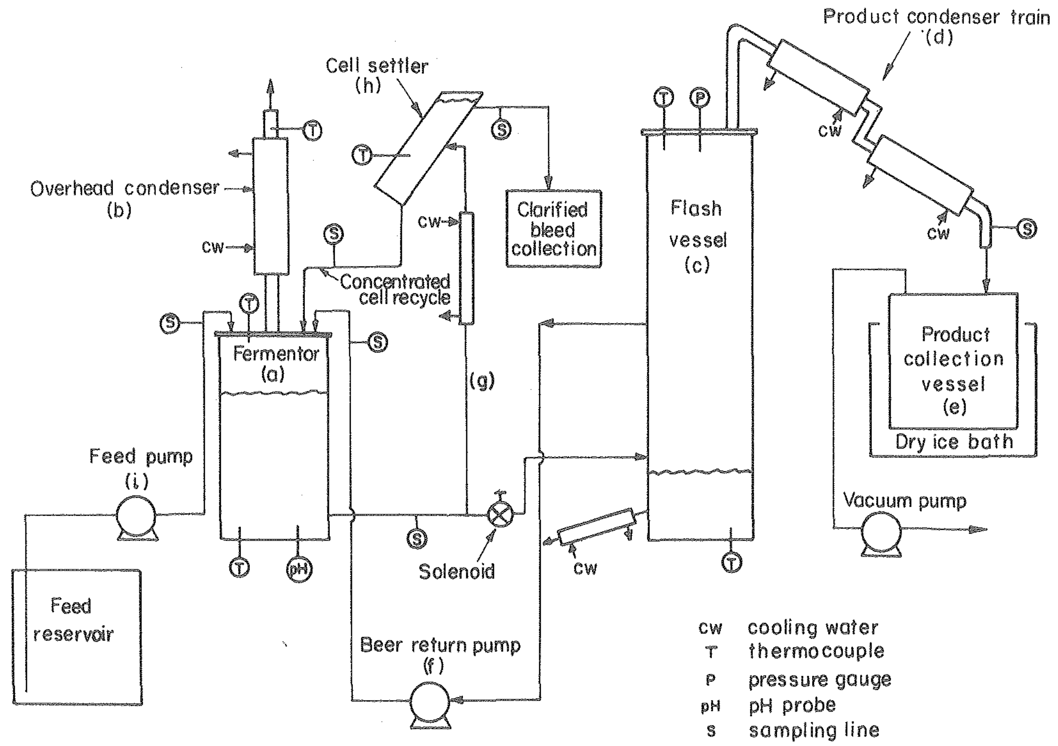

Fig. 1. Flash-ferm apparatus overview. (XBL 7912-5497)

suggested that it might be effective in enhancing the alcohol distribution coefficient.[2] Phase equilibrium experiments analyzed by gas chromatography showed the effect to be very small in the case of ethanol, however. Modifications of the idea, employing compounds with somewhat less hydrophobic character, such as tributyl phosphine oxide, are being tested.

Rather than lowering the activity of ethanol in the solvent phase, raising its acivity in the aqueous phase has also been studied as a means of improving ethanol distribution coefficients. This can be done by adding separating agents, such as sugars or salts, to the aqueous phase. A number of such compounds have been investigated by gas chromatographic analysis of batch-phase equilibrium experiments. While sugars show some enhancement of distribution coefficient, only at very high concentrations are they significant. Much more effective are some inorganic salts, including potassium phosphates and carbonate and ammonium sulfate. These salts will actually cause the formation of a separate liquid phase rich in ethanol (up to 90 wt%) when added to dilute aqueous ethanol solution. The use of such salting-out behavior depends, however, on economical recovery processes for the salt, which cannot be discarded because of its cost and possible environmental damage. Such processes are under continuing study.

Novel Fermentor Development

Equipment was built to study existing ultrafiltration (uf) modules for use as fermentors. A study of the flow pattern in the unit was made and a fermentation was attempted. Existing commercial units were unsatisfactory because of the large amount of fermentation gases that need to be vented. A new configuration to allow for easier gas-venting has now been made. In the new design, the fibers are spaced out to allow gas bubbles to rise; the shell side pressure can be regulated to control the volumetric rate of gas evolution; and the pathway for the gas to escape is less tortuous. Unfortunately, many problems in the construction of the fermentor have delayed the work.

Nutritional Requirements for Yeast Fermentation

A basic study of the nutrient requirements for yeast fermentation of sugars to ethanol is important because of the high cost contribution of the nutrients to the ethanol production cost and because of the major effects of media composition on ethanol and yeast productivities. Therefore, batch and continuous fermentations have been carried out to define the active components of the normally complex media used in yeast fermentation and to define their optimal ratios for balanced yeast growth.

It was shown that for low (10 g/ℓ) glucose concentrations, 88% of the complex component of the medium, yeast extract, could be replaced by synthetic vitamins and still increase both specific and total ethanol productivities. However, increasing the glucose concentrations to 100 g/ℓ and the other components in direct proportion led to lower ethanol productivity with synthetic vitamins relative to yeast extract. Furthermore, total sugar utilization decreased for both media with higher glucose concentrations. Possible explanations currently being investigated are the effects of substrate inhibition, nonoptimal dissolved O_2 tension, and changes in the organism.

In particular, the effect of dissolved O_2 was studied intensively because previous reports showed important but contradictory results in the very low ranges of 0 to 10 ppb dissolved O_2. Unfortunately, the use of dissolved O_2 probes, chemical tests, and gas chromatography (with thermal conductivity detector) all lacked the sensitivity to measure this level of dissolved O_2. It has been reported that a gas chromatograph with a helium ionization detector has sufficient sensitivity, but it is expensive and difficult to operate.

Instead, attention was turned to determining the effects of higher measurable concentrations of dissolved O_2, which would be the range of practical importance. Control at the reported low optimal levels, because its range is so narrow, would be impractical for industrial applications. Preliminary results show that over a wide range of about 0 to 50% of air saturation, there is little or no effect due to dissolved O_2. However, carbon dioxide was inhibitory to yeast growth and ethanol production.

Also, an interesting change, which may be an adaptation, appeared to take place in the organism when an essentially anaerobic continuous culture was aerated vigorously. The cell yield was considerably greater than that expected from fermentative growth, indicating substantial aerobic or oxidative growth was occurring. However, the ethanol yield was much greater than that expected from aerobic growth, which is expected from the residual glucose level in the medium. Therefore, both fermentative and aerobic pathways were simultaneously being utilized, and the catabolite repression (glucose effect) must have been partially lifted. Measurement of O_2 uptake and CO_2 evolution are in progress to determine the relative extents of fermentative and oxidative growth as a function of aeration conditions. If this function can be determined, the ratio of cell mass to ethanol production can be controlled. A complicating factor in this study has been the stability of the possible adaptions.

PLANNED ACTIVITIES FOR FY 1981

Flash Fermentation for Rapid Ethanol Production research during the next calendar quarter will optimize operating conditions for the flashferm process, considering such variables as feed concentration, feed rate, and flash vessel temperature and pressure.

This work will be completed and a final report evaluating the flashferm process and comparing it with alternative fermentation schemes will be submitted by late August 1981.

Alternative Ethanol Recovery research will continue investigation of the promising aspects of FY 1980 work; plans for FY 1981 include study of two new concepts in extractive fermentation and economic analysis of process designs incorporating these features. The first of these is the use of inert gas stripping of ethanol fermentation beer followed by solvent absorption of the ethanol vapor. This concept avoids the formation of emulsions which have created problems with liquid-liquid extraction processes involving fermenter beers. It also, like the vacuferm and vacuflash processes, allows increased ethanol productivity by removing ethanol continuously, thus mitigating product inhibition. Preliminary calculations show that energy requirements for inert gas recirculation are very small.

The other new concept slated for study is a means of removing alcohol from the extractant stream without heating the entire stream (as would be necessary in a conventional distillation or stripping operation). This involves using the ability of certain salts to form alcoholate complexes analogous to hydrates. Recovery of ethanol from the solid ethanolates by evaporation has the potential for less energy consumption than conventional processes.

These ideas are to be evaluated using available data and the results of experimental determinations of solvent properties using the gas chromatographic system. Results will be used to determine parameters for a process design which will be evaluated for economic feasibility.

Novel Fermentor Development research will include a fermentation using the new fermenter design. If the gas problem is overcome, the system will then be modeled using a model similar to that cited by Schuler et al.[3] The effect of fermentation gases must be incorporated into this model. If gas venting still presents a serious problem, an alternate biosystem to study the unit may need to be found.

Nutritional Requirements for Yeast Fermentation research will determine the effects of dissolved O_2 and aeration, and then the cause of low cell and ethanol productivity with 100 g/ℓ glucose will be reexamined. If O_2 is not the problem, the effect of substrate inhibition by various minerals will be studied. Also, a mass balance will be obtained for the major elements so their quantitative requirements can be determined for a balanced medium.

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THE LBL BIOMASS LIQUEFACTION PROCESS*

H. Davis, S. Ergun, C. Figueroa, C. Karatas, L. Schaleger, and N. Yaghoubzadeh

INTRODUCTION

The major objective of this program is to provide a process for converting Douglas fir wood, and other sources of biomass, to a commercially usable fuel oil. Such a product could provide a storable fuel for peak-load power plant operation, transportation or power-plant fuel for a local area, and perhaps a raw material for particular chemicals.

A process development unit (PDU) is operated on a Department of Energy (DOE) contract at Albany, Oregon by Rust Engineering. The PDU was built in the mid-1970s, based on experiments at the Pittsburgh Energy Research Center (PERC), and it has been able to generate significant amounts of oil product from Douglas fir wood chips since late 1979. The PERC process, as used in the PDU, requires excessive recycle of product oil--10 parts or more of recycled oil to one part dry wood feed --and has other economic deficiencies. The LBL process was designed to correct these deficiencies.[1] Actually, the first substantial amounts of product in the PDU were made by an improvised version of the LBL process.[2] Two relatively successful PERC-mode runs were accomplished in June[3] and October 1980.

The basic principle of the LBL process is to replace the recycled oil, used in the PERC process with slurry wood flour for feeding to the reactor with water. Wood chips undergo mild hydrolysis (at 180°C, for 45 min in 0.075% H_2SO_4); this hydrolyzes hemicelluloses and leaves the chips weak and friable.

After neutralization with alkali, the wood chip-water mixture is passed through a paper industry-style "refiner" from which a stable slurry containing up to 30% or more dry solids is obtained. This is then heated to about 360°C with a CO/H_2 synthesis gas, held for an appropriate residence time, and cooled. The oil product is denser than water at low temperatures but can be recovered in a phase separator. A significant portion of the product (7 to 12% of the dry wood feed) remains dissolved in the aqueous product.

As of October 1, 1979, serious unresolved questions remained concerning the pumpability and stability of the aqueous wood slurry, optimum reaction time, initial pH and pressurizing atmosphere, behavior of recycle streams, and properties of the product. On October 1, 1980, some information is available but considerable effort is necessary before all the questions can be answered.

ACCOMPLISHMENTS DURING FY 1980

Slurry Preparation and Stability

Slurries of partially hydrolyzed wood have been made on a large scale in the PDU and have been pumped through tubing as small as .25 in. for extended periods in the PDU and at LBL.[1] Concentrations of dry solids $>30\%$ have been handled successfully. Storage in drums for several months makes no apparent difference in pumpability.[2] An actual run in the PDU, although it used only an 8% slurry, was reasonably successful and produced several drums of product, the first substantial amounts of wood oil available from the PDU. Concentrated slurries have also been preheated successfully in small tubing at LBL. Thus the process has been demonstrated in stages.

Continuous Experimental Unit

During 1980, a bench-scale continuous experimental unit (CEU) designed to feed about 1 liter/h of wood slurry was constructed at LBL.[1] First efforts to operate this in June and July 1980 revealed several deficiencies, and it was decided to rebuild the unit from August 1980 to the present. Safety features deemed necessary were added and instrumentation and controls were improved.[4] Mechanical completion was expected in late 1980 when initial testing could begin.[4] The CEU is an essential element in providing a link between laboratory batch experimentation and continuous pilot plant and commercial operation. Basic engineering variables, e.g., reaction time, temperature, initial pH, composition of reacting gases, etc., can be studied more readily than at the PDU and results are more relevant for commercial operation than batch work results.

A small colloid mill (equivalent to a refiner) has been rented and an autoclave suitable for prehydrolysis is on order. They will permit us to study the prehydrolysis step and the preparation of slurries of various concentrations for the CEU.

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*This work was supported by the Assistant Secretary for Conservation and Solar Energy, Office of Solar Technology, Biomass Energy System Division of the U.S. Department of Energy under Contract No. W-7405-ENG-48.

A glass coil was used[5] to demonstrate the pumpability and stability of PDU wood slurry and to measure flow properties.

Batch Experimentation

During 1980, a series of factorial experiments was carried out in small "tubular bomb" reactors.[4,6] These experiments have many of the interpretation problems of batch experimentation in general in addition to a possibly serious deficiency in agitation. They have the advantage of availability of rapid heat-up and cooling (2.5 min to 360°C). The experiments are reported in some detail in the Biomass Group's fourth Quarterly Report.[4] Among the conclusions from the data are several which contradict the conventional wisdom on liquefaction.

- Synthesis gas, which may be H_2, CO, or mixtures thereof, and may include some CO_2, is essential to minimize char formation. Pressurizing with inert gas alone N_2 results in high char formation.

- At pHs near the neutral point, yields of acetone-soluble oils are higher and yields of char lower than when additional sodium carbonate is added. Sodium carbonate has been generally considered to catalyze the reduction of wood-oxygen by CO.

- At the usual reaction temperature of 360°C, yields of solubles are highest and yields of char lowest when heat-up rate is as high as possible and holding time at this temperature is very low.

This work must be checked in the continuous units. In particular, the apparent need for very short reaction times seems to contradict the results with the PERC process at the PDU, where liquid space times were of the order of two hours and the high recycle multiplied this by a large factor of the order of 20, without apparent serious effect on char formation. It is conceivable that the data are revealing the effect of agitation and gas-liquid contacting during heat-up and the subsequent slow reduction with CO and H_2.

Planned Activities for FY 1981

First order of business is the completion and testing of the CEU and an initial run under a set of standardized conditions. Once this is achieved, the CEU will be used to explore the effects of most of the pertinent process variables, particularly the variable which cannot properly be studied in batch equipment: reaction time. Studies of effects of slurry pH, gas composition, and reaction temperature will be guided by the results of batch experimentation. A serious effort will be made to obtain acceptable material balances. This has proven to be very difficult in the PDU, and data from batch autoclave work are skimpy. A flow-sheet of the CEU as it now stands is attached (Fig. 1).

A series of experiments in stirred autoclaves is planned to verify and extend the small tubular bomb results. The autoclaves are superior to the tubular bomb in at least two respects: stirring is possible and a material balance is possible. Also sizable amounts of products for chemical studies and for recycle experiments can be made. The relatively long heat-up times, however, are a serious drawback. Therefore, an effort to design and build slightly larger tubular bombs capable of agitation will be made. The larger amount of dry wood reacted in these (4-6 g versus 1-1.5 g) will also improve possibilities for a material balance.

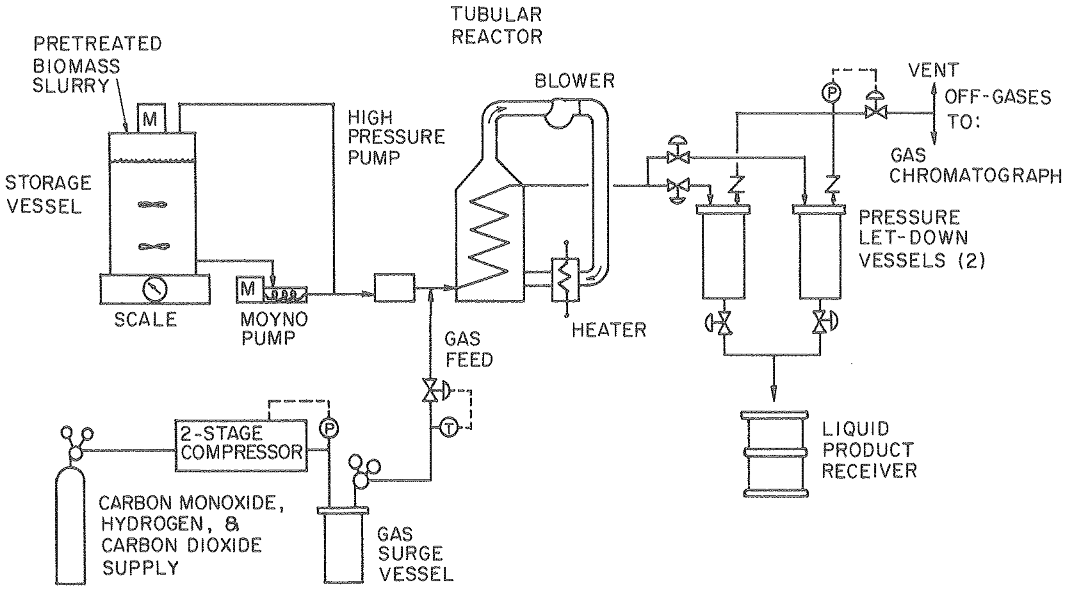

Fig. 1. LBL Process Evaluation Unit (PEU). (XBL 811-3585)

A most important effort involves the better characterization of product oils and a related effort to understand the mechanism of liquefaction. This effort employs the various methods of chromatography to effect group separations as well as individual product determinations. Samples obtained under various reaction conditions and from various feedstocks (including celluloses, hemicellulose components, and lignin) will be studied so that we can begin to understand some of the mechanisms of the many reactions which occur. This effort is discussed in a later section of this report.

While LBL no longer has monitoring responsibility for the Albany PDU operation, we have been requested to supply advice on equipment and operations and we plan to have engineers present when a definitive LBL test is made. At LBL's request, the following changes in the PDU equipment and flow sheet have been made preparatory to such an experiment:

- A direct-fired tubular preheater has been installed capable of heating 60 gal/h of feed slurry to 360°C with a total resident time of less than one min.
- A refiner has been rented so that slurry can be made on site.
- The PDU stirred-tank reactor has been repiped so that a lower product take-off, leaving about 50 to 60 gal of reactor volume, is available. This permits liquid space times of less than one h.
- Commercial phase separators for the product oil-aqueous layer separation were ordered.
- The older vertical, scraped-wall preheater has been bypassed, but can be reinstalled as a standpipe reactor (~17 gal capacity) with the scraper removed.

Neither the stirred-tank nor the standpipe constitutes the reactor we would prefer. This should be tubular-really an extension of the preheater to allow an appropriate time at temperature. As of October 1, 1980, however, we were hopeful that one or both of these available reactor systems would work. Judging from the batch experimentation work discussed above, we would get the least amount of charry residue and the largest amount of product (if not the best quality) by stopping reaction after the tubular preheater.

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CHEMISTRY OF BIOMASS LIQUEFACTION*

H. Davis, D. Kloden, and L. Schaleger

INTRODUCTION

The liquefaction of wood, municipal waste, and other forms of biomass has been studied for many years. The present efforts stem from work done by H. Appel, I. Wender and others at the U.S. Bureau of Mines' Bruceton Station, (later known as PERC and referred to now as PETC) in the 1960s and early 1970s. It was found that treatment of biomass materials in an autoclave at temperatures of 300-400°C under pressures of water vapor and CO gave an oil-like product. The product was definitely not hydrocarbon. It contained up to 15% O_2, including substantial amounts of carbonyl and phenolic hydroxyl groups. Its heating value was therefore considerably lower than that of a petroleum fuel oil. Still, it burned, and was substantially free of sulfur, nitrogen, and ash, making it a desirable nonpolluting fuel. A process development unit (PDU) was therefore designed and construction began

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*This work was supported by the Assistant Secretary for Conservation and Solar Energy, Office of Solar Technology, Biomass System Division of the U.S. Department of Energy under Contract No. W-7405-ENG-48.

on it at Albany, Oregon in 1974. It operates on Douglas fir wood chips, and was designed both to scale-up the process and to convert it from a batch to a continuous process.

Over the years various efforts have been made to deduce the stoichiometry and mechanism (or mechanisms) of the conversion and the chemical make-up of the product. At all levels of operation, tests with good material balances have been lacking. There has been argument as to the role of CO or of the CO-H_2 mixtures usually substituted for it. Catalysts have been tested, supported, then abandoned. The original U.S. Bureau of Mines' work indicated that an alkaline system--achieved by adding Na_2CO_3--was necessary for CO to be effective. Even this is questioned today.

Nuclear magnetic resonance (NMR) analysis and physical properties of the oil from wood chips show it to be highly aromatic. This suggests that much of the oil product comes from the lignin portion of wood (∿32% in Douglas fir) rather than from the aliphatic polysacharide portions. Experiments with cellulose, sugars, and lignin feeds bolster this conclusion.

The temperatures at which liquefaction takes place (the PDU operates at 360°C) are in a range where pyrolysis readily occurs. Large amounts of CO_2 and water are formed. The liquefaction is therefore a controlled pyrolysis accompanied by a reduction reaction.

Characterization of the reaction and the product oil has been inhibited by the wide variety of reaction conditions and feed stock tried in batch experiments. The present existence of two reasonably well identified processes (PERC and LBL), both operable in the PDU and both leading to reasonably consistent products, makes a renewed effort on characterization attractive.

Accomplishments During FY 1980

Stoichiometry

The lack of good material balances and the variety of processing conditions has left the stoichiometry of the process somewhat uncertain. The best material balances for the PDU to date were obtained in test run 8,[1] using the PERC process. An analysis of the data[2] shows that several classes of reactions definitely occur, and that the stoichiometry can be described at least semi-quantitatively. From 100 lb of dry wood approximately 0.6 lb-mol of CO_2 and 0.5 lb-mol water were formed essentially by pyrolysis, while about 0.6 mol CO reacted to further reduce O_2 in the product oil and, of course, form an additional 0.6 mol CO_2. There is no net usage of H_2. In fact, the reaction medium, the reactor, or both, catalyze the water-gas shift reaction. Additional CO reacts with water to form H_2 and CO_2.

Material balance closure demands that roughly 45 lb of the wood be accounted for as $CO_2 + H_2O$ (plus a trace of methane) and roughly 55 lb as liquids or solid product. However, the PDU run showed only 41% oil yield plus 4% char residue. Thus our forced balance requires an additional 10%. A portion of this is probably material dissolved in the aqueous effluent or volatiles lost overhead. The rest simply indicates the limits of our current ability to obtain (and to calculate) a material balance.

The LBL process differs from PERC in a fundamental way: the feed to the process is an aqueous slurry of partially hydrolyzed wood, as opposed to a slurry of wood flour in recycled product. Since in the PERC process as carried out in the PDU, the feed is 90% recycled oil, the overall residence time in the reactor is many hours (as opposed to about one hour for LBL). The presence of larger excesses of water and the absence of recycled oil may also have secondary effects on the process chemistry. Also, the portion of overall product dissolved in the larger aqueous effluent will be greater in the LBL process.

Nevertheless, the same general processes must occur. Apparently, to obtain a product, other than char, with less than about 10-15% O_2 some reduction by synthesis gas must occur. (See Table 1.) We suggest the following as a resonable goal for either process:

$$100\ \text{lb dry wood} + 0.6\ \text{mol CO} \xrightarrow[4000\ \text{psig}\ H_2O,\ H_2,\ CO]{360^\circ}$$

$$0.5\ \text{mol}\ CO_2 + 0.5\ \text{mol}\ H_2O + 55\ \text{lb nonvapor product.}$$

The above requires about 430 ft^3 of synthesis gas per 100 lb of dry wood. The "nonvapor product" includes an amount of water solubles dependent on process and process conditions. It also includes solid char residue, that must, however, be minor if the process is to be acceptable.

Characterization of Products

The gross product of liquefaction has been characterized largely by elemental analysis, by simple physical properties, such as density and viscosity, and occasionally by distillation (typically 60 to 70% is vaporizable in a laboratory vacuum still). Numerous individual compounds have been identified in the lower boiling fractions.

Table 1. Product analysis.

Wood (wt%)	Nonvapor Product (wt%)
C 53.2	C 83.9
H 5.6	H 8.3
O 40.5	O 7.5
N 0.13	N 0.1
Others 0.6	Others 0.2
Total 100.0	Total 100.0

These are largely cyclic ketones, phenols, and cyclic ethers, with few if any hydrocarbons (other than those in the PERC product, which may have come from the initial anthracene oil). Alkaline extractions have indicated 10 to 40% acidic components (primarily phenols), depending on the process and the treatment method.

A list of compounds identified by steam distillation of an LBL process product oil is reproduced as Table 2, from the LBL fourth *Quarterly Report*.[3] Somewhat similar materials have been extracted from aqueous effluent or from other oil products.

While the majority of the compounds identified in Table 2 are aliphatic and of low molecular weight, the more typical compounds must be quite different. Distillation curves and gel permeation chromatography show the average molecular weight to be about 300 or more. Physical properties, H:C ratio and NMR studies show that well over 50% of C atoms are aromatic--probably 90% of the compounds are aromatic. The identification of any very high percentage of these as individual compounds is a difficult, nearly impossible task and not a very rewarding one. Accurate and well-characterized methods of dividing the product by functional type and by molecular weight range have long been needed.

PLANNED ACTIVITIES FOR FY 1981

With the addition of a graduate chemist and a chemical technician to our staff, we hope to make real progress in the development of rapid type-analyses. Equipment available includes gas chromatography, gas chromatography plus mass spectrometry, high precision liquid chromatography, gel permeation chromatography, and the usual techniques of solvent extraction.

The objective is twofold: first to know what the product is and second to be able to follow changes in the product as the process changes. There are many ways, of course, in which such a product might be characterized. At this point, we would be well-satisfied if a given sample could be divided into four or five fractions according to molecular weight and if each of these (except perhaps the heaviest) could be separated into four or five fractions according to polarity. Within each fraction, gross properties would be known. These include elemental analysis, average molecular weight, molecular weight distribution, viscosity, and density. Types of compounds concentrated in each fraction would be known at least semiquantitatively, e.g., aromatic and aliphatic hydrocarbons, phenols (mono and dihydric), methoxy phenols, ethers, cyclic ethers, and ketones. Estimates of aromaticity, ring structure, and degree of ring

Table 2. Major components of steam distillate of TR-7 oil.[*][†]

No.[‡]	c	Time(s)	Mass	Probable Identity	Type[§]
1		429	84	cyclopentanone	CK-S
2*		446	98	cyclohexanone	CK-S
3		486	98	3-methylcyclopentanone	CK-S
4		694	112	cycloheptanone (tentative)	CK-S
5		853	110	dimethyl-2-cyclopentenone isomer	CK-S
6*		941	96	2-methyl-2-cyclopentenone	CK-U
7		1114	124	dimethyl-2-cyclopentenone	CK-U
8*		1173	110	dimethyl-2-cyclopentenone isomer	CK-U
9		1246	110	dimethyl-2-cyclopentenone isomer	CK-U
10		1302	124	trimethyl-2-cyclopentenone isomer	CK-U
11*		1412	-	(computer omission)	-
12		1467	-	(computer omission)	-
13		1498	138	alkyl cyclohexenone (tentative)	CK-U
14		1527	138	alkyl cylcohexenone (tentative)	CK-U
15*		2184	124	guaiacol	MP
16		2389	138	4-methylguaiacol (creosol)	MP
17*		2477	136	$C_9H_{12}O$ (alkyl phenol)	P
18		2548	152	4-ethylguaiacol	MP
19		2630	122	C2 phenol isomer	P
20		2639	150	alkyl phenol	P
21		2709	166	4-n-propylguaiacol	MP
22		2817	122	ethylphenol isomer	P

[*] Obtained from Albany Drum #5 (sample TR-7 - 190 LBL Process).

[†] GC conditions: OV-225 SCOT column; 50°C for 3 min, then 30/min to 250°C and hold.

[‡] The six most abundant components are starred.

[§] CK-S; cyclic ketone, saturated; CK-U: cyclic ketone, unsaturated; MP; methoxyphenol; P: phenol.

substitution would be available. Compounds present in significant percentages would be identified and measured.

Comparison with the slow international progress in defining properties of coal products suggests that this is only partly achievable by a small group. Not all of it is necessary for following the reaction or finding uses for the products. But we should at least be able to follow the concentration of major product types like phenols, acids, and furans as they are affected by process variables. We should also be able to follow changes in molecular weight, boiling range, and aromaticity. In FY 1981 we hope to achieve a goal somewhere between this minimum and the ultimate: a truly well-identified product.

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THE SOLVOLYSIS OF DOUGLAS FIR WOOD IN ACIDIFIED ORGANIC SOLVENTS*

G. Yu, T. Vermeulen, and H. Davis

INTRODUCTION

There are two major engineering and economic problems of wood liquefaction. These arise from the difficulty of feeding the substrate into a reaction system (the "front end" problem) and the need for a reaction temperature near the critical temperature of water, and consequently for a high operating pressure. The front end problem is currently met by feeding a liquid and biomass slurry. This is wood flour-recycle product oil in the PERC process and prehydrolyzed wood-water in the LBL process.

The objective of the present work was to find an alternate method of liquefying wood to solve the front-end problem by producing a material easily fed into a liquefaction reactor that might yield an interesting product, thereby totally bypassing the present liquefaction reaction system.

This report summarizes work done mainly during FY 1980 by G. Yu as part of work on his doctoral thesis under Professor T. Vermeulen of the Department of Chemical Engineering at the University of California, Berkeley, and carried out in the laboratories of the LBL Coal and Biomass Group.

ACCOMPLISHMENTS DURING FY 1980

Solvolysis Process

Based on wood chemistry concepts, a process capable of solubilizing more than 95% of wood under some mild conditions has been developed. Unlike the PERC and LBL processes, no H_2 or CO is required. The product is a soft, black, bitumen-like solid at room temperature and melts readily at 140°C. Its heating value is estimated to be roughly 11,000 Btu/lb.

The process concept is based on two well-known reactions, lignin alcoholysis and cellulose hydrolysis. The former involves solubilization of lignin using alcohol under conditions such as 5-24 reaction time at 40-120°C. It is apparently a very slow and low-yield process. Cellulose hydrolysis, however, requires hydrolyzing cellulose to glucose in an aqueous acidic medium. In both cases, either carbohydrate or lignin is left as a solid residue. A combination of acid and alcohol, however, could conceivably enable both the lignin and cellulose to depolymerize and be solubilized. Essential ingredients of the process are, therefore, an alcohol (or phenol) and dilute strong acid.

Table 1 depicts some results of our process feasibility and process solvents evaluation study. The solvents can either be derived from cellulose or from lignin. The results showed that alcohols with a small amount of acid added are good media for solubilizing wood. An estimated reaction temperature of 250°C is needed to define a high degree of solubilization in an acceptable time. Analysis of reactor off-gas showed that the synthesis gas used to pressurize the reactor did not participate in the reaction. We made our trials, therefore, with acidified alcohols (or phenols) under an initial condition of 1 atm N_2. At reaction temperature, the atmosphere consists largely of the vapors of solvent and water from the wet alcohol feed.

Effects of Product Variables

Figures 1 and 2 illustrate effects of process variables such as temperature and time on the degree of wood solubilization. In both cases, opti-

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*This work was supported by the Assistant Secretary for Conservation and Solar Energy, Office of Solar Technology, Biomass System Division of the U.S. Department of Energy under Contract No. W-7405-ENG-48.

Table 1. Preliminary process feasibility and solvents evaluation study.

Solvent[*]	Unreacted Wood (%)
methanol[†]	47.81
methanol	27.82
ethanol[†]	39.25
ethanol	25.30
propanol	19.43
butanol	16.52
pentanol	18.77
hexanol	13.80
ethylene glycol	15.29
glycerol	26.67
cyclohexanol	6.60
phenol	4.18
catechol	1.02
cresol	4.33
guaiacol	4.78
water[‡]	42.64
water[‡]	45.73

[*] Process condition: solvent = 50% alcohol: 50% water (pH 2.5); solvent: wood = 4:1; gas = 400 initial psig CO:H_2(1:1); and temperature:time = 250°C for 1 h.

[†] pH 2.0 @ 180°C.

[‡] pH ∿ 7.0.

mum conditions exist for maximum solubilization. In the case illustrated, i.e., 0.1% H_2SO_4 at 250°C, maximum solubilization occurs after about 0.5 h.

Not surprisingly, some solvent is incorporated into the wood. This incorporation may be considered a stabilization step which prevents depolymerized species from repolymerizing. Table 2 shows the result of our solvent incorporation study. Excessive incorporation obviously adds greatly to cost and has a negative effect on equipment size and process energy recovery. Recovery of solvent will be necessary unless we can use a solvent intended as a fuel anyway and incorporated to only a modest degree. Various types of hydrolysis have been suggested as recovery steps. "Gasohol," alcohol and wood, or coal liquefaction products are examples of possible solvents which, being themselves fuels, could be left in the product.

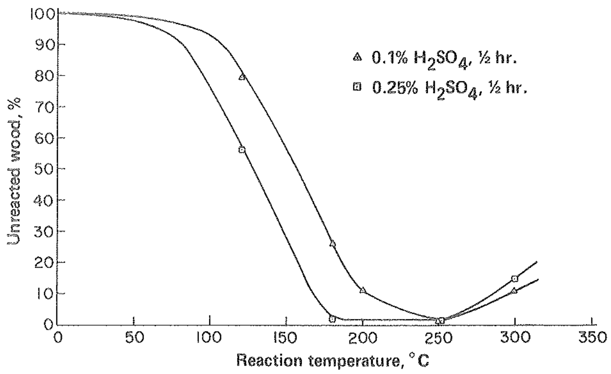

Fig. 1. Degree of solubilization by phenol as a function of reaction temperature and acid concentration. (XBL 809-1874)

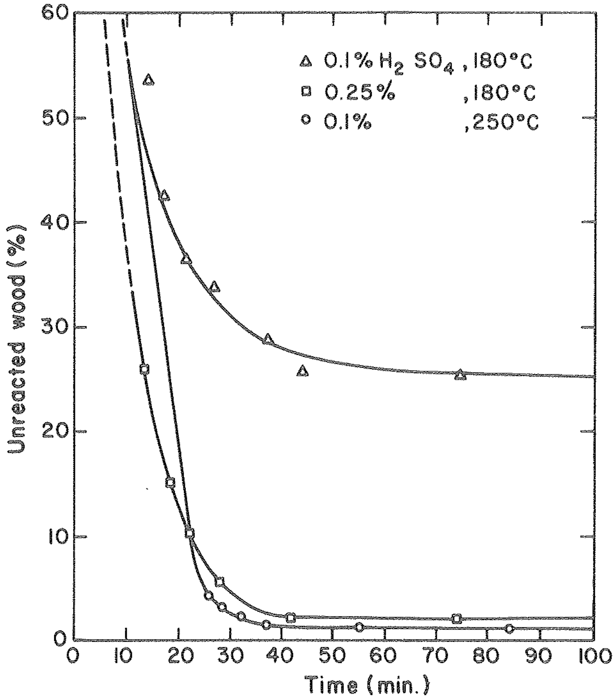

Fig. 2. Degree of solubilization by phenol as a function of time and acid concentration. (XBL 809-1859)

Table 2. Solvent incorporation study.

Solvent[*]	Solvent Incorporated (%) Based on Initial Solvent	Solvent Incorporated (%) Based on Initial Dry Wood	Water Produced (%) Based on Initial Dry Wood
butanol[†]	2.32	10.18	9.96
ethylene glycol	2.23	9.82	12.38
cyclohexanol	2.87	12.60	11.14
phenol	17.56	77.14	23.30

[*] Process condition: solvent:wood = 4:1; speed of stirring = 140 rpm; 0.1% H_2SO_4 @ 250°C for 0.5 h.

[†] 0.25% H_2SO_4 @ 180°C for 1 h.

The product, after recovery of the unincorporated process solvent, is a soft bitumen-like material at room temperature. It melts and starts flowing at around 140°C. Elemental analysis of the product shows a reduction of 25 to 50% of the O_2 compared to original wood. Since almost no CO_2 is formed, this reduction must be achieved through formation of water. Table 3 depicts a comparison between our solvolytic oil and other materials.

Planned Activities for FY 1981

At present, the solvolysis must be considered primarily as a source of information for subsequent work. As part of a liquefaction process, it constitutes the front end, i.e., a method by which wood, or other biomass material may be put into a form suitable for feeding into a reactor. There the solubilized product may be further reacted--perhaps in tubular or stirred reactors in the presence of CO and H_2 as in present liquefaction processes. Other possibilities include the passage of the product as a solution across a catalyst giving reduction under relatively mild conditions.

Table 3. Comparison between solvolytic oil and other materials.

	Wood	Solvolytic "Oil"	Lignite	Subbituminous Coal -- Wyodak
N	0.13	0.15	0.93	0.92
S	0.05	0.06	0.55	1.20
Ash	0.50	0.58	16.90	14.09
H/C	1.27	0.78	0.89	0.96
O/C	0.57	0.28	0.24	0.19

We expect that the program for FY 1981 will include assessing the usefulness of the solvolysis step and gaining a better understanding of the kinetics and mechanism of this very complex reaction, or mix of reactions. Only limited experimental work required to clear up identified problems is planned until specific possibilities for using results are identified. Answers to certain questions, including those below, are very worthwhile obtaining:

- Can a recycled product-oil with a high expected phenolic hydroxyl content be used as the "solvent"? If so, solvolysis could be a viable front-end step.
- Are there specific catalytic reactions we could easily carry out in parallel or in sequence with solvolysis?
- Do alcohols simpler than butanol, cyclohex and phenol work well at supercritical pressures?

SELECTIVE HYDROGENATION OF COAL*

E. Grens, T. Vermeulen, D. Bowyer, J. Edwards,
F. Hershkowitz, J. Maienschein, C. Onu, and G. Zieminski

INTRODUCTION

Coal liquefaction processes currently under development involve thermal decomposition (pyrolysis) of the coal in an organic liquid medium followed by hydrogenation of the initial pyrolysis products, often with the aid of heterogeneous catalysts. The thermal degradation reactions are not selective and do not take advantage of reactive bond types in the coal structure. They produce a wide range of products, including light hydrocarbon gases and refractory char. The former contribute to high H_2 consumption while the latter require special processing (e.g., gasification) for their utilization. The coal pyrolysis is required because reactions of coal with available solvent media are far too slow below pyrolysis temperatures, and solid catalysts can not promote the reaction of the solid coal material.

This project's aim is to convert coal to liquid products by using homogeneous catalysts that can promote selective scission of certain linkages in the coal structure below coal pyrolysis temperature. These linkages join conjugated hydroaromatic groups in the coal, and include aliphatic and O_2 (ether) bridges. The catalysts are dissolved in, or constitute, a liquid reaction medium, which has access to the extensive interior pore surfaces in the coal.

Included in this research program are studies of the interaction of organic solvent media with coals, the effects of homogeneous catalysts in promoting reactions at moderate temperatures, and the use of inorganic, Lewis-acid type melts as catalytic media for coal conversion. The action

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of the catalytic treatments on model chemical compounds containing certain types of bond structures found in coal is examined to elucidate the mechanisms of coal decomposition. Transport processes for coal reaction products and dissolved H_2 gas are considered to determine the extent to which these processes may limit conversion rates. Since 1978 the major effort has been directed to the use of mixed organic-inorganic treatment media, in particular $ZnCl_2$ melts in combination with hydroaromatic solvents (e.g., tetralin) or with alcohols (e.g., methanol). This type of coal treatment was found to be much more effective than treatment with either organic or inorganic media separately, doubling or tripling conversions compared to those obtained with treatment in a single medium under the same temperature conditions.

ACCOMPLISHMENTS DURING FY 1980

The major project activities during FY 1980 included studies of the kinetics of coal/organic solvent interactions, investigation of coal conversion in both $ZnCl_2$/tetralin and $ZnCl_2$/methanol treatment media, and model compound studies to test proposed reaction mechanisms. Product analyses and characterization, with emphasis on hexane-soluble products ("oils"), were conducted to provide insight into the behavior of the conversion process.

Interaction of Coal with Organic Solvents

(by E. Grens and G. Zieminski)

Investigation of the dissolution rate of coal in hydroaromatic organic solvents was continued in a specially designed apparatus having a time resolution of about 30 s. These experiments examined the interaction of Wyodak subbituminous coal with tetralin in the temperature range of 200-300°C, and they arose from previous investigations of the action on coal of a number of organic solvents.[1] The dissolution rates observed indicate that at least two distinct classes of soluble material are involved: one dissolves almost instantaneously (if exposed at sufficiently small particle size) and is apparently associated with exinite macerals in the coal; the second dissolves much more slowly, at least partly under pore diffusion control, and exhibits an activation energy on the order of 10 kcal/gmol for the dissolution reaction. The effect of coal particle size was examined to help clarify the rate-controlling mechanism, but this effect was, to a degree, obscured by the considerable comminution of the coal particles that occurs with solvent contact. This suggests that reported solubilities of coals in given solvents, and of temperature effects on these solubilities, reflect the rate phenomena involved and the contact times chosen. At 250°C, contacts of more than 200 h may be required to approach equilibrium.

Coal Conversion in Zinc Chloride/Tetralin Mixtures

(by E. Grens, J. Edwards, and F. Hershkowitz)

Our recent investigations of coal conversion in mixed organic-inorganic media have been primarily on one two-phase system, $ZnCl_2$/tetralin, and one single-phase system, $ZnCl_2/CH_3OH$.[2] The treatments of coal in $ZnCl_2$/tetralin have so far involved essentially equal weights of subbituminous coal and organic solvent in the presence of excess $ZnCl_2$ melt. During FY 1980 these studies concentrated on the effects of treatment temperatures and on the yields and properties of the hexane-soluble fraction of the products.[3]

The yields of oils, as well as of asphaltenes (toluene solubles) and total conversion (cumulative pyridine solubles) increase significantly with increasing temperature below the initial pyrolysis temperature of the coal (325°C) as shown in Figure 1. The relatively greater increase of the oils, and corresponding decrease in preasphaltene yield (soluble in pyridine but not toluene) is important, since oils are desirable products while preasphaltenes offer severe difficulties for downstream processing. Examination of conversion rates indicates that reaction times of about 30 min are appropriate at 325°C while times up to 60 min may be required at 250-300°C. Experiments in which asphaltenes and preasphaltenes were separated from oils for continued treatment have demonstrated the effectiveness of this approach to further increase oil yields and offer the possibility of use of higher temperatures for this subsequent processing without exposing the oils, or initial coal, to undesired pyrolysis conditions.

Characterization of oil products by proton nuclear magnetic resonance (NMR) and gel-permeation chromatography (GPC), as well as elemental analysis, leads to a structure for a representation "oil molecule," with a molecular weight of about 500, composed of two linked four-ring hydroaromatic clusters. This "oil molecule" has a formula $C_{40}H_{38}$, with 37% of the H atoms and 70% of the C atoms being involved in aromatic structures. This is a less aromatic material than that produced by most liquefaction processes operating at higher temperatures.

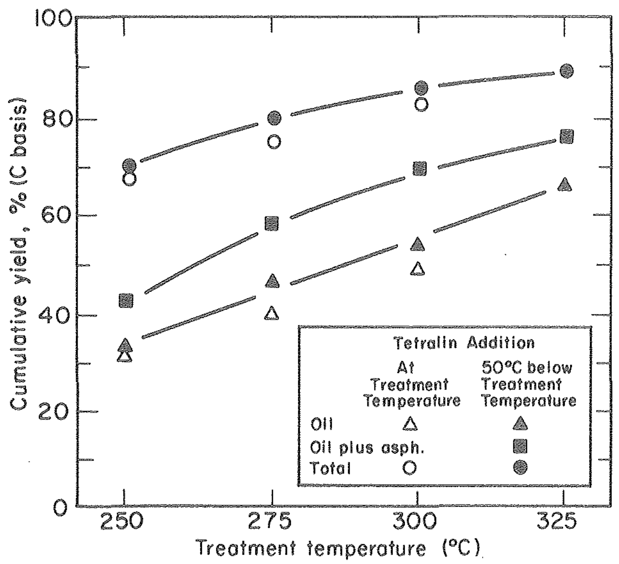

Fig. 1. Effect of treatment temperature on the conversion of coal to soluble products. Treatment of 50 g Wyodak coal for 60 min with 273 g $ZnCl_2$, 27 g H_2O, 50 g tetralin, and 3.5 MPa total pressure. (XBL 811-3584)

Coal Conversion in a Zinc Chloride/Methonal Melt

(by T. Vermeulen, C. Onu, and D. Bowyer)

When CH_3OH addition is used in $ZnCl_2$ treatment of subbituminous coal, to depress the freezing point of the melt and act with the $ZnCl_2$ so that it can be used without a recycle solvent (e.g., tetralin), relatively high conversions to solvent-soluble products are obtained. Total conversion levels approaching 90% at 250°C, 95% or better at 275°C, and nominally 100% at 300°C have been reported previously.[4]

Further experiments have been conducted to determine the effect of temperature staging on the yield of oils, which preferably would be very high. Addition of 1.5 to 3.0 wt% of metallic Zn to the melt increases the oil content of the product by 10% or more. (It is likely, also, to diminish corrosion by the $ZnCl_2$ in cases where corrosion is a problem.) Results are shown in Table 1.

The following conclusions can be drawn from the tabulated data and from earlier experiments:

1. Heating at 300°C for 30 min, alone, is not significantly better than at 275°C. However, less time (e.g., 20 min) at 300°C might also produce the same result.

2. Oils production at 325°C is clearly better than at 300°C, suggesting the onset of another kind of bond-breaking. However, total conversion is slightly reduced. The preasphaltene fraction (pyridine-soluble but toluene-insoluble) from 325°C operation began to melt at 200°C, with nearly 30% melted by 400°C; whereas the 300°C product did not show any melting below 400°C (the limit of the test). In GPC, the 325°C preasphaltene shows a lower average molecular weight, with fewer aromatic fused rings and consequent reduced ultraviolet absorption.

3. In last year's report, it was noted that a short step at 340°C diminished the oils production. It also raised the mean melting point of the oils fraction from ∿60°C to ∿90°C, indicating a deterioration in quality.

To improve the understanding of $ZnCl_2/CH_3OH$ catalysis, and to assess its potential for converting materials with intermediate levels of coalification (such as peat and lignite), the solubilization of wood, as chips or flour, and of wood-derived lignin and cellulose, has also been examined in the $ZnCl_2$-CH_3OH catalytic medium. Experiments at 250°C for 40-60 min show a carbon recovery of 79% for cellulose and 90% for both wood flour and chips. Under treatment, wood changes markedly in form and O_2 content before solubilization begins, as shown by both scanning electron microscopy and elemental

Table 1. Effect of temperature staging in treatment of 50 g Wyodak coal at 55 bars hydrogen, with 3% Zn and 14% CH_3OH (relative to 250 g $ZnCl_2$).

Run	Temp. (°C)	Time (min)	Extractibles Oil.	Asphaltene	Caf (%) Preasphaltene	Atomic H:C
51	275	30	32	15	54	0.99
77	300	30	33	17	50	1.04
72	325	30	46	14	37	1.08
73	275	15	54	10	36	1.19
	300	15				
	325	30				
82	275	15	35	18	45	1.10
	300	30				
81[a]	250	10	39	13	48	1.20
	275	10				
	300	10				
	325	10				
86[b]	250	10	41	12	47	1.25
	275	10				
	300	10				
	325	10				

[a] 18% CH_3OH

[b] 24% CH_3OH. Results similar to Run 78 at 14% CH_3OH (reported previously) except for 1.06 HC determined in Run 78.

analyses. Subsequently, the bulk of the wood is converted rapidly to preasphaltenes, with asphaltenes and oils being formed and additional oxygen being removed as the reaction progresses.

Model Compound Studies

(by E. Grens and T. Maienschein)

A number of pure organic compounds, chosen to contain bond types similar to those that are thought to be affected during coal conversion, have been subjected to $ZnCl_2$ catalysis under conditions similar to those used in coal treatment.[6] In these experiments a nonreactive solvent (dodecane) containing a small amount of the compound of interest was contacted with excess $ZnCl_2$ melt (with 10% water) at 175-275°C and (usually) 1.4 MPa H_2 pressure for times up to 60 min. To facilitate identification of initial reaction products, excess aromatic substrates (benzene or ethylbenzene) were often added to provide location for alkylation by carbonium ions (or radicals) formed; this prevented polymerization of the model compounds to "tars."

The two principal classes of model compounds investigated were those having aromatic groups (i.e., phenyl and naphthyl) joined by aliphatic bridges and those having aromatic groups joined by ether linkages, either directly or removed by a methylene group from the ring (e.g., benzyl). These classes are representative of aliphatic and ether linkages in coals.

At 250°C only aliphatic bridges consisting of a single methylene group are cleaved, with a rate constant of about .02 min^{-1} for diphenylmethane. Bridges of length 0, 2, or 3 are not affected. Polarization of one of the aromatic groups by addition of an OH substituent greatly increases the reaction rate; 4-hydroxydiphenylmethane has a rate constant of about 0.6 min^{-1} at 250°C. Aromatic ethers, with the exception of diphenyl ether, are cleaved quite rapidly at 250°C. Phenylbenzyl ether has a rate constant of about 1 min^{-1}, and hydroxy substitution again increases this rate.

Examination of reaction products by gas chromatography indicates that the $ZnCl_2$ promotes cleavage of aliphatic bridges preferably adjacent to the least polarized aromatic group, and that the resulting carbonium ions alkylate the available aromatic centers. With aromatic ethers the cleavage occurs between the O and any methylene groups in the bridge, with the resulting carbonium ion again alkylating an aromatic substrate.

These model-compound results are good evidence that $ZnCl_2$ catalysis of coal liquefaction can act through cleavage of both aliphatic and ether linkages in the coal. In subbituminous coals the ether links, which are expected to often involve also a two-carbon aliphatic chain, are very likely the location of much of the initial decomposition.

PLANNED ACTIVITIES FOR FY 1981

The results achieved thus far in this program have demonstrated the possibility of homogeneously-catalyzed coal liquefaction processes, operating below the pyrolysis temperature of the coal and giving high yields of "oils," with corresponding low productions of light gases, refractory char, and tar. Much additional work is still required to determine processing conditions and sequences for best yields and to develop continuous coal treatment and catalyst recovery processing techniques.

The support of this work by the Office of Basic Energy Sciences has not been extended to cover these future activities, and their accomplishment will depend on other sources of funding.

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PROCESSING TO ACHIEVE ENVIRONMENTAL COMPATIBILITY

COAL DESULFURIZATION*

T. Vermeulen, S. Ergun, S. Lynn, E. Petersen,
L. Clary, G. Cremer, D. Mixon, and M. Smith

INTRODUCTION

Coal is most economically used directly as boiler fuel. Its S content is converted during combustion to SO_2, which is discharged in the stack gases. Environmental constraints make it necessary to limit the S content of the effluent gas by imposing chemical treatment to remove S either from the entering coal or the exiting gases.

In previous years this problem was investigated on a broad scale, first with support from the Office of Basic Energy Sciences, and in 1979 under the auspices of the Office of Fossil Energy in the Division of Coal Mining and Preparation.

ACCOMPLISHMENTS DURING FY 1980

Coal Alkalinization Prior to Combustion

(by E. Petersen and M. Smith)

Earlier studies at LBL suggested that impregnation of sulfur-bearing coal with alkaline compounds could cause trapping of SO_x produced during combustion, thus eliminating the need for stack-gas cleaning. Experiments during the past year have involved impregnation, followed by drying and controlled combustion. Combustion at a nominal 800-1000°C gives substantially cleaner stack gas than at 1200°C. Without alkali, 25% of the total initial S (inorganic plus organic) is retained by the solid. With 15% of added Na_2CO_3 (about 1.5 times the stoichiometric requirement), 90% of total S is retained at 800-1000°C.

Such use of Na_2CO_3 would tend to be more expensive than stack-gas cleaning, and would thus be desirable only in special cases. The possibility arises that seawater or other saline brines, alone or with accessory use of CO_2 and CaO from $CaCO_3$, might be used economically to impregnate coal with $Mg(HCO_3)_2$. This prospect will be investigated further.

Oxidation of Organic Sulfur[1]

(by S. Lynn, and L. Clary)

Model-compound experiments were run in order to test their conversion under pyrite-oxidation conditions. Dibutyl sulfide reacts rapidly, and diphenyl sulfide slowly (15% per hour), under these conditions; dibenzothiophene is refracting except in the presence of VO^{2+} (which corrodes stainless steel and actively oxidizes the carbon of coal). The products were mainly sulfoxides and sulfones, with scant evidence of S-C bond breaking. Aqueous $ZnCl_2$, or $FeCl_3$ at 200°C was found ineffective for hydrolytic decomposition of sulfones, other than dibutyl sulfone.

Although pyrite-oxidation treatments do not remove organic S from coal, the results just cited suggest that S compounds in coal are somewhat altered. Exploratory extractions with liquid SO_2 at 150°C gave ambivalent results, sometimes yielding a modest reduction and sometimes an increase. The use of two or more reaction steps in series is now viewed as essential and is believed to constitute a promising approach.

Pyrite Oxidation in Coal[2]

(by T. Vermeulen, S. Ergun, S. Lynn, G. Cremer, and D. Mixon)

S removal from coal has been investigated with the use of an aqueous oxidizing medium comprising $Fe_2(SO_4)_3$, O_2, and H_2SO_4. This mixture markedly reduces water consumption and waste disposal; the by-products of coal treatment can be recovered in marketable form. About 90% conversion of pyrite, entirely to sulfate, is obtained in treatment at 130-150°C for 1 h at 30 atm O_2 pressure. Conversion is higher for more finely powdered coal (Table 1). Illinois No. 6 coal was mainly studied using four different samples; two other high-sulfur coal (three samples) showed similar behavior.

Reaction-kinetics analysis was made for both pyrite in coal and bulk FeS_2. Although the effects of O_2 and Fe^{3+} are not entirely separate, the rate depends primarily on Fe^{3+} concentration at low pressures of O_2, and becomes first-order in O_2 pressure at elevated pressures (Table 2). The rate is nearly constant as H_2SO_4 concentration increases (Table 3), decreases somewhat as ferric sulfate concentration increases, and increases somewhat with temperature (Table 4). It is possible that Fe^{+++} is more effective in a partial oxidation to elemental S and that O_2 is more effective in completing the oxidation. Although a standard reaction time of one h was selected because of initially conversion low rates, an almost equal degree of pyrite removal at the optimum temperature and pressure apparently could be obtained in 30-40 min (with less C oxidation in proportion to the residence time).

A proposed process layout is shown in Figure 1. After conventional crushing and grinding to minus

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*This work was supported by the Lawrence Berkeley Laboratory's Director's Office under Contract No. W-7405-ENG-48 with the U.S. Department of Energy.

Table 1. Effect of particle size on pyrite removal (1 h, 150^{o}C, 420 psi O_2).

Sample Number	1	2	5	7	3	4	6
Tyler screen range	-20+35		-20		-100+150		-100
Effective average mesh size	25		50		125		175
Pyrite removed (%)	--	64*	77	73	84	80	91

*Estimated.

Table 2. Effect of oxygen pressure on pyrite removal (150^{o}C, 1 h, various treating solutions).

Mesh	-20+35			-100+150	
Psi	150	200	280	280	400
Removal (%)	21	43	56	75	83

Table 3. Effect of acid strength on pyrite removal [-100+150 mesh, 1 h, 12 wt % $Fe_2(SO_4)_3$].

Strength (wt %)	5	15	25
Sample 3 (150^{o}C)	76%	-	84%
Sample 4 (130^{o}C)	80%	80%	75%

Table 4. Effect of temperature on removal (420 psi O_2, 1 h).

Coal Sample	Mesh Size	Treating Solution	Temperature (^{o}C)	Removal (%)
4*	-100+150	25/12	100	62
4*			110	67
4*			120	70
4*			130	75
4*			140	80
4*		5/12	150	76
3*		25/12	150	84
6+	-100		100	60
6+			150	91

*Illinois No. 6.

+Bevier.

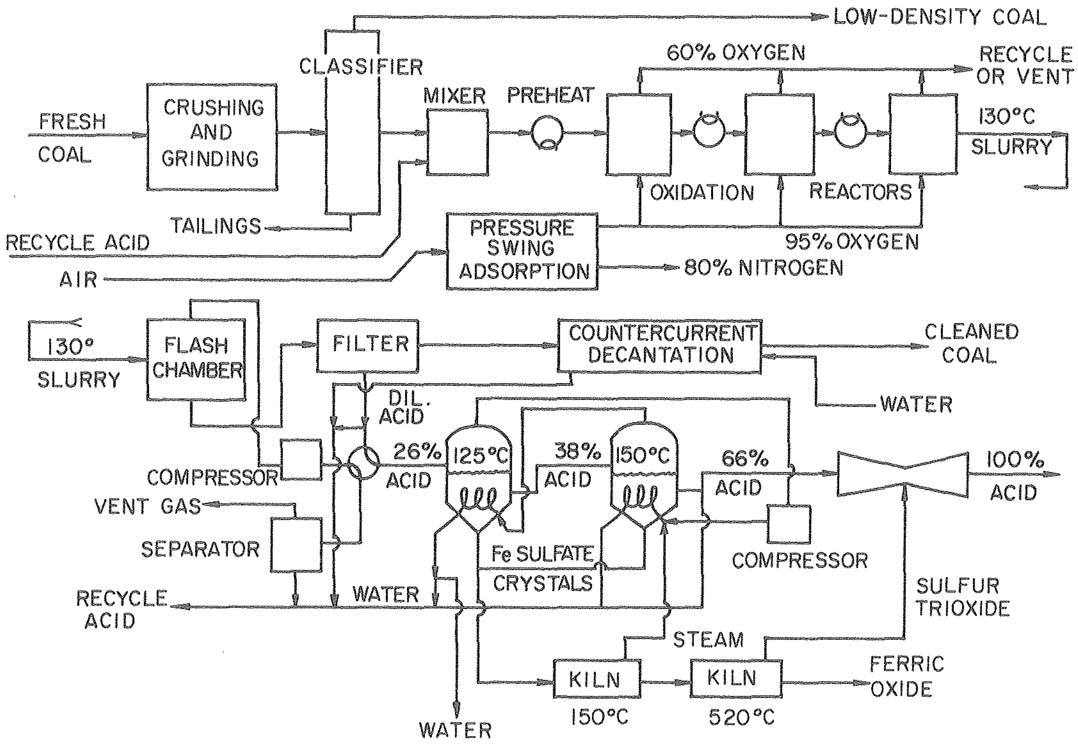

Fig. 1. Proposed flowsheet for chemical desulfurization of coal by the acidic iron sulfate process. (XBL 811-3587)

100 mesh, hydraulic classification of the sized fractions would be used to separate low-, medium-, and high-density materials. Only medium-density material would be subjected to chemical cleaning, the low-density material being adequately low in S content and the high-density material being considered unusable. The prepared feed would be blended into recycle acid in a 1:2 volume ratio, passed through a slurry pump, and fed in series to a bank of autoclaves (at 130°C and 40 atm abs). Ninety-five percent O_2 would be prepared by pressure-swing adsorption through molecular sieves. The off-gases would be withdrawn at 60% O_2. The treated slurry would then enter a flash tank where its pressure would be reduced to atmospheric, and from there it would pass to a rotary filter for removing the acid. The coal would be washed with minimum amounts of water by counter-current decantation, and the wash water would be returned to the process.

The acid fed to the reactors would contain 25% H_2SO_4 and 15% $Fe_2(SO_4)_3$, and the product acid liquor from the filters would contain about 26% and 20%, respectively. About two-thirds of this acid would be recycled directly. The other one-third would go to double-effect evaporation and crystallization, actuated by vapor compression of steam from the first effect. The acid strength leaving the first effect would be 38%, the temperature in that effect would be about 130°C, and the iron sulfate concentration would be about 22%. The second effect, at 150°C, would discharge 66% acid with 2% of iron sulfate. About 85% of this product acid would be returned to the process, diluted with condensate and with wash liquor from the decantation to restore it to feed composition.

$Fe_2(SO_4)_3$ crystallized from the evaporators would be washed, drained dry, and fed to two kilns in series. The first, at 150°C, would discharge chemically bound water, the off-gases being cooled to condense out water and then conveyed to vent-gas disposal. The second kiln, at 520°C, would discharge gaseous SO_3 and solid $Fe_2(SO_4)_3$ in marketable form. The relatively small stream of 66% acid diverted from the process after evaporation would pass first to a chilling crystallizer to lower its temperature to 50°C and reduce its $Fe_2(SO_4)_3$ content to 0.2%. It would then enter a venturi-mixer unit fed with SO_3 produced from the $Fe_2(SO_4)_3$ so as to bring the acid product to a concentration level of 96-98% H_2SO_4.

With suitable management of the water and reaction-product flows, coal nearly free of inorganic sulfur would be provided, along with H_2SO_4 and $Fe_2(SO_4)_3$ as marketable by-products.

PLANNED ACTIVITIES FOR FY 1981

These studies will be continued on a reduced scale, with special attention given to Coal Alkalinization Prior to Combustion. The entire program will be reactivated and extended if the opportunity arises.

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KINETIC STUDIES OF REACTIONS INVOLVED IN THE INTERACTION BETWEEN SO_2 AND NO_x IN AQUEOUS SOLUTIONS*

S. G. Chang, S. Oblath, S. Gomiseck, R. Clem, and T. Novakov

INTRODUCTION

Many concurrent and consecutive reactions[1-6] can take place as a result of interaction between SO_2 and NO_x in aqueous solutions. Although the kinetics of many of these reactions have been studied, the results of previous work by other scientists showed conflicting conclusions[7-9] on some reactions, while the kinetics of some other reactions[6] have not been well characterized yet. We have investigated the kinetics of reactions between nitrite and bisulfite, and hydroxylamine and bisulfite as part of an effort to acquire a fundamental understanding of the chemical interaction between SO_2 and NO_x in aqueous solutions and to develop and investigate the potential of chemical additives for lime/limestone flue gas desulfurization (FGD) scrubbers to upgrade performance in environmental control of SO_2 and NO_x.

ACCOMPLISHMENTS DURING FY 1980

Reactions of Nitrite and Bisulfite

We studied the nitrite and bisulfite reaction over the pH range of 4.5 to 7 and found two concurrent processes for the formation of hydroxylamine disulfonate. These two processes can be expressed mathematically by the following equation.

$$-\frac{d\left[NO_2^-\right]}{dt} = k_1 \left[H\right]^+ \left[NO\right]_2^- \left[HSO\right]_3^- + k_2 \left[NO\right]_2^- \left[HSO\right]_3^{-\,2} .$$

An additional process independent of bisulfite ion concentration was proposed by Seel and Knorre[9] and by Yamamoto and Kaneda.[8]

We have recently carried out experiments to determine the presence or absence of this pathway at lower reactant concentrations by employing various buffer reagents. Nitrite concentrations (initially 0.5 to 10 mM) were monitored by visible spectrophotometry. Bisulfite ion concentration was between 5 and 40 mM. The pH was maintained by using oxalate, tartrate, or phthalate buffers with an ionic strength of 0.2M.

Results of our experiments indicated that there is no process occurring that is independent of bisulfite concentration. A process independent of bisulfite ion concentration observed by other scientists might be attributed to the employment of acetate buffer, a medium believed to catalyze the formation of NO^+ in nitrous acid/nitrite solution.

We have also performed a kinetic study of this reaction at low pH (<3) and found the formation of nitrous oxide in addition to hydroxlamine disulfonate. It appears that nitrosulfonic acid, an intermediate resulting from the reaction between nitrous acid and bisulfite, can undergo either further sulfonation to produce hydroxylamine disulfonate or hydrolysis to form sulfuric acid and nitrous oxide. The ratio of the amounts of sulfite to nitrite consumed will be two if the former reaction takes place, whereas this ratio is expected to be one if the latter reaction occurs. By determining this stoichiometric ratio as a function of pH or bisulfite concentration, we have found that the ratio of the rate constant of sulfonation to that for hydrolysis is 1.7 ± 0.5. The value of each individual rate constant cannot be determined under the experimental conditions and analytical techniques employed because the rate-controlling step is the formation of the nitrosulfonic acid.

If sulfonation of nitrosulfonic acid takes place in wet flue gas scrubbers, then at least 2 mol of SO_2 are needed to remove 1 mol of NO. However, if the hydrolysis reaction takes place, only 1 mol of SO_2 is needed.

Reactions of Hydroxylamine and Bisulfite

Hydroxylamine, one of the species produced as a result of reaction between NO_x and SO_2 in aqueous solution, can undergo further reaction[10-12]

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with SO_2 to form either sulfamic acid or ammonium bisulfate. We have performed kinetic studies of this reaction as a function of temperature by monitoring the concentration of total hydroxylamine with a PAR differential polarograph.

The reaction follows the rate law

$$-\frac{d[\text{total hydroxylamine}]}{dt} = k_{obs}[\text{total hydroxylamine}][\text{total sulfite}].$$

The rate of reaction was found to be independent of the ionic strength of the solution. The rate constant k_{obs} in l/mol-sec was determined at two temperatures: 7.67×10^{-3} at 35°C and 1.48×10^{-3} at 22°C. Sisler and Audrieth[10] and Fraser[12] suggested that formation of both sulfamic acid and ammonium bisulfate involves attack by the $SO_2 \cdot H_2O$ on the NH_2OH. The reaction can therefore be expressed as

$$NH_2OH + SO_2 \cdot H_2O \begin{array}{l} \xrightarrow{k_a} NH_2HSO_3 + H_2O \\ \xrightarrow[k_b]{} NH_4HSO_4 \end{array} . \qquad (1)$$

The rate law can be written as

$$-\frac{d[\text{total hydroxylamine}]}{dt} = (k_a + k_b)[NH_2OH][SO_2 \cdot H_2O] . \qquad (2)$$

To evaluate the rate constant and activation energy of both reactions using our experimental measurements, Equation 1 is expressed in terms of the concentration of reaction species NH_2OH and $SO_2 \cdot H_2O$. Because [total hydroxylamine] = $[NH_2OH] + [NH_3OH^+]$ and [total sulfite] = $[SO_2 \cdot H_2O] + [HSO_3^-] + [SO_3^=]$, Equation 1 can be rewritten as

$$-\frac{d[\text{total hydroxylamine}]}{dt} = k_{obs}\left\{1 + \frac{[H^+]}{K_n}\right\}\left\{1 + \frac{K_1}{[H^+]} + \frac{K_1K_2}{[H^+]^2}\right\} \cdot [NH_2OH][SO_2 \cdot H_2O], \qquad (3)$$

where K_n, K_1, and K_2 are respectively the acid dissociation constant for hydroxylamine and the first and second dissociation constants for sulfurous acid.

By comparing Equations 2 and 3, we obtain the following relationship:

$$k_a + k_b = k_{obs}\left\{1 + \frac{[H^+]}{K_n}\right\}\left\{1 + \frac{K_1}{[H^+]} + \frac{K_1K_2}{[H^+]^2}\right\}$$

The ratio k_a/k_b can be obtained by the corresponding ratio of the products $[NH_2HSO_3]/[NH_4HSO_4]$; this ratio was determined by Fraser[12] at several temperatures. The following values of k_a/k_b were obtained from interpolation of Fraser's results: 9 at 22°C and 19 at 35°C. By applying the transition-state theory, the enthalpy and entropy of activation for the formation of both sulfamic acid and ammonium bisulfate can be calculated as shown in Table 1. The results of this study are in fairly good agreement with those of Fraser.

PLANNED ACTIVITIES FOR FY 1981

The kinetics of the following reactions will be investigated:

1. Production of hyponitrous acid and sulfates from the reaction of hydroxylamine monosulfonate with nitrite.
2. Reactions of ferrous and nonferrous chelates with NO to form nitrosyl metal chelate complexes.

Table 1. The enthalpy and entropy of activation for the formation of sulfamic acid and ammonium bisulfate by the reaction of NH_2OH with $SO_2 \cdot H_2O$.

	Sulfamic Acid		Ammonium Bisulfate	
	$\Delta H_a^{\ddagger}$ (kcal/mol)	$\Delta S_a^{\ddagger}$ (e.u.)*	$\Delta H_b^{\ddagger}$ (kcal/mol)	$\Delta S_b^{\ddagger}$ (e.u.)*
Fraser	10.9	-16	1	-56
This work	13.4	- 6.1	3.0	-45.8

*e.u. = entropy unit.

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REACTIONS OF SULFITE AND NITRITE IONS IN AQUEOUS SOLUTIONS*†

S. G. Chang and D. Littlejohn

INTRODUCTION

Lime/limestone scrubbers represent the current generation of technology for power plant flue gas desulfurization (FGD). The important chemical reactions that take place after dissolution of flue gas in an aqueous lime and limestone slurry must be identified so that a scrubber with better performance and reliability can be constructed. Because power plant flue gas contains hundreds of ppm of both SO_2 and NO_x, it is essential to understand the chemistry between SO_2 and NO_x in aqueous solutions. This scientific understanding could also aid the development of a wet simultaneous desulfurization and denitrification process based on the addition of reagents and additives to the existing lime or limestone FGD scrubbers.

We have reviewed the literature[1-5] and found that many concurrent and consecutive chemical reactions can occur as a result of the interaction between NO_x and SO_2 in liquid water. Nitrous (III) and nitric (IV) acids are produced in the aqueous phase after NO_x are absorbed into liquid water, and sulfite/bisulfite ions (IV) are formed if SO_2 dissolves in water. We have examined the kinetic studies of reactions that can take place as a result of interactions between sulfite/bisulfite and nitrite ions and calculated the concentration profile of species produced in this system as a function of reaction time.

ACCOMPLISHMENTS DURING FY 1980

Review of Previous Kinetic Studies

Nitrous acid and sulfite react to form nitrosulfonic acid, which then continues along one or more of three reaction paths:

1. Further sulfonation to produce hydroxylamine disulfonate and amine trisulfonate. These can hydrolyze to form sulfuric acid and reduced N species. The latter can undergo further reaction with bisulfite and nitrite.

2. Hydrolysis to form sulfuric acid and hyponitrous acid. The latter decomposes to produce nitrous oxide.

3. Reaction with nitrous acid to yield sulfuric acid and nitric oxide. The extent to which these three different paths will contribute to the system depends on the

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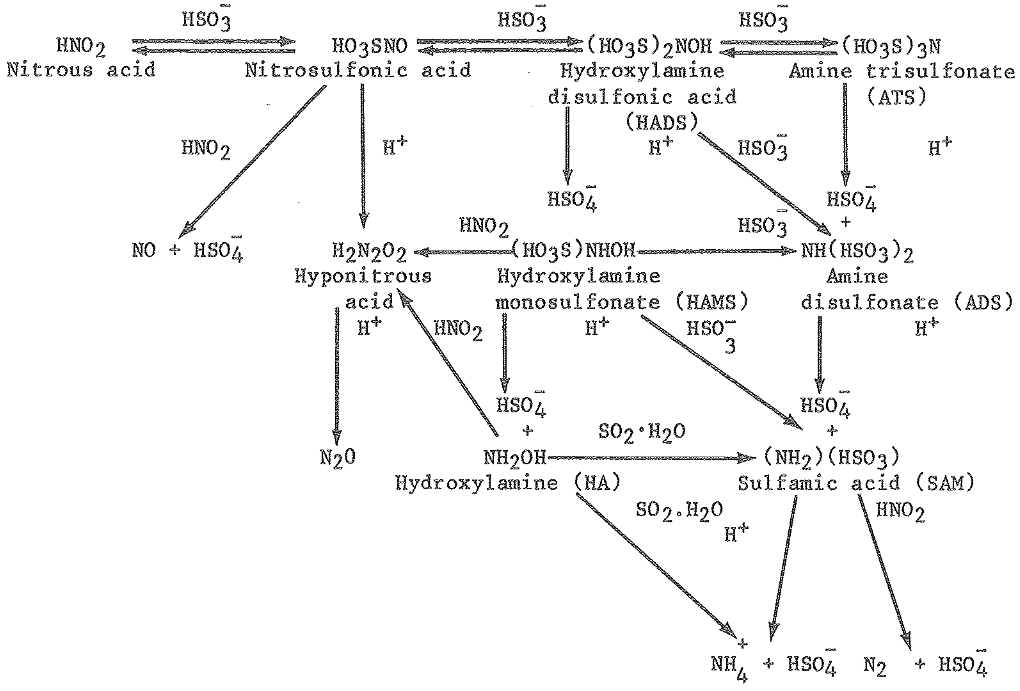
† Condensed from S. G. Chang, Reactions of Sulfite and Nitrite Ions in Aqueous Solutions, Lawrence Berkeley Laboratory report LBL-11800, 1980.

pH, temperature, and concentration of nitrite and sulfite species. A summary of reactions that can take place as a result of interaction between sulfite and nitrite ions is shown in the following reaction scheme:



The kinetic information on the reactions involved in this system has been obtained (Table 1).

Chemical Kinetics Modeling

Table 1 lists elementary reactions considered and rate constants used. The following assumptions were made in this calculation:

1. Gas dissolution and liberation rates are much larger than chemical reaction rates.
2. Any reaction involving HNO_3, NO(aqueous [aq.]), NO_2(aq.), N_2O_3(aq.), and N_2O_4(aq.) is neglected.
3. The equilibrium is maintained all the time for the following reaction pairs: 3, 4; 10, 11; 12, 13; 14, 15; and 16, 17. The rate constants of these ten reactions were adjusted to satisfy the equilibrium condition.
4. Oxidation of NO to NO_2 (both in gas phase and aqueous solution) is discounted.
5. The pH of the solution was assumed to be constant throughout the reaction.

Figures 1-4 and 5-6 show the time-resolved concentrations of species in a batch reactor at various pH's, temperatures, and initial partial pressures of SO_2 and NO_x for the first 2 and 24 hours respectively. The gas-to-liquid ratio (G/L) is 75. Figure 1 (at P_{SO_2} = 1000, P_{NO} 450, and P_{NO_2} = 50 ppm, pH = 5, and T = 328K) demonstrated that the removal efficiency of NO is only about 10% although NO_2 can be almost completely removed because NO alone cannot be converted into HNO_2. The major product is HADS within the initial 1.5h;

Table 1. Some reduced nitrogen species identified in a few flue gas wet simultaneous desulfurization and denitrification processes.

Process	Additives	Reduced Nitrogen Species Identification
Asahi	Na_2SO_3, Fe^{+2}(EDTA*)	$NH(SO_3Na)_2$, N_2
Chisso	$(NH_4)_2SO_3$, Fe^{+2}(PCC†)	$NH(SO_3NH_4)_2$, $NH_2(SO_3NH_4)$ $(NH_4)_2SO_4$
Chiyoda	O_3	N_2O, N_2
Ishikawajima Harima	O_3	$Ca(NH_2SO_3)_2$, N_2
Mitsubishi	O_3	$Ca[NH(SO_3)_2]$, $Ca[NOH(SO_3)_2]$ NH_2OH, N_2O, N_2

*Ethylenediaminetetraacetic acid.

†Proprietary chelating compound.

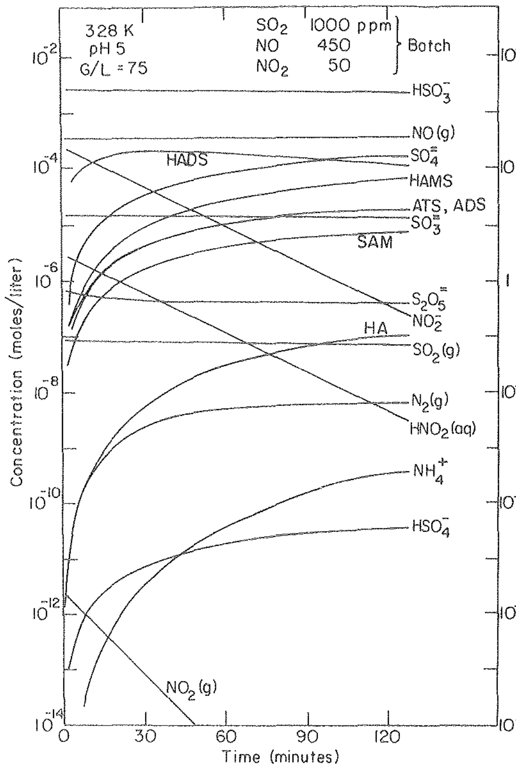


Fig. 1. The concentration profile of species as a function of reaction time in a batch reactor (ph = 5 and temp = 328K) at the following initial condition: $P_{SO_2} = 1000$, $P_{NO} = 450$, and $P_{NO_2} = 50$ ppm. The gas to liquid ratio, G/L is 75. (XBL 8011-6246)

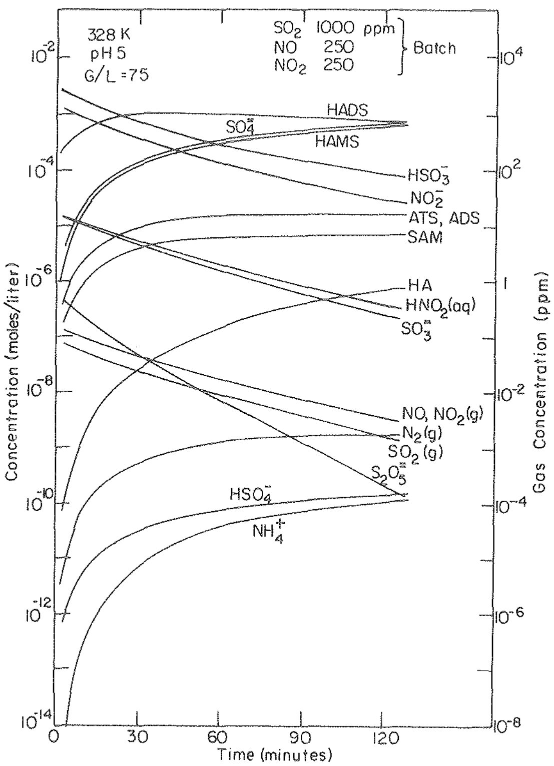


Fig. 2. The concentration profile of species as a function of reaction time in a batch reactor (pH = 5 and temp = 328K) at the following initial condition: $P_{SO_2} = 1000$, $P_{NO} = P_{NO_2} = 250$ ppm. The gas to liquid ratio, G/L is 75. (XBL 8011-6247)

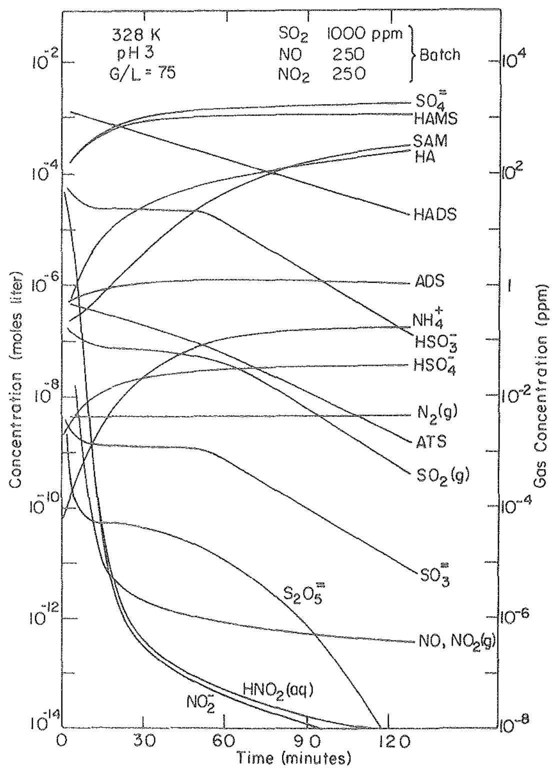


Fig. 3. The concentration profile of species as a function of reaction time in a batch reactor (pH = 3 and temp = 328K) at the following initial condition: $P_{SO_2} = 1000$, $P_{NO} = P_{NO_2} = 250$ ppm. The gas to liquid ratio, G/L is 75. (XBL 8011-6245)

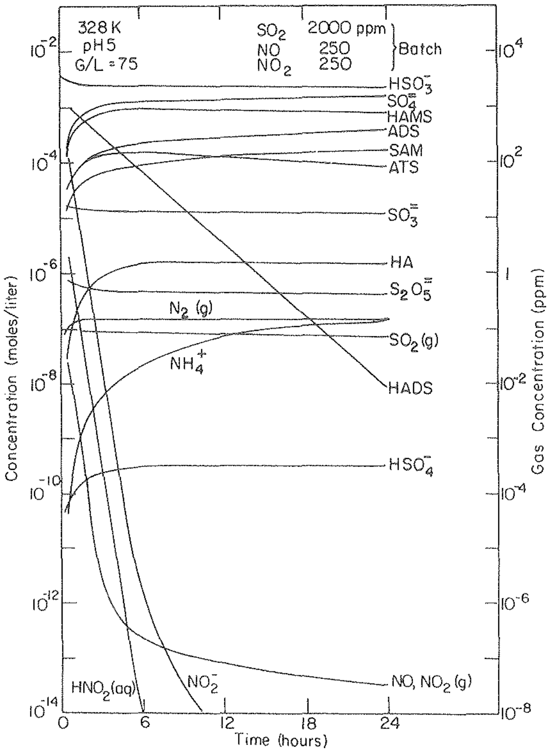


Fig. 4. The concentration profile of species as a function of reaction time in a batch reactor (pH = 5 and temp = 328K) at the following initial condition: $P_{SO_2} = 2000$, $P_{NO} = P_{NO_2} = 250$ ppm. The gas to liquid ratio, G/L is 75. (XBL 8011-6250)

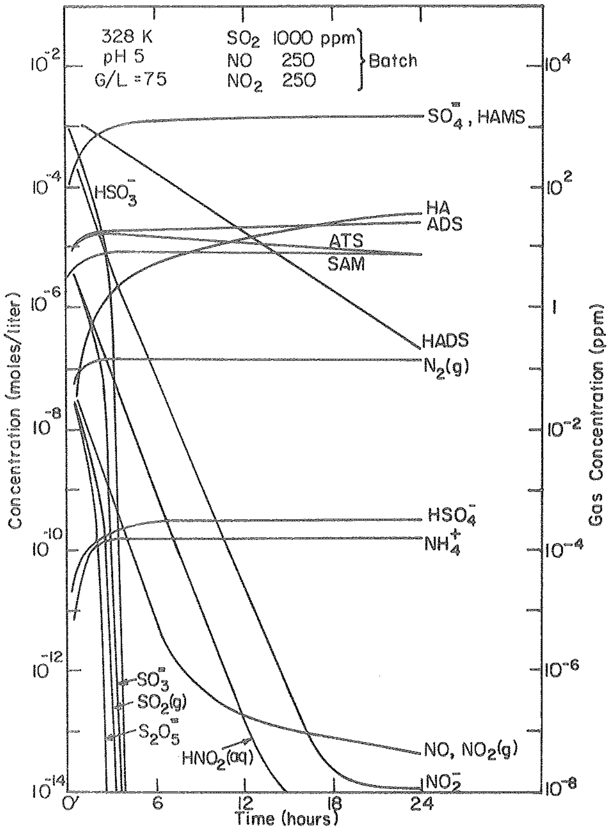


Fig. 5. The concentration profile of species as a function of reaction time in a batch reactor (pH = 5 and temp = 328K) at the following initial condition: P_{SO_2} = 1000, P_{NO} = P_{NO_2} = 250 ppm. The gas to liquid ratio, G/L is 75. (XBL 8011-6253)

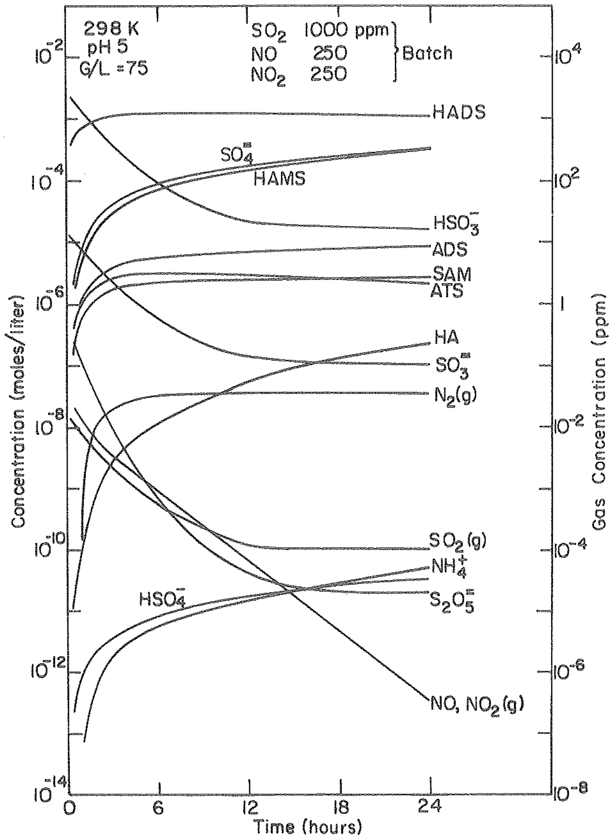


Fig. 6. The concentration profile of species as a function of reaction time in a batch reactor (pH = 5 and temp = 298K) at the following initial condition: P_{SO_2} = 1000, P_{NO} = P_{NO_2} = 250 ppm. The gas to liquid ratio, G/L is 75. (XBL 8011-6252)

the concentrations of HAMS and sulfate increase while that of HADS decreases as the reaction time continues. If the reaction is allowed to continue, the final products will be NH_4^+, N_2, and sulfate. Because we disregard the reaction of HAMS and HA with HNO_2 and the hydrolysis of nitrosulfonic acid, no N_2O is formed.

The effect of the oxidation of NO to NO_2 on the reaction is illustrated in Figure 2 (P_{SO_2} = 1000, P_{NO} = P_{NO_2} = 250 ppm, pH = 5, and T = 328K). The result indicates enormous improvement in NO_x removal efficiency. The concentration of HADS, HAMS, ATS, and other species is larger (compared to Figure 1) because of the larger concentration of nitrite/nitrous acid in the solution. By the same token, HSO_3^- is consumed at a larger rate.

The effect of the pH of the solution on the reaction is shown in Figure 3 (P_{SO_2} = 1000, P_{NO} = P_{NO_2} = 250 ppm, pH = 3, and T = 328K. The reactions are faster at a lower pH (between pH 5 and 3), and NO_x is reduced at a larger rate. The concentration of HAMS is larger than HADS after about 20 min. Similarly, larger concentrations of HA, SAM, N_2, and NH_4^+ are observed at a given time because the hydrolysis reaction is acid catalyzed, and therefore low pH conditions would favor the formation of hydrolysis products.

If the concentration of SO_2 is increased while that of NO_x is held constant, i.e., at larger SO_2/NO_x ratios as in Figure 4 (P_{SO_2} = 2000, P_{NO} = P_{NO_2} = 250 ppm, pH = 5, and T = 328K), the production rates of ATS, ADS, and SAM increase because this larger SO_2/NO_x ratio favors sulfonation reactions. It is interesting to note that the NH_4^+/N_2 ratio increases with the increase in the SO_2/NO_x ratio because the rate of formation of N_2 is only slightly affected by the change in the SO_2/NO_x ratio. (The effect due to the increase in SAM concentration is offset by that due to the decrease in HNO_2 concentration.) However, the rate of formation of NH_4^+ increases as the concentration of SAM increases at a constant pH.

The effect of temperature is demonstrated in Figure 5 (P_{SO_2} = 1000, P_{NO} = P_{NO_2} = 250 ppm, pH = 5, and T = 328K) and Figure 6 (P_{SO_2} = 1000, P_{NO} = P_{NO_2} = 250 ppm, pH = 5, and T = 298K. The results indicate that the overall reaction rate increases at higher temperatures.

Table 1 shows that some reduced N species identical to those discussed in this paper have been identified in a few flue gas wet simultaneous desulfurization and denitrification process[6] based on both oxidation-absorption-reduction and absorption-reduction principles.

Further exploration of reagent/additives to promote the absorption of relatively insoluble NO in aqueous solution and investigation of the kinetics of reactions subsequently involved in the system could permit the simultaneous removal of NO_x in lime/limestone FGD scrubbers without requiring major capital investment.

PLANNED ACTIVITIES FOR FY 1981

The formation of N_2O by the reaction of hydroxylamine monosulfonate and hydroxylamine with nitrite ion will be included in the calculation. The effect of HNO_3, NO, NO_2 and metal ions in the solution will be considered.

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ABSORPTION OF NO BY FE^{+2}•NTA SOLUTION[*]

R. J. Demyanovich and S. Lynn

INTRODUCTION

As cited in the previous section, work in Japan has shown ferrous ion complexed with ethylenediaminetetraacetic acid (EDTA) to be an effective absorbent for NO. Nitrilotriacetic acid (NTA) is less expensive than EDTA and has been shown in previous work to be effective as a buffer for absorbing SO_2,[1] as a catalyst for the reaction between O_2 and ferrous ion,[2] and as a chelating agent for both Fe^{+2} and Fe^{+3}. The present work is investigating the absorption of NO and SO_2 by Fe^{+2}•NTA solutions.

The need for the presence of a chelating agent results from the finding, reported in the previous section, that NO is not readily absorbed by a sulfite or hydroxide solution unless an equimolar quantity of NO_2 is also present. Since 90% or more of the NO_x in a typical flue gas is in the form of NO, this has led some Japanese workers to advocate the introduction of ozone to promote oxidation of part of the NO to NO_2. Others have advocated the use of Fe^{+2}•EDTA to allow absorption of NO. In none of the latter cases was the fate of the NO after absorption discussed.

ACCOMPLISHMENTS DURING FY 1980

Semiquantitative experiments have shown that a solution that is 0.10 $\underline{M}$ in $FeSO_4$ and 0.11 $\underline{M}$ in NTA absorbs pure NO rapidly and quantitatively until a limit of 1 NO per Fe^{+2} is reached. Subsequent sparging of the solution with O_2 produces darkening, indicating oxidation of Fe^{+2} to Fe^{+3}, but no NO is released by the solution. The rate of absorption of NO and the relative quantity of NO absorbed are greater in the presence of NTA than in its absence.

PLANNED ACTIVITIES FOR FY 1981

The investigation of the chemistry of this system will be continued. Of particular interest are the following: the fate of the NO after absorption; the reactions, if any, between absorbed NO and SO_2 in the presence of Fe^{+2}, Fe^{+3}, and NTA; and the stability of NTA in this reactive medium in the 50°-60°C temperature range of aqueous scrubbing.

The mass-transfer characteristics of this system will be studied to determine the rate-limiting step under conditions of interest to scrubber operation.

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PROCESSING OF CONDENSATE WATERS FROM COAL CONVERSION*

C. J. King, D. Mohr, J. Hill, P. Mackenzie, and J. MacGlashan

INTRODUCTION

Coal-gasification and coal-liquefaction processes produce large volumes of condensate water, formed from reactor effluents as they are cooled. This water typically contains large quantities of ammonia, neutralized by near-equivalent quantities of dissolved acidic gases (CO_2, H_2S). It also contains substantial amounts of dissolved polar organics, reflected by a high chemical oxygen demand (COD). There can also be dissolved nonvolatile salts and lower concentrations of other problem substances, such as polynuclear aromatics, N and S compounds, and cyanides. Condensate waters from other synthetic fuel processes, such as shale retorting and pyrolysis of biomass, have similar characteristics.

Conventional biological treatment (1) has given nonreproducible results for these waters, (2) is subject to upsets from high or varying feed concentrations, and (3) removes about 60 to 70% of the COD at best. Biological treatment is also a destructive process and so does not allow recovery of chemicals such as phenol in unchanged form. The purpose of this project is therefore toward developing solely physicochemical processing methods that will enable recycle of the process condensate waters as cooling-tower make-up. This leads toward process configurations which will build up large concentrations of contaminants in condensate waters before the water is processed, as opposed to the dilution of these waters which is sometimes practiced for biological treatment. A typical physicochemical processing scheme might involve solvent extraction and stripping, followed by carbon adsorption or ozonation, as necessary to provide sufficiently complete removal of problem organics.

Our work to date has focused on four different areas--analysis of individual constituents of typical condensate waters, extraction with novel solvents which will allow more complete COD removal, interpretation of rates of stripping NH_3, CO_2, and H_2S from samples of real condensate waters, and innovative combinations of extractions and stripping which can substantially decrease the energy consumption required for removal and recovery of ammonia.

Our initial results relating to extractability of phenols by different conventional solvents, the effects of pH and temperature on extractability, and means for recovering residual dissolved solvent from extraction processes are described in the FY 1979 report and in a recently prepared summary.[1]

ACCOMPLISHMENTS DURING FY 1980

Sampling and Analysis of Condensate Waters

Samples of condensate waters were obtained from the Ft. Lewis, Washington Solvent Refined Coal (SRC) liquefaction plant. These were adjusted to different pH values for different portions immediately on arrival and were stored cold in the dark. Analyses of this water and of synthetic solutions of different phenols show that the polyhydric phenols had probably largely degraded before the sample was received. The polyhydrics are subject to rapid free-radical polymerization on contact with O_2 or light, as is evidenced by darkening of the solution. The process configuration of the Ft. Lewis plant collects condensate water in an open tank. There is no simple way to obtain a sample of water that has not already been thoroughly exposed to O_2.

Samples of condensate water were then obtained from the slagging-bed gasifier plant at the Grand Forks Energy Technology Center (GFETC). This water had not been exposed to air, and was sampled and stored under N_2 and in the dark, with different portions changed to different pH values. Most of our subsequent work has been carried out with this water, which does appear to be stable over time.

A gradient-solvent high-performance liquid chromatography (HPLC) technique (methanol/water gradient with C-18 μBondapak column) has been developed to analyze different organic solutes in condensate waters both qualitatively and quantitatively. We have modified the standard COD titration procedure to remove interferences from thiosulfate and sulfide. Components reliably identified in the GFETC gasifier condensate water are shown in Table 1 and account for about two-thirds of the total measured COD. These components are largely phenol and nonalkylated and slightly alkylated mono- and polyhydric phenols. Nearly all of the remaining COD apparently is organic and much of it is composed of highly polar substances. We are pursuing identification and quantification of the components that are important contributors to the remainder of the COD. Techniques being employed are HPLC with a methanol/water gradient, a more polar column and preconcentration of portions of HPLC effluent, followed by combined gas chromatographic and mass spectrometric (GC/MS) analysis.

A striking difference between the SRC and GFETC waters concerns the dihydric phenol isomers --pyrocatechol (1,2), resorcinol (1,3), and hydroquinone (1,4). In the condensate water from the SRC process, the amount of resorcinol is large

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Table 1. Substances identified in GFETC slagging-bed gasifier condensate water.

Compound	Concentration (ppm)
phenol	4430
cresols	2640
pyrocatechol	990
dimethyl cresols	400*
resorcinol	70
hydroquinone	20
acetophenone	15
2-naphthol	20

*Approximate.

(3,200 ppm), and equal to the concentration of phenol itself. In the GFETC gasifier water, the concentration of pyrocatechol is much larger than those of the other two isomers. Other published analyses for dihydric phenols in gasification and liquefaction condensate waters are sparse, but those few that have been published support the same strong directional difference in the isomeric distribution of the dihydric phenols between gasification condensates and liquefaction condensates.

Extraction of Condensate Waters

We have carried out extraction studies in which removals of both individual identified components and overall COD are monitored, with the aim of evaluating the effectiveness of different solvents as well as obtaining useful information on the chemical characteristics of as yet unidentified constituents.

Table 2 shows results obtained for extractions of GFETC gasifier condensate with methyl isobutyl ketone (MIBK), which was shown in our earlier work[1,2] to be much more effective than the more conventionally used diisopropyl ether (DIPE). For measurements of residual COD after extraction, the aqueous raffinate was first stripped extensively with N_2 to remove volatile, dissolved MIBK solvent. The removal of MIBK was confirmed gas-chromatographically. About 76% of the COD is removed with a single-stage extraction, including essentially all of the COD associated with those components identified in Table 1. Little additional COD is removed by a second extraction at system pH, indicating that the residual COD is associated with components that are very poorly extracted by MIBK. About 30% of the remaining COD is removed by a second extraction at low pH, indicating that the substances thus removed have characteristics of moderate to moderately strong acids.

As shown in the 1979 report and in the following section, we have found that trioctyl phosphine oxide (TOPO) is a very effective extractant for phenolics, including polyhydric phenols. It is a much stronger Lewis base than MIBK, is available commercially at about $8/lb, and is now being used extensively in the hydrometallurgical industry.

Table 2 shows results of extractions with a mixed solvent composed of 25% wet weight (w/w) TOPO in MIBK, the MIBK diluent being used to dissolve TOPO and form a solvating medium for reaction complexes. A significantly greater fraction of the COD is removed at system pH than for extraction with MIBK alone. Again, the vanishingly small additional removal in a second extraction indicates that the components giving the remaining COD are poorly extracted by TOPO/MIBK at system pH. A second extraction at low pH removed about 50% of the remaining COD, indicating again that these additional substances have moderate to moderately strong acid character, or at least are transformed at low pH into a form more attracted by the Lewis base.

Table 2 also shows results for successive extractions by MIBK and then methylene chloride (CH_2Cl_2). Since CH_2Cl_2 is a Lewis acid, the additional COD removed by extraction into it is a measure of the amount of COD with a basic character. Only a small percentage of the COD remaining after MIBK extraction appears to have this basic property, even when the pH is raised to 12.

The results shown in Table 2 are encouraging with regard to the likely ultimate success of extraction processes for bulk COD removal.

Raffinates from these extractions are being examined further by the analytical methods indicated above, as a supplemental approach for identifying the principal constituents contributing to the COD not already identified in Table 1.

Extraction of Phenol with TOPO/DIBK

In earlier work,[3,4] we observed that pyrogallol (1,2,3-trihydroxybenzene) exhibits a very high equilibrium distribution coefficient (K_D = weight fraction in solvent phase/weight fraction in aqueous phase, at equilibrium) of the order of 100 when extracted from water into a solvent mixture of 25% w/w TOPO in diisobutyl ketone (DIBK). We have carried out more extensive measurements of extraction of phenol itself from water into TOPO/DIBK.

Table 3 reports a series of measurements in which the phase ratio, and thereby the stoichiometric ratio of TOPO to phenol, was varied for a solvent of fixed initial composition. From these results it can be seen that TOPO is a very strong extractant for phenol and that the values of K_D found are at least qualitatively consistent with the Law of Mass Action.

Stripping of NH_3, CO_2, and H_2S from Condensate Waters

A batch, one-stage stripping apparatus was used to follow removals of NH_3, CO_2, and H_2S from samples of condensate water as N_2 was sparged through at ambient temperature.[5] The pH and concentrations of the three solutes in the remaining solution were monitored using a pH meter and specific-ion electrodes, respectively. Partial pressures of the solutes in the effluent gas were determined by means of an acid/base chemical-absorption train.

Table 2. COD removals by extractions of GFETC gasification condensate water.*

Conditions	% Removal of COD†	Number of Measurements Used in Finding Average
1. Extraction with methyl isobutyl ketone (MIBK)		
One extraction, without pH adjustment	76.1 ± 0.6	3
Two successive extractions, without pH adjustment	77.7 ± 0.4	2
One extraction without pH adjustment, followed by one extraction at pH < 2	83.6 ± 1.1	2
2. Extraction with 25% (w/w) trioctylphosphine oxide (TOPO) in MIBK		
One extraction, without pH adjustment	81.4 ± 0.2	3
Two successive extractions, without pH adjustment	81.4 ± 0.1	2
One extraction without pH adjustment, followed by one extraction at pH < 2	90.5 ± 0.1	3
3. Extraction with MIBK, followed by extraction with methylene chloride (CH_2Cl_2)		
Two successive extractions with MIBK, followed by one extraction with CH_2Cl_2, all without pH adjustment	79.5	1
Two successive extractions with MIBK, without pH adjustment, followed by one extraction with CH_2Cl_2 at pH = 12	80.3	1

*Equal volumes of aqueous and solvent phases used in all extractions.

†Initial COD = 30,200 ppm; raffinate stripped thoroughly for removal of residual volatile solvent.

Table 3. Extraction of phenol from water into TOPO/DIBK*

Solvent/Feed (vol./vol.)	Temperature (°C)	Mols TOPO/Mols Phenol (Stoichiometric Ratio) Total Feed	Extract	K_D
1.00	20.6	10.2	10.2	474
0.50	21.8	5.1	5.1	406
0.25	22.0	2.55	2.56	332
0.125	22.2	1.28	1.34	208
0.0625	23.8	0.64	0.78	86
0.0400	24.5	0.40	0.64	56

*Solvent composition: 25% w/w TOPO in DIBK; each result is the average of 2-3 separate measurements; feed phenol concentration = 4900 ppm w/w.

Figure 1 shows observed results for N_2 stripping of condensate water from the Ft. Lewis, Wash. SRC coal-liquefaction plant. A general result is that H_2S is removed more readily than CO_2 and NH_3. Also shown in Figure 1 are the partial pressures predicted from the prevailing solution compositions using the theoretical model of Edwards et al.,[6] which allows for activity coefficients and Henry's Law constants of the three solutes in solution, neglecting any effects from other solutes. It can be seen that the theoretical prediction matches the experimental results well up to the point where H_2S has been fully removed. Subsequently the pH drops to a lower value than predicted, and the NH_3 and CO_2 partial pressures become concomitantly lower and higher, respectively, than the predictions. Apparently additional anions were formed by an oxidation mechanism after H_2S was removed, causing the observed trends. The observed results late in the stripping process can be rationalized[5] by adding a certain constant amount of nonvolatile strong-acid anions to the model of Edwards et al.

We have made similar measurements for a sample of Omega 9 retort water from in-situ retorting of oil shale. Here the results can be rationalized by allowing for an excess of nonvolatile strong-base cations (e.g., Na^+) in the theoretical model.[5]

Combined Stripping and Extraction

Steam requirements for stripping ammonia from condensate waters tend to be very large (e.g., boil-up of 10 to 15% of the total water). This results from the simultaneous presence of acid gases (CO_2, H_2S) in solution with the basic ammonia. The water thereby acquires a pH (typically 8.5 to 9.0) where all these species are ionized to a large extent, and the volatility of the ammonia is considerably suppressed below what it would be in the absence of the acid gases. Similarly, the volatilities of the acid gases are also considerably suppressed compared to what they would be in the absence of the ammonia. The presence of large concentrations of multiple volatile species also complicates isolation of ammonia as a salable product.

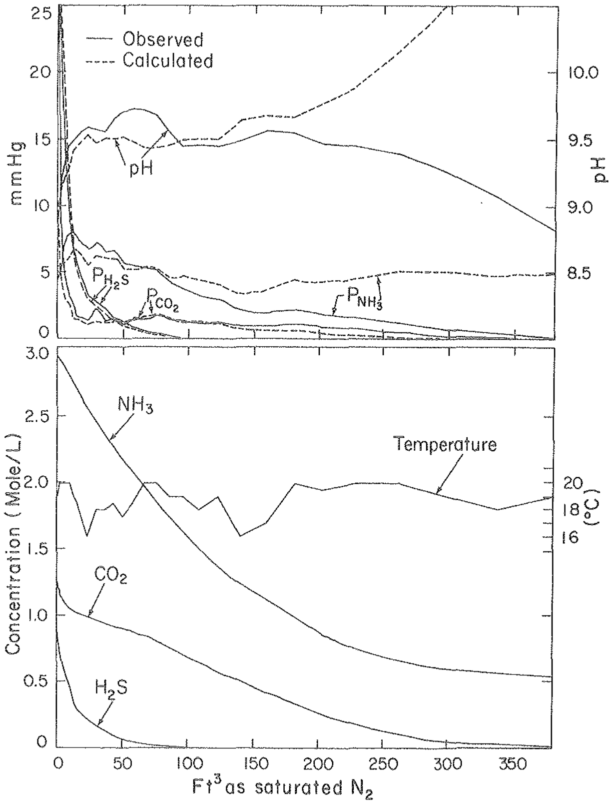

Fig. 1. Experimental results for stripping of SRC condensate water, and comparison with model of Edwards et al.[6] (XBL 806-1211)

We are exploring a novel approach whereby two separation processes are combined to function simultaneously, with one serving to remove and isolate the ammonia and the other serving to remove the acid gases. This concept follows from a suggestion originally made by Cahn et al.[7] in the context of liquid-membrane processes. In our work, we are combining extraction with stripping, i.e., we are trying to achieve the goal of removing ammonia (or acid gases) by extraction while removing acid gases (or ammonia) by stripping. Removal of the one solute by extraction should increase the volatility of the other, thereby reducing the steam requirement for stripping.

As an example, for a condensate water initially containing 8,500 ppm NH_3 and 12,000 ppm CO_2, with other solutes contributing negligibly to the pH, selective extraction of 25% of the NH_3 should increase the partial pressure of CO_2 by 250%, while selective extraction of 25% of the CO_2 should increase the partial pressure of NH_3 by 60%. The percentage increases are less at lower NH_3 and CO_2 concentrations, but it is the behavior at the highest (feed) concentration that should set the steam requirement, since the pinch on an operating diagram usually occurs at the feed end of the column.[8] Thus extraction of 25% of the ammonia at the feed end could reduce stripping steam requirements to about 30% of those without extraction.

In work through FY 1980, we have explored the Lewis bases tributyl phosphate, TOPO, Alamine 336 (tertiary amine), Adogen 283 (secondary amine), and dimethylaniline as possible selective extractants for CO_2, without particularly encouraging results. We are exploring neodecanoic acid, ethylhexanoic acid, and di-2-ethylhexyl phosphoric acid (D2EHPA) as selective extractants for ammonia, and have found very encouraging results for D2EHPA. These results have so far been difficult to quantify, however, because of complications due to a washable acid impurity in the D2EHPA, which we are now removing before use of D2EHPA. This impurity would not be a complication in a practical process. We have also experienced a phase-settling problem with D2EHPA, and we are taking steps to understand and overcome this. D2EHPA is a commonly used extractant in commercial hydrometallurgical processing.

PLANNED ACTIVITIES FOR FY 1981

We are continuing investigations by HPLC and GC/MS to identify the most important remaining constituents composing the COD in condensate waters. This work will be coupled with extractions using various chemically specific solvents in order to generate information on the chemical classes of unidentified components. We shall continue to emphasize GFETC gasifier condensate water, with additional samples of it and other condensate waters obtained as warranted.

Experimental studies are continuing with MIBK, TOPO, and other candidate solvents to monitor removal of COD as related to removals of specific chemical constituents in condensate waters. These measurements will be followed by conceptual design calculations to assess the relative attractiveness of these and other candidate solvents. In the case of TOPO, different diluents and different methods of regeneration will be considered. Other factors, such as rate of extraction and settling properties, will be evaluated and measured as needed.

Measurements are also continuing on the extraction of specific phenols (phenol, resorcinol, pyrogallol, etc.) from aqueous solution under controlled conditions using TOPO/diluent solvent mixtures. These measurements are directed toward a fuller understanding of the chemical-equilibrium factors at work, and should aid in the identification of attractive solvent compositions and operating conditions. Similar studies will be made as needed with other extractants effective for compounds found or expected to be at substantial concentrations in condensate waters.

An immediate goal in our studies related to combined stripping and extraction for removal and isolation of ammonia is quantitative understanding of the effectiveness of selective extraction of ammonia by D2EHPA with various diluents. We are also exploring ways of enhancing the settling characteristics of this system. Other potentially selective solvents for H_2S or NH_3 are being investigated. This work is guided by design concepts of how the simultaneous stripping-extraction approach could be used most effectively in practice. In this, we are open to the possibility that the extraction portion of this step could also be effective toward the goal of bulk COD reduction.

We are also investigating other general design approaches through which the energy consumption of extraction and/or stripping processes for condensate waters could be reduced.

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ELECTROCHEMICAL ENERGY STORAGE

APPLIED BATTERY AND ELECTROCHEMICAL RESEARCH PROGRAM*†

E. J. Cairns and F. R. McLarnon

INTRODUCTION

Lawrence Berkeley Laboratory (LBL) has lead mission responsibility for management of the Applied Battery and Electrochemical Research Program, which is supported by the Office of Advanced Conservation Technologies of the Department of Energy (DOE). This program provides the applied research base which supports all of DOE's Electrochemical Systems missions, and the general objective of the program is to help provide electrochemical systems that can satisfy economic, performance, and schedule requirements. The specific goal of the project is to identify the most promising electrochemical technologies and transfer them to industry and/or another DOE program for further development and scaling-up.

The general problem areas which the program deals with include the identification of new electrochemical couples for advanced batteries; the determination of technical feasibility of the new couples; improvements in components of batteries under development by other Electrochemical Systems projects funded by DOE; and the establishment of engineering principles applicable to batteries and electrochemical processes. Major emphasis is given to applied research which will lead to superior technical performance and lower life-cycle costs. The program is divided into three major research areas: Exploratory Battery Research and Development, Engineering-Science Research and Materials Research.

ACCOMPLISHMENTS DURING FY 1980

Both the Implementation Plan and Program Charter for the Applied Battery and Electrochemical Research Program were approved by DOE. LBL placed 25 subcontracts in FY 1980 and conducted a vigorous in-house research program.‡

The Exploratory Battery Research and Development area includes studies of new electrochemical couples or of new approaches to known battery systems. High-temperature systems under investigation include Ca/molten salt/FeS_2, Li/LiI·Al_2O_3/TiS_2, and Na/β"-Al_2O_3/SCl_3^-NaCl-$AlCl_3$. Ambient temperature systems being studied are $LiSO_2$/CZn/NaOH/$Fe(CN)_6^{\equiv}$. New electrode/electrolyte formulations for Zn/KOH/NiOOH and Li/organic electrolyte/TiS_2 cells are being investigated, and a status study of ambient temperature secondary Li batteries was conducted.

Projects grouped under Engineering-Science Research include morphological and optical studies of battery electrodes in Pb/H_2SO_4/PbO_2, Zn/KOH/NiOOH, and metal/air cells; and a thermal management study of the high-temperature Li/molten salt/FeS battery. Improvements in alkaline (Zn/NiOOH and Fe/NiOOH) battery performance are being sought by investigating the effect of temperature on electrode kinetics, measurements of thermodynamic efficiencies, and detailed studies of electrode restructuring phenomena.

The Materials Research effort seeks to identify, characterize, and improve the materials and components to be used in batteries and electrochemical processes. Basic investigations of new materials for battery components have led to the discovery of a novel all-solid electrode structure for possible use as negative electrodes in molten salt cells. New ternary Li-transition metal oxides have been identified as possible positive electrode reactants for use in similar systems. Projects aimed at developing improved separators for high-temperature Na/S and Li/S cells are focusing on such materials as β"-alumina, nasicon, conducting glasses, and novel superionic conductors. New polymeric separators are being studied for use in ambient-temperature Li/TiS_2 cells, and composition profiles in molten-salt electrolytes are being analyzed.

PLANNED ACTIVITIES FOR FY 1981

New projects will include studies of novel photoelectrochemical cells, new ambient-temperature Li batteries and dendritic growth in Zn/halogen cells.

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†The LBL participants 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.

‡"Development of Electrochemical Synthesis and Energy Storage" is described in both the 1980 Materials and Molecular Research Division Annual Report and elsewhere in this report (under "Battery Electrode Studies").

BATTERY ELECTRODE STUDIES*

E. J. Cairns, F. R. McLarnon, M. Katz, and J. Nichols

INTRODUCTION

This project's purpose 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 $Zn/Fe(CN)_6^{\equiv}$) and rechargeable molten salt cells ($Li\text{-}Al/FeS$, $Li\text{-}Al/FeS_2$, $Li\text{-}Si/FeS$, $Li\text{-}Si/FeS_2$, and $Na/\beta\text{-}Al_2O_3/NaCl\text{-}AlCl_3\text{-}SCl_4$). The approach used in this investigation is to study the life- and performance-limiting phenomena under realistic cell operating conditions. Further background information can be found elsewhere.[1-3]

ACCOMPLISHMENTS DURING FY 1980

Investigations have focused on the zinc electrode, which exhibits satisfactory performance in rechargeable alkaline cells ($Zn/NiOOH$, Zn/AgO) but has an inadequate cycle life. The short lifetime and continual capacity loss of the zinc electrode are closely related to a phenomenon known as shape change,[4-6] the redistribution of active material over the electrode's face as the cell is cycled.

Computer-Control of Electrode Performance Experiments

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

Cycle-life performance testing of battery electrodes requires continuous control and/or monitoring of a variety of cell parameters (electrode overpotential, cell current, cell voltage, temperature). Design of a suitable control system must take into consideration several possibly conflicting requirements: the system should be capable of continuously cycling up to 50 cells simultaneously and independently. It must be reliable, accurate, cost-effective, and flexible enough to permit a wide variety of cell charge and discharge regimes. It also must be suitable for convenient data reduction, storage, and display.

An appropriate computer-controlled test system has been designed, constructed, and partially tested. The system configuration is shown in Figure 1. The core of the system is a microcomputer (DEC LSI 11/23) with 128K of RAM and two hard memory disks (RL01), each with five megabytes of storage. The CPU is provided with a 16-bit I/O card and a four-channel D/A card. Two prototype current controllers were constructed to permit operation of eight independent cells from a single power supply.

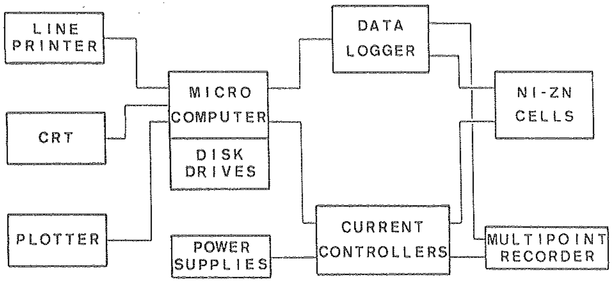

Fig. 1. Test system. Microcomputer: DEC LSI 11/23, RL01 Disk drives. Line printer: LA-120. Data logger: Fluke 2240B. (Other components are being designed and specified.) (XBL 811-7880)

Zinc Electrode Research

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

Researchers have recognized[2,4-7] that reduced solubility of zinc species in alkaline electrolyte would reduce shape change and thereby improve the lifetime of $Zn/NiOOH$ and Zn/AgO cells. The focus of this project is to identify candidate electrolytes and characterize the effect of lowered zinc solubility on the cycle-life performance of $Zn/NiOOH$ cells.

A tri-electrode cell (Fig. 2) was designed, constructed and tested. A 2.6 A-hr zinc electrode is sandwiched between two 1.3 A-hr NiOOH electrodes. Vacuum-table methods were employed to construct teflon-bonded zinc electrodes, and the nickel electrodes were generously supplied by battery manufacturers.[8] Analytical techniques[9] for the determination of zinc, hydroxide, and carbonate concentrations are being adapted to selected battery electrolytes.

PLANNED ACTIVITIES FOR FY 1981

The computer-controlled electrode testing system will be completely implemented, and cycle-life testing of $Zn/NiOOH$ cells will be initiated. Work on rechargeable molten-salt cells will begin.

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*This work was supported by the Assistant Secretary for Conservation and Solar Energy, Office of Advanced Conservation Technologies, Division of Energy Storage Systems of the U.S. Department of Energy under Contract No. W-7405-ENG-48.

†This project is part of a larger effort, "Electrochemical Synthesis and Energy Storage," which is reported in the Materials and Molecular Research Division 1980 Annual Report.

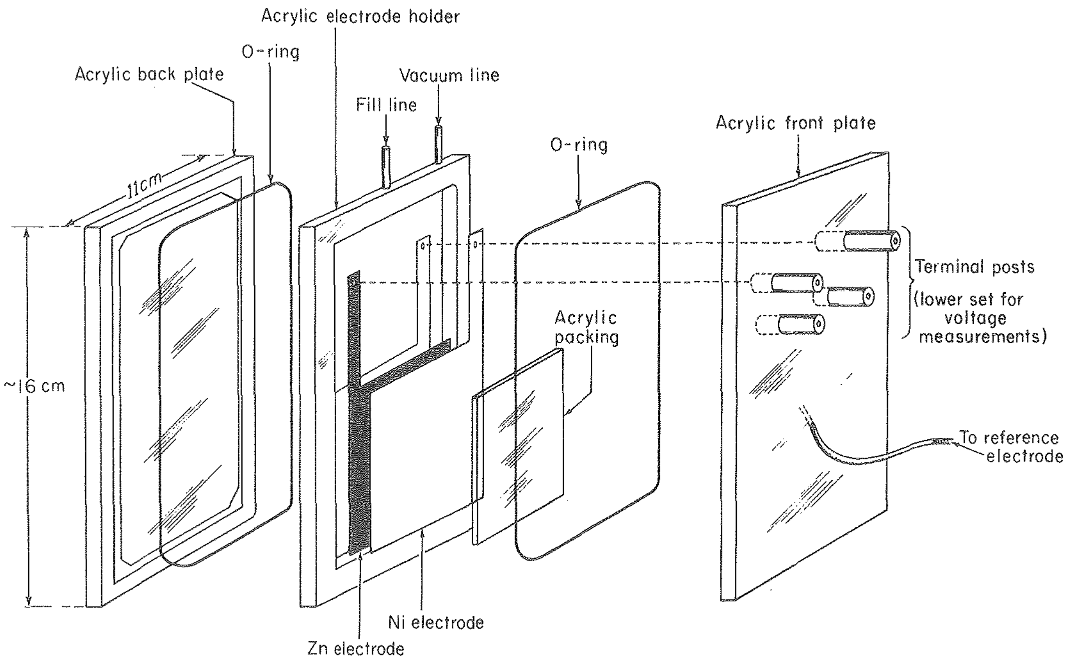

Fig. 2. Test cell. (XBL 811-31)

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