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ENERGY & ENVIRONMENT DIVISION

CHEMICAL PROCESS RESEARCH AND DEVELOPMENT PROGRAM

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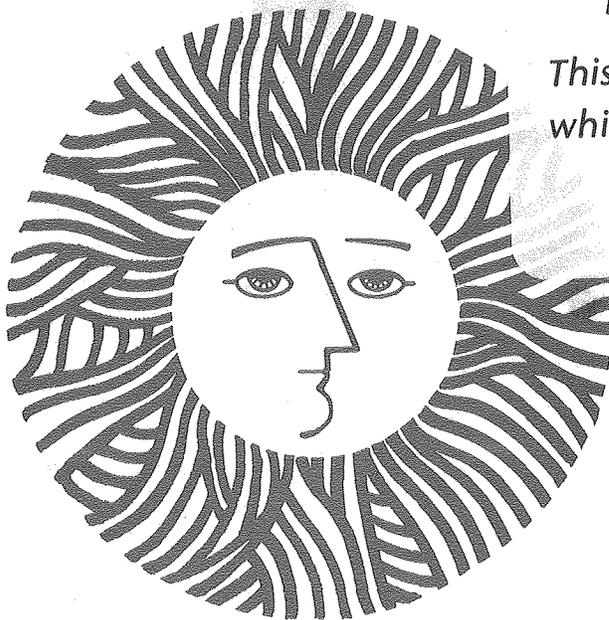
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**CHEMICAL PROCESS
RESEARCH AND DEVELOPMENT PROGRAM**

FY-1979

The research reported in this volume was undertaken during FY 1979 within the Energy & Environment Division of the Lawrence Berkeley Laboratory. This volume will comprise a section of the Energy & Environment Division 1979 Annual Report, to be published in the summer of 1980.

CONTENTS

Introduction	4-1
Process Development Studies on the Bioconversion of Cellulose and Production of Alcohol C. Wilke, H. Blanch, S. Rosenberg, S. Tangnu, A. Sciamanna, and R. Freitas	4-2
Low-Cost, Low-Energy Flash Ethanol Fermentation B. Maiorella, H. Blanch, and C. Wilke	4-9
Studies on the Physiology and Enzymology of Lignin Degradation S. Rosenberg and C. Wilke	4-14
Status of Biomass Liquefaction at Lawrence Berkeley Laboratory S. Ergun	4-18
Pretreatment of Biomass Prior to Liquefaction L. Schaleger, N. Yaghoubzadeh, and S. Ergun	4-19
Catalytic Liquefaction of Biomass M. Seth, R. Djafar, G. Yu, S. Ergun, and T. Vermeulen	4-21
Monitoring the Biomass Liquefaction Process Development Unit at Albany, Oregon S. Ergun, C. Figueroa, and C. Karatas	4-24
LBL Continuous Biomass Liquefaction Process Engineering Unit (PEU) S. Ergun, C. Figueroa, C. Karatas, and J. Wrathall	4-26
Selective Hydrogenation of Coal E. Grens, T. Vermeulen, J. Edwards, F. Hershowitz, P. Joyce, J. Mainenschein, C. Onu, J. Shin, and G. Zieminski	4-27
Coal Desulfurization S. Ergun, S. Lynn, E. E. Petersen, T. Vermeulen, J. A. Wrathall, L. Clary, G. Cremer, J. Mesher, D. A. Dixon, and M. C. Smith	4-32
Processing of Condensate Waters from Solid-Fuel Conversion C. King, S. Lynn, D. Hanson, D. Greminger, G. Burns, D. Mohr, J. Hill, and N. Bell	4-34
Applied Battery and Electrochemical Research Program E. Cairns and F. McLarnon	4-37
Battery Electrode Studies E. Cairns and F. McLarnon	4-38

CHEMICAL PROCESS RESEARCH AND DEVELOPMENT PROGRAM

INTRODUCTION

The Chemical Process Program focuses upon three principal areas--1) production of synthetic fuels, and 2) processing of effluent or recycle water and gas streams to achieve environmental compatibility, and 3) energy storage. The common thread is the use of principles of transport, thermodynamics, kinetics, separations and physical chemistry to improve fundamental, mechanistic understanding, and to develop improved processing approaches.

Two major projects are concerned with conversion of biomass (wood chips, agricultural waste, newsprint, etc.) to fuels. In one of these, a fungus enzyme is used to convert cellulose to glucose, which is then converted to ethanol by fermentation. Ethanol is a candidate as an alternative to, or a diluent for, gasoline (e.g., "gasohol"). The energy efficiency of such a process is critically dependent upon the energy consumed for separation of ethanol from water; improved distillative methods for carrying out that separation are being sought. Related research on fundamentals of fermentation and enzymatic processes supports this project. The second major endeavor deals with direct, reductive conversion of biomass to a fuel oil, using homogeneous catalysis. Here LBL monitors a process-demonstration unit in Albany, Oregon, operated under DOE contract, and at the same time carries out more fundamental research directed towards improvements of various components of that process. A signal accomplishment in 1979 was production of the first barrel-sized quantities of oil from the PDU, following a breakthrough in methodology for catalysis and digestion of wood chips.

Another project directed toward production of synthetic fuels concerns coal liquefaction. Lewis-acid homogeneous catalysts, such as zinc chloride, mixed with certain organic solvents, such as tetralin, provide substantial liquefaction of coal at temperatures markedly lower than those contemplated for other coal-liquefaction processes. Current research is directed toward understanding fundamental aspects of the underlying chemical reactions, as well as the influence of the pore structure of coal and transport characteristics.

In the area of processing for environmental control, one project deals with desulfurization of coal before combustion. Work to date has involved comparison of the relative capabilities of several different oxydesulfurization processes for removing both pyritic and organic sulfur, as well as chemical research probing mechanisms of reaction of coal sulfur in metallic sodium dispersions, sodium sulfide, or acidic aqueous media. These latter studies could lead to novel and more effective methods for sulfur removal from coal.

Sulfur can also be removed from flue gases formed after combustion. In a recently started project, we are exploring solution chemistry (thermodynamics and kinetics) underlying aqueous-scrubbing methods for removal of SO_2 and NO_x from combustion flue gases. Particular attention is being paid to iron chelates, which offer the possibility of simultaneous removal of SO_2 and NO_x .

Nearly all approaches for converting coal, oil shale, or biomass to liquid and/or gaseous fuels produce large amounts of process-condensate water, which is highly contaminated with organics, ammonia, sulfides, etc. These waters have proved to be very difficult to treat by conventional biological processing. We are exploring and evaluating the use of physico-chemical techniques alone as a roughing treatment for such waters, removing enough chemical oxygen demand and ammonia to allow recycle of the water as cooling-tower make-up. Particular attention is being paid to the use of novel solvents to allow effective removal of mono- and poly-hydric phenols by solvent extraction, and to innovative ways of combining solvent extraction and stripping to reduce the very considerable energy requirement for stripping of ammonia.

In the final area of energy storage, new programs are directed toward improved batteries, such as are needed to enable widespread use of electric cars.

PROCESS DEVELOPMENT STUDIES ON THE BIOCONVERSION OF CELLULOSE AND PRODUCTION OF ALCOHOL*

C. R. Wilke, H. W. Blanch, S. L. Rosenberg,
S. K. Tangnu, A. F. Sciamanna, and R. P. Freitas

INTRODUCTION

In most lignocellulosic materials, that are considered as residues, the cellulose is relatively inaccessible to hydrolysis by enzymes. This is mainly due to the crystalline structure of the cellulose and the presence of protective and interspersed layers of lignin and pentosans.

One aspect of increasing the accessibility is by changing the crystalline structure of cellulose to a less ordered system. There are various physical and chemical treatments that can be performed to accomplish this, however, these methods must be relatively very low in cost. Most physical methods are relatively expensive.

Various agricultural and forest residues have been subjected to various chemical pretreatments as part of the ongoing studies on raw materials and process evaluation performed in our laboratory.

The most economical of the pretreatments studied has been the dilute acid process whereby, generally, at least one half of the pentosans, the so-called "hemicellulose fraction," is hydrolyzed to pentoses. Thus, a partial separation of the pentoses from the hexosans is obtained. There is the additional feature of generally doubling the conversion of the carbohydrates to sugars as otherwise occurs on enzymatic hydrolysis of the natural state of these residues.

Promising results have been obtained and reported¹ on the agricultural residues such as the straws of wheat, barley, rice, sorghum, rice hulls, and corn stover. The forest residues such as populus, sycamore, sweet gum, and spruce were studied. These woods are considerably more resistant to attack and stronger chemical treatment were tried with moderate degrees of improvement.²

BIOCONVERSION OF CELLULOSE

Most recently, two fractions of bagasse were analyzed in the continuing work on raw materials analysis and evaluation. The rind fiber and pith fractions were analyzed and enzymatically hydrolyzed. They were also subjected to acid pretreatment followed by enzymatic hydrolysis. The acid pretreatment was accomplished by boiling the above substrates in about 6 w% suspensions for 5 1/2 hours in 0.9 w% sulfuric acid. On enzymatic hydrolysis of the rind fiber fraction there was a 5.7% carbohydrate conversion, and with the pith fraction there was about an 18% conversion. Enzymatic hydrolysis with the acid treated substrates above and including the sugars in the acid liquors, there was a 35% and 57% carbohydrate conversion, respectively.

It would appear that bagasse pith fraction is well worth retaining for hydrolysis and the rind fiber fraction used for direct power production.

Because of the encouraging results obtained with the sulfuric acid hydrolysis's on ground wood such as populus and reported,^{2f} work was extended to try other acids, especially those with appreciable vapor pressures at moderate vacuum, thus leading to acid recovery and recycle.

Enzymatic Hydrolysis

In the past year, a new strain of cellulolytic fungus produced at Rutgers University, and labelled Rut-C-30, was introduced for general study by interested groups throughout this country. Preliminary studies on its performance on corn stover, as a base case, can conservatively be called outstanding relative to the strain T. reesei QM-9414.

Batch Cellulase Production (Rut-C-30).

Fermentation operations were conducted in 5 and 14 liter New Brunswick fermentors. Three cellulose concentrations, S₀, (1, 2.5 and 5.0%) were tested to determine the maximum levels of cellulase activity obtainable in submerged culture. Temperature-pH profiling was tried to increase viable cell mass to maximum levels and thereby enhance fermentor productivity at the higher substrate levels. The effect of Tween-80 and urea concentration on cellulase production were also determined.

Various batch experiments were undertaken to determine the optimum conditions for cellulase production. Various combinations of temperature and pH programming were examined, and the results are summarized in Table 1.

From the above concentrations it can be concluded that a temperature of 25°C and pH controlled not to go below 5.0 are optimum for enhanced cellulase production.

In runs #15 and 16, higher levels of cellulase (2.5 and 5.0%), respectively, were used. There is a substantial increase in cellulase activities as well as in soluble production.

Table 2 shows the comparison of Rut-C-30 with Trichoderma viride QM-9414. If we compare runs #2 and 3, the filter paper activity in #3 is slightly higher but β -glucosidase activity is higher by 10 times versus run #2. This higher level of β -glucosidase would permit more rapid conversion of cellobiose to glucose. This would then decrease the cellobiose inhibition of the C₁ enzyme and hence increase the rate of depolymerization of crystalline cellulose.

If we compare runs #1 and 3, there is an increase in filter paper activity, β -glucosidase and soluble protein by about 3.7, 2.5, 7 and 1.6 times, respectively. All of these experiments demonstrate the superiority of Rut-C-30 over T. viride QM-9414.

Table 1. Effect of environmental conditions on enzyme activity of Rutgers C-30.

Operating Conditions			S ₀ (%)							
Run	pH	Temp °C*	S ₀ (%)	T-80(%)	C/N	FPA	β-glu.	C ₁	C _x	S.P.
1	4 up to 48 hrs, after 48 hrs decrease to 3.3 and was controlled not to go below 3.3	31° 0-2D	1.0	0.02	8.4	1.6	2.3	0.06	38	3.4
2		28° 2-8D	1.0	0.02	8.4	1.7	2.3	0.06	40	3.3
3	Controlled not to go below 4.0	31° 0-2D	1.0	0.02	8.4	2.0	3.55	0.169	44	3.4
4		25° 2-8D	1.0	0.02	8.4	2.1	3.35	0.173	44	3.25
5	Controlled not to go below 5.0	31° 0-36H	1.0	0.02	8.4	2.1	4.25	0.2	40	3.45
6		25° RT	1.0	0.02	8.4	2.1	4.75	0.17	40	3.2
7	Controlled not go below 5.0	31° 0-9H	1.0	0.02	8.4	2.6	2.75	0.18	59	2.78
8		25° RT	1.0	0.02	8.4	3.1	3.3	0.195	84	3.3
9	Controlled not to go below 5.0	25° 0-8D	1.0	0.02	8.4	3.0	4.3	0.26	105	3.3
10		28° 0-2D	1.0	0.02	8.4	2.9	3.9	0.23	115	3.45
11	Controlled not to go below 4.0	25° 2-8D	1.0	0.02	8.4	2.6	1.85	0.2	54	3.15
12		25° 0-8D	1.0	0.02	8.4	2.1 ^a	1.6	0.23	50	3.35
13	Controlled at 4.0	25° 0-8D	1.0	0.02	8.4	2.8	3.3	0.24	110	3.6
14	Controlled at 6.0	25° 0-8D	1.0	0.02	8.4	2.5	3.1	0.17	70	2.6
15	Controlled at 5.0	25° 0-8D	2.5	0.02	10.29	5.2	10	0.48	210	8.2
16	Controlled not to go below 5.0	25° 0-8D	5.0	0.02	8.1	14.4	26	1.03	348	20

^aWith urea (0.3 g/L).

*D = Days, H = Hours, RT = Remainder of Time

Table 2. Comparison of *T. viride* strains Rut-C-30 and QM-9414.

Run No.	S ₀ (%)	Strain	FPA U/mL	β-Glucosidase U/mL	Solution Protein mg/mL	Remarks
1	5.0	Rut-C-30	14.4	26	20	pH 5.0, T-80 level = 0.02%, 25°C
2	2.5	Rut-C-30	5.2	10	8.2	pH = 5.0, T-80 level = 0.02%, 25°C
3	5.0	QM-9414	6.1	1.01	12.68	(0-1 day)pH allowed to fall to 4 (1-2 day)pH allowed to fall to 2 (2 day) raised to 3.3 and controlled not to go below pH 3.3
4	2.5	QM-9414	4.3	1.15	5.94	same as above

Continuous Cellulase Production (*T. viride* strain QM-9414. It was observed in previous work that increasing the cell density or substrate concentration did not proportionally increase enzyme productivity. Extensive studies were carried out in order to optimize individually the 1st and 2nd stage of the two-stage continuous system for cellulase activity by manipulating pH, temperature, Tween-80 level, substrate concentration and dilution rates. The results are shown in Table 3. The experiments were run continuously for about 3 1/2 months.

Runs #1 and #2 show that decreasing Tween-80 level by half increases the filter paper activity by 60% in the first stage of the two-stage fermentation. There is a considerable drop in the filter paper activity in the first stage at pH 5.0 than at other pH levels which severely affects the productivity in the second stage. Although, the filter paper activity of run #1 in the first stage is about 70% less than in run #3, the productivity is higher in the second stage. If run #1 was operated with 0.1% Tween-80 level, it could lead to higher productivity. Similarly, if the second stage of run #2 was operated at pH 5, it could also lead to higher productivity. Hence for all practical purposes the first stage can be operated between a pH range of 3.75--4.25 and the second stage at pH 5. In terms of inlet substrate concentration, 1.75% gives as good a filter paper activity as 2.5%. If the first stages of run #2 and run #9 are compared, it is seen that there is a decrease in filter paper activity and enzyme productivity from 4.2 and 0.084 to 2.54 and 0.053, respectively. If enzyme activity and production in the second are taken into consideration, then it would be profitable to use SW-40 rather than BW-200, as the substrate. Table 4 gives the optimum operating conditions of the two-stage continuous cellulase production system using *T. viride* QM-9414.

Xylanase Production. In shake flasks, *Streptomyces xylophagus* nov. sp. grows in pellet

Table 4. Optimum operating conditions for cellulase production by *T. viride* QM-9419.

Control Variables	1st Stage	2nd Stage
pH	3.75-4.25	5.0
Temperature (°C)	28°	28°
Dilution Rate (hr ⁻¹)	0.02	0.027
Inlet Substrate (%) Conc.	1.75	--

form. The size of pellets varies from flask to flask, some being very fine and the largest about 1 mm in diameter. As pellets grow, the color of the broth changes from milky white to brown. The organism growing in wheat bran medium is thus difficult to observe directly.

The results of batch growth studies are shown in Table 5. The enzyme production rate in shake flask and 14-liter fermentor showed a marked difference in final enzyme activity in using washed wheat bran compared with washed-dried wheat bran. In the 14-liter fermentor where the pH was controlled, wheat bran shows a considerable improvement in enzyme activity as compared to shake flask studies.

In continuous culture, a dilution rate of 0.027/hr gives an enzyme activity of 7.25 mg/mL-hr while lower or higher dilution rates seem to affect the enzyme activity, soluble protein and cell dry weight. It thus appears that a dilution rate of approximately 0.027/hr is optimal.

Composition of Cellulase. Cellulase is composed of three distinct types of activities. These are roughly characterized by activity towards crystalline cellulose, amorphous cellulose and cello-

Table 3. Two-stage continuous production of cellulase from QM-9414.

Run No.	Controlled Variables								Results ^a				Results (Past Process)			
	Inlet Sub ^b Conc. (g/L)	Tween-80 Level (%)	Temp (°C)		pH		Dilution Rate (hr ⁻¹)		Productivity		FPA		System	S ₀ (g/L)	D (hr ⁻¹)	FPA
			F ₁	F ₂	F ₁	F ₂	F ₁	F ₂	F ₁	F ₂	F ₁	F ₂				
1	25	0.2	28	28	4.0	5.0	0.02	0.02	0.053	0.112	2.64	5.6	Single-stage	7.5	0.02	2.7
2	25	0.1	28	28	4.0	4.0	0.02	0.02	0.084	0.087	4.2	4.36	no re-cycle	7.5	0.03	1.9
														1.50	0.03	1.4
														1.50	0.02	2.5
3	25	0.1	28	28	3.75	3.3	0.02	0.02	0.089	0.105	4.44	5.24				
4	25	0.1	28	28	4.25	4.0	0.02	0.02	0.088	0.104	4.39	5.2	Single-stage	10	0.02	3.7
5	25	0.1	28	28	5.0	3.75	0.02	0.02	0.025	0.053	1.25	2.66	recycle			
6	25	0.1	28	28	4.0	5.0	0.027	0.027	0.054	0.116	2.0	4.3				
7	17.5	0.1	28	28	4.0	5.0	0.027	0.027	0.054	0.11	2.0	4.1				
8	17.5	0.1	28	28	4.0	5.0	0.054	0.054	0.038	0.099	0.7	1.84				
9	17.5 ^c	0.1	28	28	4.0	4.00	0.02	0.02	0.05	0.096	2.54	4.8				

^aFor non-recycled system F₁ = first stage; F₂ = second stage

^bBall-milled Solka Floc (200 mesh)

^cSolka Floc (40 mesh)

Table 5. Xylanase production.

Mode of Operation	Type of Substrate	Results		
Shake Flask (200 mL medium in 500 mL flask)	Larchwood (L) 1% Wood Gum (WG) 1% Wheat Bran (W) 7%	Final Enzyme Activity		
		6.97+ 5.17 3.11++	6.89* 7.55 4.19**	
		+Bacto peptone 3g/L *Bacto peptone 8g/L	++Washed & dried wheat bran **Washed wheat bran	
Submerged Fermentation Fer vol = 14L Liq vol = 10L	L; WG; W	9.82*	8.53* (1.61)+; pH, 7.4 6.08 (1.75) pH, 7.9 6.83 (1.79) pH, 8.4 7.77 (1.81) pH, uncontrolled 7.83 (1.56) pH, 8.4 bacto-pep-2g/L ⁻¹ 2.79 pH 8.4, no bacto-peptone	9.44 (3.16+)
	1% 1% 7%		*Enzyme activity (mg/mL) +Soluble protein (mg/mL)	
Continuous (in 14-litre fermenter)	WG(1%)	Dilution rate (hr ⁻¹)		Steady-State Value
		0.02	6.75*(1.6)** (5.25)***	
		0.027	7.25 (1.75) (6.5)	
		0.034	5.7 (1.5) (7.25)	
		0.04	3.25 (1.4) (5.5)	
		*Enz. Act (mg/mL)	**Soluble protein (mg/mL)	***Cell dry wt. (g/L)

biose. To describe the kinetics of cellulose hydrolysis, these components of the cellulase complex are separated.

Figure 1 shows a scheme for such a separation. The raw culture filtrate, in 0.05 M citrate buffer, pH 5.0, 0.02% NaN₃, is concentrated by ultrafiltration with an Amicon UM2 membrane, which removes material of molecular weight less than 1,000. The concentrate is then subjected to gel permeation chromatography (GPC), which results in two fractions. The low-molecular weight fraction contains nonessential material. The high-molecular weight fraction containing enzyme is concentrated by freeze-drying, resuspended in citrate buffer, and subjected to ion-exchange chromatography in a 95 x 1.5 cm column packed with DEAE-Sephadex and eluting with an ionic gradient from 5 mM citrate to 50 mM citrate at pH 5.5. β -glucosidase is eluted first, followed by two separate components of C_x and a single C₁ component.

Two dimensional polyacrylamide gel electrophoresis was used for the analysis and detection of the enzyme at various stages in the separation. This technique gives the molecular weights and isoelectric points of the four components which were resolved. Xylanase and protease activities have not localized in a single fraction.

PRODUCTION OF ALCOHOL

Ethanol Production

Optimization of the Ethanol Fermentation Medium. According to the processing cost distribution of Wilke, Yang, Sciamanna and Freitas³ for the bioconversion of corn stover to ethanol, the greatest cost for ethanol production exclusive of the sugars cost is that for the medium chemicals going

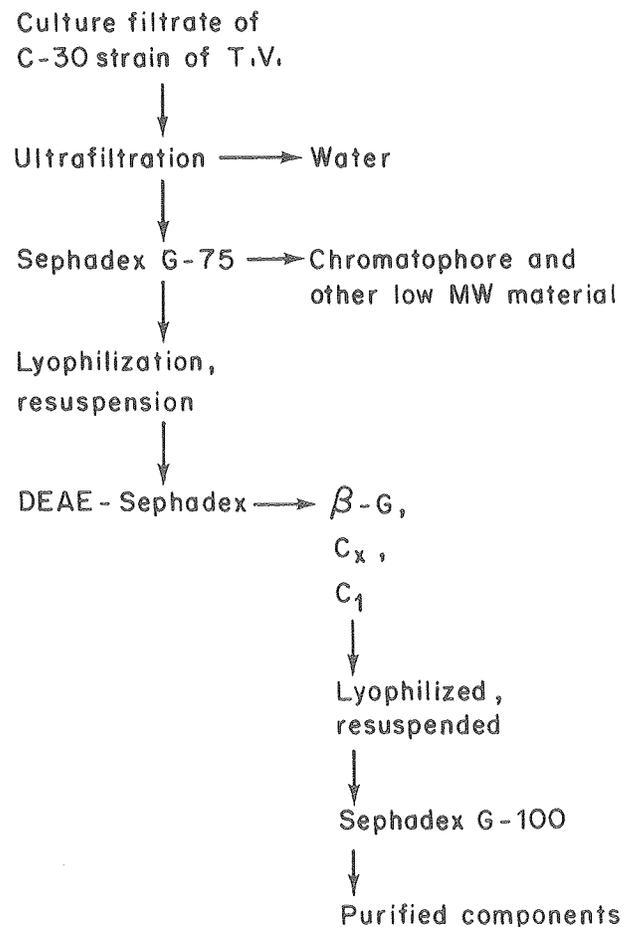


Fig. 1. Separation scheme for cellulase complex. (XBL 801-76)

into the ethanol fermentation. Of the chemical costs, 95% can be attributed to the protein nutrients in the form of antolyzed yeast. To reduce these chemicals cost, basic studies have been undertaken to determine the active components of yeast extract and their quantitative requirements as well as the minimal minerals requirement. It will then be possible to optimize the source and quantity of these active components and minerals for various raw materials.

The following conclusions were drawn from batch ethanol fermentations using glucose as the substrate.

From Shake Flasks:

1. *Saccharomyces cerevisiae* var. *Anamensis* (ATCC-4126) can synthesize all growth factors needed with sufficient time (Fig. 2).
2. Vitamin deficient media produce lower cell mass yields but higher ethanol yields (Fig. 3).
3. Biotin synthesis is the rate-limiting step in cell growth if no external growth factors are added (Fig. 2).

From 1 liter batches:

1. Vitamins and amino acids can increase the specific growth rate. A synthetic mix of vitamins can achieve 85% of the maximum specific growth rate produced with yeast extract (Fig. 4).

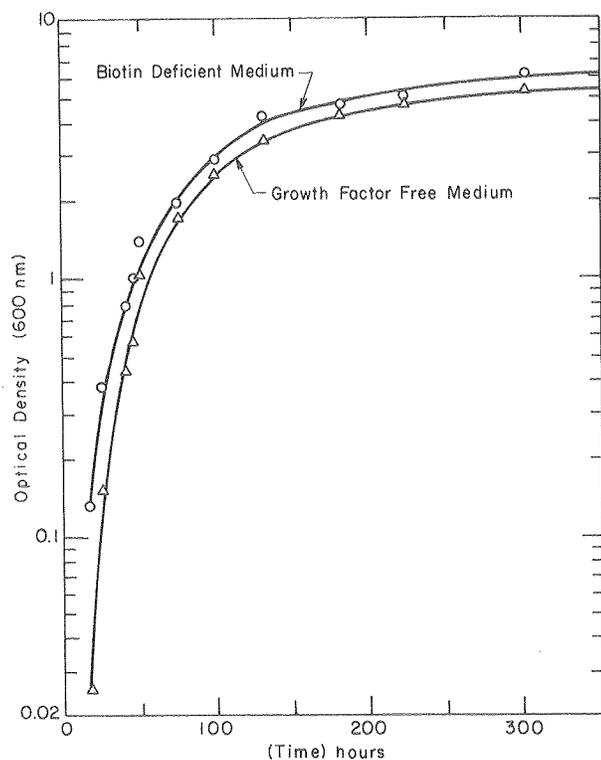


Fig. 2. Comparison of growth in biotin deficient and growth free medium. (XBL 795-6359)

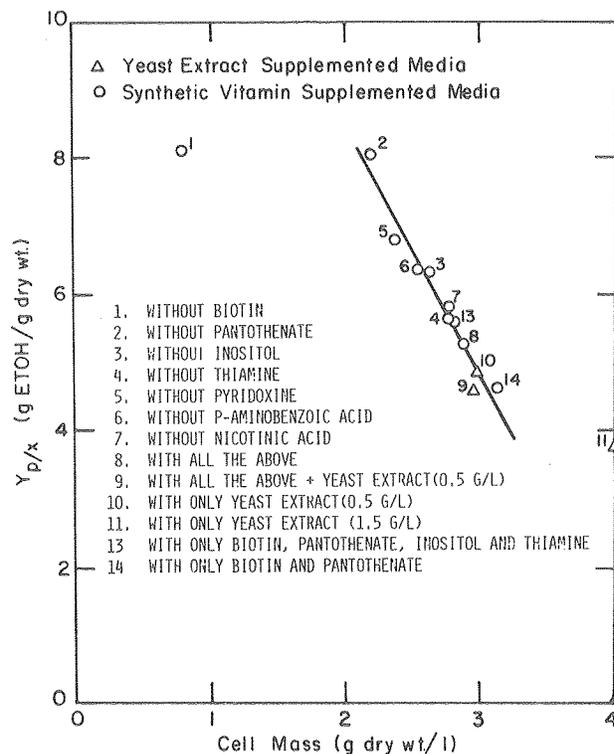


Fig. 3. Effect of various growth factor combinations on cell yield and ethanol yield per gram of cells in shake flasks. (XBL 795-6358)

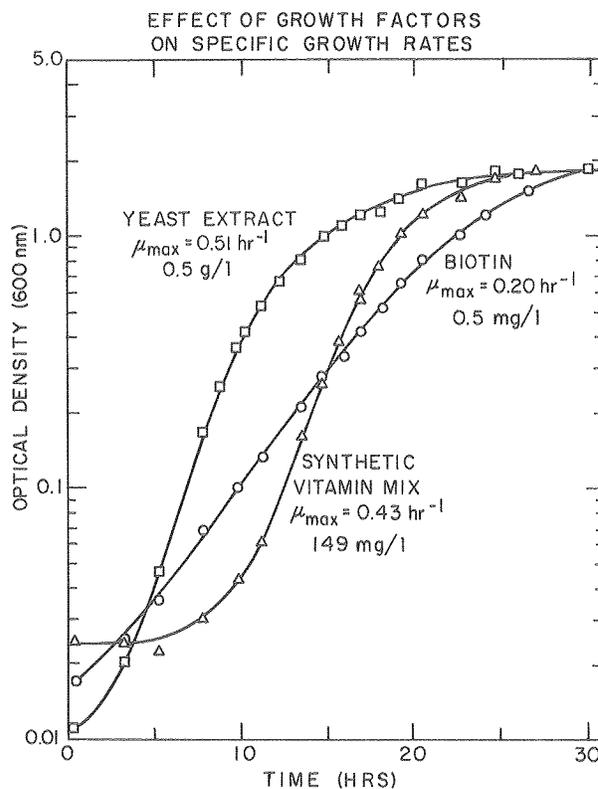


Fig. 4. Effect of growth factors on specific growth rates. (XBL 795-6365)

After the identification of the important growth factors in batch fermentation, continuous cultures were started to determine the optimum levels of all the medium components in ethanol fermentation. A novel procedure extending developments by Mateles and Battat⁴ was employed. Each medium component is made the limiting substrate in terms of cell and ethanol yields. The limiting nutrient is first determined by observing which components when injected as a concentrated shot directly into the fermenter produces a transient increase in cell mass and/or ethanol. When this limiting nutrient is found, its concentration in the feed reservoir which is feeding at a steady state dilution rate, is increased such that it is no longer yield limiting up to a given level of cell mass and ethanol. When the component was limiting from the steady-state yield, then the stoichiometric requirement of that component per quantity of cell mass as well as the ethanol yield per quantity of cell mass can be determined. This component can then be eliminated from further testing as the other components in turn are each made yield limiting.

Using this procedure, the effect of the important growth factors for yeast growth in continuous culture was determined for 10 g/L glucose concentrations that are summarized in Table 6. With a minimal level of yeast extract of 0.1 g/L, the cell yield in grams/liter dry weight (which is approximately equal to the optical density) was about 0.33. Increasing the yeast extract to 0.35 g/L resulted in total sugar utilization and about 1.22 g/L dry weight, indicating the growth limiting factors were in yeast extract.

It was then shown that the first growth factor deficiency which has to be satisfied before the effects of the other vitamin deficiencies could be discerned is that for biotin. Increasing the concentrations of the other vitamins had no effect with biotin was not added. With biotin added, increasing the pantothenic acid and then the pyridoxine concentrations each increased the cell yield.

With these three vitamins in excess, further addition of other vitamins had no significant effect

on cell yield but may have increased the ethanol yield. In fact, with all the vitamins in excess it appeared that the sugar was totally utilized but with more ethanol and less cell mass than with high (0.35 g/L) yeast extract concentration.

Work is now in progress to determine the effects of decreasing the present levels of growth factors and minerals and increasing the level of glucose for scaleup to the higher sugar concentrations called for in the vacuum fermentation systems described elsewhere. The above results for batch and the initial results for continuous ethanol fermentation were presented at the annual meeting of the American Society for Microbiology.⁵

Ethanol Production from Xylose. Xylose represents the most significant component monomer of hemicellulose, and work has been undertaken to convert pentose sugars, arising from hemicellulose hydrolysis, to ethanol. The organism Bacillus macerans has been selected as the most promising ethanol producer.

Early work was performed in batch cultures. Figure 5 shows a typical batch culture on 2% xylose. The maximum specific growth rate is 1.5/hr and with a significant amount of unconverted substrate remaining even though growth is essentially finished. The curve for acetic acid departs from that for ethanol at about 0.07% (after 45 hr). This departure coincides with the slowing of the specific growth rate and is followed by the appearance of acetone. More precisely, when the concentration of acetate in the medium reaches approximately 0.07%, the organism begins shifting its metabolic pathway so that it produces more acetone and less acetate. When B. macerans produces acetate, it makes an extra ATP. When it slows acetate production it makes less ATP per xylose molecule, hence the growth rate slows. It should be pointed out that to balance oxidation states, Bacillus macerans must make one mole of acetate for every mole of ethanol or one mole of acetone for every two moles of ethanol. It also produces formic acid which it is also capable of converting to hydrogen and carbon dioxide. It does not produce lactic acid.

Table 6. Effects of growth factors on continuous yeast cultures for 10 g/L glucose.

Growth Factors	Optical Density dry wt. (g/L)
Yeast extract (0.1 g/L)	0.33
Yeast extract (0.35 g/L)	1.22
Yeast extract (0.1 g/L) + Biotin (4µg/L)	0.43-0.53
Yeast extract (0.1 g/L) + Biotin (4µg/L) + Pantothenic Acid	0.733
Yeast extract (0.1 g/L) + Biotin (4µg/L) + Pantothenic Acid + Pyridoxine (1.25 mg/L)	0.91
Above + all other vitamins	0.95

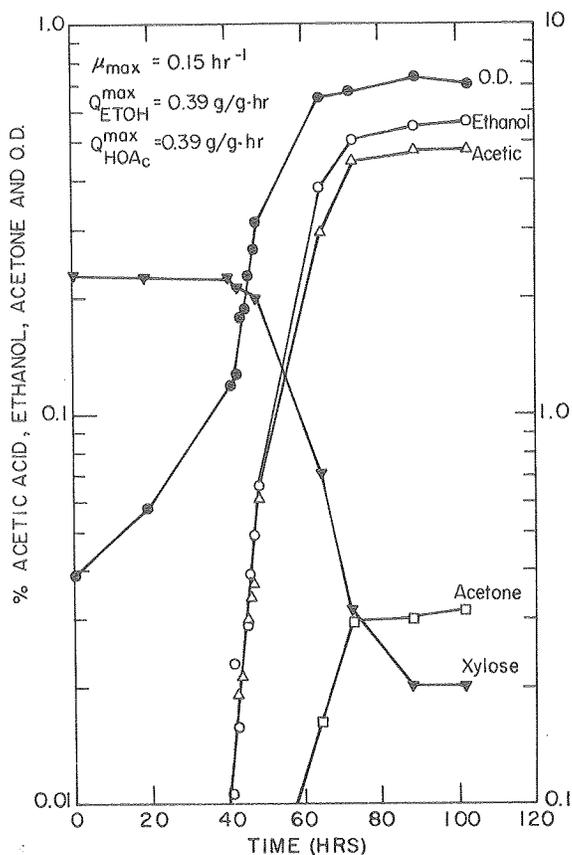


Fig. 5. *Bacillus macerans* growth on xylose.
(XBL 795-6364)

Following batch culture experiments, continuous culture experiments were begun. Several runs were made using 2% xylose at dilution rates of approximately 0.03, 0.06 and 0.09/hr, i.e., 20%, 40% and 60% of μ_{max} , respectively. Several runs were made at the same dilution rates, but with 0.5% ethanol added to the inlet medium. For all of these, nitrogen was sparged through to sweep out CO_2 . The sparging rate was 0.05 VVM. The results showed a

good conversion to ethanol. The theoretical maximum yield by the metabolic pathways of *Bacillus macerans* is 26%. The yields obtained were poor. At a dilution rates of 0.09/hr only half of the xylose was consumed. The lower dilution rates showed better consumption, up to 98% utilization at 0.03/hr. The addition of ethanol to the feed caused poorer utilization, but no significant decrease in cell density.

Future work will include quantifying inhibition by ethanol, acetone, and acetate. The nitrogen sparging rate will be changed to determine if CO_2 is an inhibitor. There is some evidence that xylose is an inhibitor at concentration in the range of 6 to 8 w% and above.

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LOW-COST, LOW-ENERGY FLASH ETHANOL FERMENTATION*

B. Maiorella, H. W. Blanch, and C. R. Wilke

INTRODUCTION

Ethanol production from renewable agricultural resources is an important potential supplement for petroleum-derived fuels and chemicals. Ethanol can be mixed in up to a one to nine ratio with gasoline for automotive fuel without modification to the standard auto engine. With modifications (primarily to the carburetor) ethanol can be used exclusively. After a chemical shift to ethylene, a wide range of petrochemicals can be synthesized from fermentative ethanol.

Two major problems are associated with the use of ethanol to replace petroleum derived fuel and chemicals. The cost of fermentation derived ethanol is high (Table 1) and large amounts of energy are required for ethanol production.

The major cost component of fermentative ethanol is sugar costs (63% of finished product cost). Currently, sugar from molasses sells¹ for \$0.19/kg, which alone accounts for a charge of \$0.32/ liter for ethanol.

The second major cost factor is fermentation plant production cost. Fermentative ethanol is traditionally produced by labor and capital intensive batch techniques. Based on 94.6 M liter-per-year batch-plant design by Cysewski and Wilke,² the capital cost of a new batch fermentation plant would be 25.4 million dollars, with an ethanol manufacturing cost, exclusive of feed materials costs and without profit, of \$0.14/liter.

Production of sugar by hydrolysis of agricultural wastes is under study by many researchers^{3,4} and offers promise of major reductions to the raw material costs. New fermentation techniques, described here, greatly reduce production costs.

Energy requirements for fermentative ethanol production must be considered on a global basis, including energy consumed in farming (Table 2).

A substantial net positive energy return can be claimed by including energy from the burning of farm by-products.⁵ If sugar is to become less costly though, the by-products must be used for hydrolysis to produce more sugar raw material, and not for plant steam production. The distillation energy requirement is equivalent to almost one-half of the energy available in the ethanol produced, and this energy requirement must be reduced.

VACU-FERM PROCESS

The vacu-ferm process, developed concurrently by Cysewski and Wilke,⁶ and Ramalingham and Finn⁷ was a major step forward in reducing capital equipment and production costs for fermentative ethanol manufacture and is shown in Fig. 1. Fermentation is conducted under vacuum (51 mm Hg). Ethanol is boiled away at 35°C as it is produced, maintaining beer ethanol concentration at 3.5 wt%. Thus, end product inhibition is removed. Specific ethanol productivity is increased from 0.6/hr, the average rate over the course of an atmospheric batch fermentation, to a continuous 0.8/hr for vacu fermentation. With cell recycle to achieve high cell concentrations (123 g/L) in the continuous vacuum fermentor, overall productivities of 80 g ethanol/L-hr are achieved. The twenty-eight, 189 m³ fermentors of the batch plant can be replaced by a single, high efficiency, 151 m³ continuous vacuum fermentor.

Energy for boil-up in the vacuum fermentor could be provided by external heating. To reduce energy requirements, vapor recompression heating is used instead. Rather than compressing the vapor mixture entirely to atmospheric pressure, the main compressor compresses the vapor to only 118 mm Hg. At this pressure, the vapors can be passed through a fermentor reboiler with heat exchange providing for boil-up in the fermentor. The liquid ethanol-water mixture can now be pumped with low energy costs to distillation column pressure. A second compressor is required to remove the noncondensable CO₂ and O₂ gases (along with an equilibrium amount of ethanol and water) from the system.

Table 1. Ethanol production and market costs.

Fermentative Ethanol Manufacturing Cost: (94.6 M Liter per year from conventional operating batch plants not including profit)	\$0.47/liter
Ethanol Chemical Market Price:	\$0.34/liter
Cost of Energy Equivalent Gasoline: (One liter of ethanol contains the same chemical energy as 0.7 liters of gasoline.)	\$0.18/liter
Federal Supported Price for Fermentative Ethanol Blended into Gasohol: ^a	\$0.45/liter

^aAdditional tax supports are provided by many states.

Table 2. Estimated global energy balance for production of ethanol from molasses (energies are in kJ per liter anyhdrous ethanol).^a

Energy Consumption		Energy Production	
Farming	13,155	Ethanol	21,071
Sugar Milling and Concentration	6,912	Fusel Oils and Aldehydes	307
Feed Sterilization	139	Farm By-products (cane bagasse for steam generation)	34,700
<u>Distillation</u>			
To Azeotrope	6,996		
To Anhydrous	2,090		
Yeast Product Drying	390		
Subtotal	29,672		56,078
		Net Energy Production	26,406

^aCompiled from estimates by Vogelbush, Scheller, Black, and Cysewski.

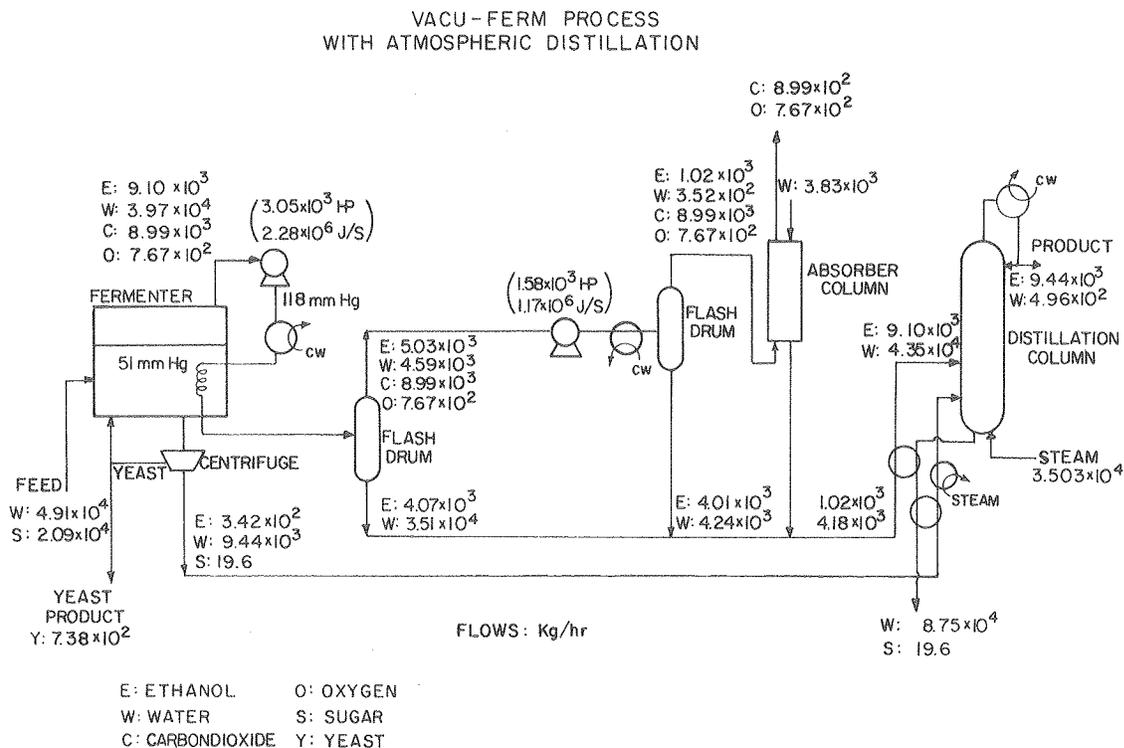


Fig. 1. Flash-ferm process with vacuum distillation.
(XBL 799-7051)

Capital and manufacturing costs (exclusive of feed) are greatly reduced to \$13.9 million and \$0.0763/L, respectively.

Many potential points for improvement remain in the vacu-ferm design. Oxygen solubility in the beer is greatly reduced under vacuum, and to meet the yeast oxygen maintenance requirement, pure oxygen must be sparged into the fermentor. Carbon dioxide is produced along with the ethanol. All this CO₂ gas must be processed by the vacuum compressors. Compressor size and energy requirements are thus much larger than if only the equilibrium ethanol-water vapor product was compressed. Ethanol is recovered from the compressed gas stream by condensing in the fermentor reboiler and auxiliary exchangers. Non-condensable CO₂ and O₂ gases interfere with condensation, decreasing effective heat transfer coefficients and increasing required heat exchanger surface area. The final CO₂ and O₂ gas stream exiting the compressor carries along a substantial fraction (11%) of the ethanol product, and a large ethanol absorber column is required to recover this.

FLASH-FERM PROCESS

The flash-ferm process, originally proposed conceptually by Wilke,⁸ addresses the limitations of the vacu-ferm process and makes several improvements (Fig. 2). An atmospheric distillation is combined with a beer vacuum flashing step. Fermentation is carried out in a single (1.51x10⁵ liters) atmospheric pressure fermentor. Yeast maintenance

oxygen requirement is met with inexpensive sparged air. CO₂ is evolved and vented directly from the fermentor (with no compression required).

To remove ethanol, 3.5% ethanol beer is rapidly cycled between the fermentor and a small vacuum flash vessel where ethanol is boiled away. 2.5 wt% ethanol beer is returned to the fermentor. Only the small amount of CO₂ dissolved in the cycling beer is carried into the flash vessel, and only this CO₂ must be processed through the compressors. Vapor recompression heating is again used. Because the ethanol concentration in the flash vessel must be maintained at less than the 3.5 wt% desired in the fermentor, the equilibrium amount of water carried overhead with the ethanol product is increased relative to that in the vacu-ferm process. This added water vapor through the first compressor offsets the greatly reduced CO₂ flow. The main compressor is made slightly larger than in the vacu-ferm case. The capacity requirement of the second compressor is greatly reduced, however, and an overall energy and capital cost savings results. Very little ethanol (less than 1% of the total product) is carried away with the CO₂ finally vented, and this can be largely recovered by sparging the CO₂ back through the dilute beer solution in the fermentor. The costly ethanol absorber is thus eliminated.

With the flash-ferm process, ethanol manufacturing cost (exclusive of feed) is further reduced to \$0.0697/L as compared to \$0.0763/L for the vacu-ferm and \$0.136/L for the batch process.

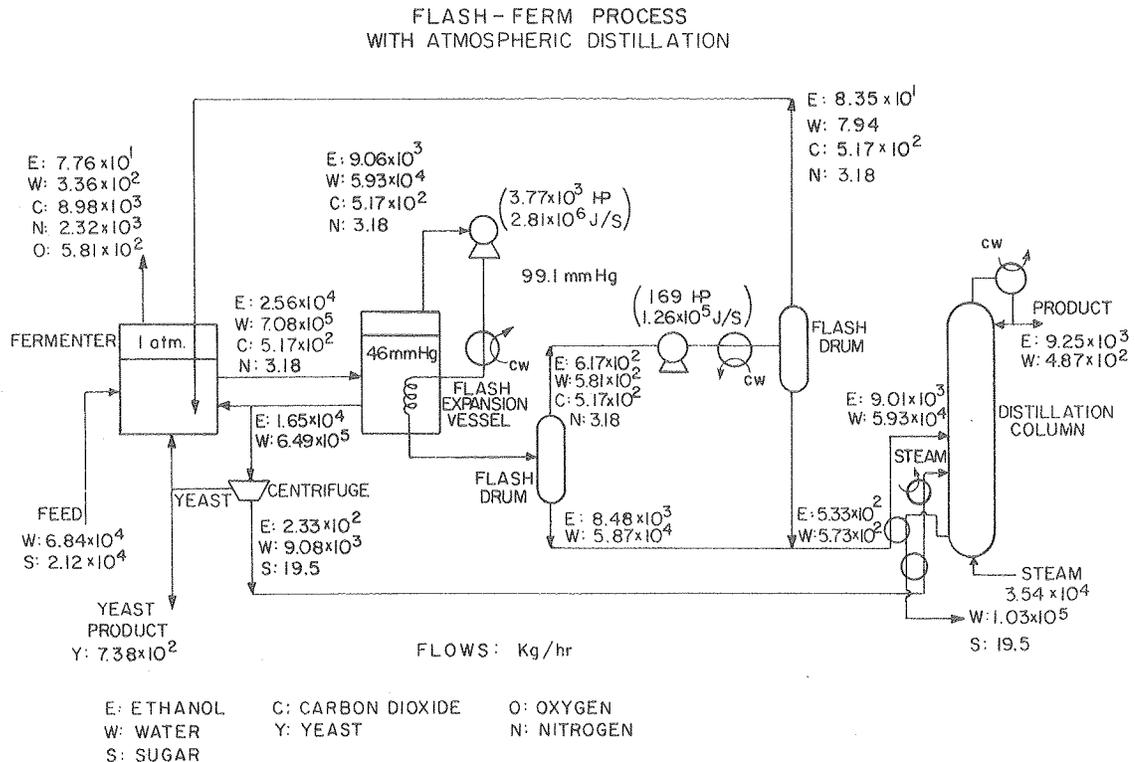


Fig. 2. Flash-ferm process with atmospheric distillation. (XBL 799-7052)

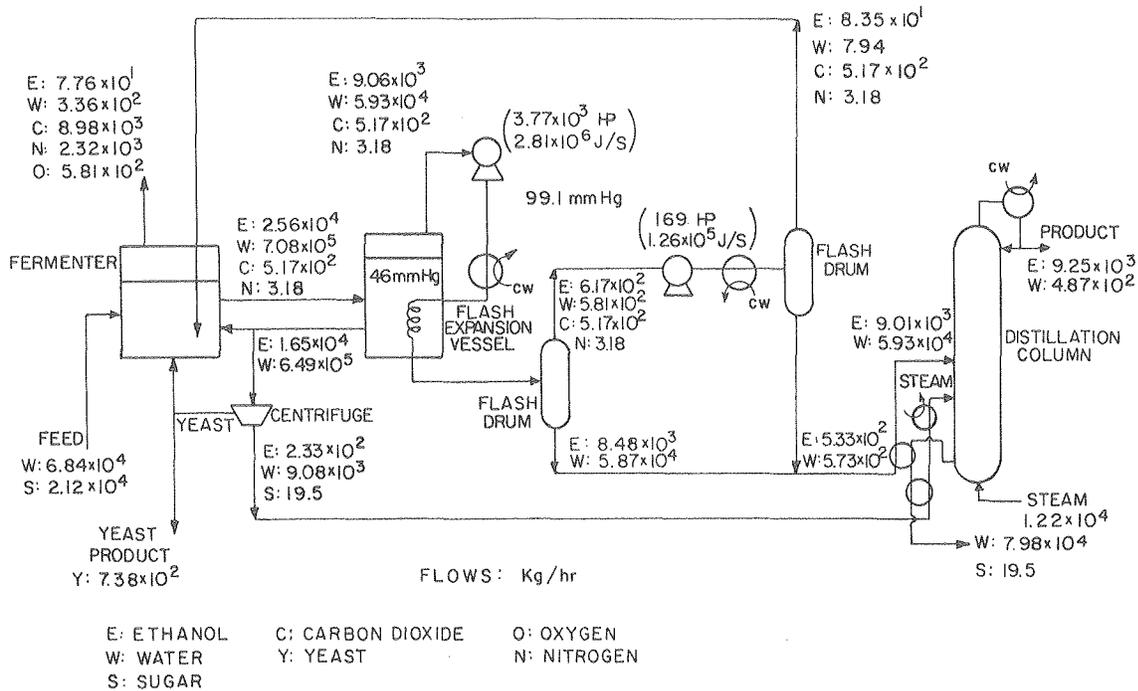
FLASH-FERM PROCESS
WITH VACUUM DISTILLATION

Fig. 3. Vacu-ferm process with atmospheric distillation. (XBL 799-7053)

The overall energy requirement (including feed sterilization and yeast product drying) is 8.36×10^6 J/L, which is reduced from the vacu-ferm energy requirement of 1.09×10^7 J/L, but still higher than the energy requirement for a batch process which requires no vacuum compressors.

It should be noted that the assumption that the pressure shift has no adverse effect on ethanol productivity has not been fully substantiated experimentally. Experiments conducted by Wilke and Yang⁹ involving simultaneous shifts in both pressure and temperatures (35°C to 45°C) resulted in loss of cell viability and reduced ethanol production. A further preliminary experiment, however, indicated that the pressure shift alone has no adverse effect. Additional experiments are in preparation to test the isothermal operation and fully prove the flash-ferm process.

VACUUM DISTILLATION

The flashing operation of both the vacu-ferm and flash-ferm processes provides an initial concentration step. Ethanol concentration in the main feed to the distillation column of the flash-ferm process is 13.2 wt%, much higher than the 5 wt% column feed in the batch process. Yet, the distillation energies in both cases are similar— 6.74×10^6 J/L for batch, 6.63×10^6 J/L for flash-ferm.

Most of the energy for the distillation to 95 wt% goes to providing boilup for the high required reflux. Little reduction in distillation

energy results from the initial flash concentration step because the atmospheric pressure distillation reflux is fixed by a high concentration pinch point, not by the feed composition (as would ordinarily be the case).

Advantage can be taken of the initial concentration step afforded by the vacuum flashing operation if vacuum distillation is used. The ethanol-water equilibrium behavior is altered at reduced pressures, the high end pinch becomes less extreme.¹⁰ The reflux ratio can be reduced from 8.00 to 2.59 with corresponding substantial reduction in required distillation energy (Table 3).

The distillation reboiler and feed preheat energies can now be met entirely with exhaust steam from the compressor drivers (Fig. 3) and considerable operating cost savings result.

Total manufacturing cost for the combined flash-ferm and vacuum distillation process (exclusive of feed materials) is only \$0.0621/L, a reduction of 54% as compared with the traditional batch process (Table 4). The overall energy requirement is reduced to 3.57×10^6 J/L, a 42% savings.

CONCLUSIONS

The flash-ferm process is an advance upon the earlier vacu-ferm process, offering advantages in reduced operating costs and energy consumption. When combined with a vacuum distillation, the initial ethanol concentration step provided by the

Table 3. Ethanol separation energy requirements J/L 95 wt%.^a

Process	Compressors	Column Feed Preheat	Column Reboiler Energy	Total
Batch Fermentation and Atmospheric Distillation	0	2.58×10^5	6.74×10^6	7.00×10^6
Vacuum Fermentation and Atmospheric Distillation	1.26×10^6	1.64×10^5	6.58×10^6	8.00×10^6
Flash-Ferm and Atmospheric Distillation	1.07×10^6	1.26×10^5	6.63×10^6	7.83×10^6
Flash-Ferm and Vacuum Distillation	1.07×10^6	9.17×10^4	2.41×10^6	3.57×10^6

^aThese figures do not include scavenging of 600 psia compressor exhaust steam.

Table 4. Manufacturing cost comparison of processes.

	Batch-Ferm (1 ATM Column) ¢/L	Vacu-Ferm (1 ATM Column) ¢/L	Flash-Ferm (1 ATM Column) ¢/L	Flash-Ferm (Vacuum Column) ¢/L
Direct Costs:				
Raw Material	33.180	33.748	33.180	33.180
Operation	<u>9.138</u>	<u>4.766</u>	<u>4.731</u>	<u>3.838</u>
Total Direct Cost	42.336	38.514	37.914	37.121
Fixed Cost	3.027	1.662	1.617	1.712
Plant Overhead	<u>1.432</u>	<u>0.642</u>	<u>0.631</u>	<u>0.655</u>
Total Manufacturing Cost	46.795	40.820	40.162	39.385
General Expenses	<u>3.260</u>	<u>1.992</u>	<u>1.944</u>	<u>2.039</u>
Total Production Cost	50.108	42.809	42.106	41.425
Gross Income				
Ethanol Sales	44.909	44.909	44.909	44.909
Yeast Sales	5.944	5.944	5.944	5.944
Gross Profit	0.745	8.044	8.747	9.428
Tax (50% gross profit)	0.372	4.021	4.375	4.713
Net Profit (annual after tax)	0.372	4.021	4.375	4.713
Return on Investment	1.45%	28.12%	31.43%	32.00%

flashing operation is taken advantage of, and energy requirements are reduced to very low levels.

With these improvements, the fermentation and distillation processes have been optimized. Further steps toward reducing fermentative ethanol cost must come from development of cheap supplies of sugar raw material.

ACKNOWLEDGMENT

The assistance of Tom Glenchur in carrying out many of the detailed design and economic calculations is gratefully acknowledged.

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STUDIES ON THE PHYSIOLOGY AND ENZYMOLOGY OF LIGNIN DEGRADATION*

S. L. Rosenberg and C. R. Wilke

Studies of biological lignin degradation were undertaken in order to see if this process could be incorporated in our current scheme for the bioconversion of lignocellulosic materials to ethyl alcohol. The presence of lignin in natural cellulosic materials protects some of the cellulose and other carbohydrates from enzymatic attack. Removal of the lignin increases the amount of carbohydrate subject to enzymatic saccharification and, thus, the amount of ethanol obtainable. The goal of this research was the demonstration of a cell-free lignin-degrading enzyme system.

Before a cell-free system could be demonstrated, it was necessary to learn how to grow the organisms (molds) rapidly under conditions where lignin degradation was actually occurring. It was found that both intimate cell-substrate contact and high oxygen concentrations were required for lignin (but no carbohydrate) degradation. Figures 1-3 illus-

trate these conclusions. Only in stationary, non-submerged cultures (Fig. 2) or in submerged but oxygenated cultures (Fig. 3) was lignin degraded to a significant degree.

Having a culturing system where rapid lignin degradation was known to occur (Fig. 2) we next attempted to extract the enzymes involved by a number of conventional methods and demonstrate their activity in the absence of the living cells. These attempts were unsuccessful.

Since it was possible that the presence of cells was necessary for the regeneration of needed co-factors or the continued production of unstable components, an apparatus was developed to indicate the presence of diffusible enzyme systems in the presence of growing cells. The apparatus, termed a diffusion chamber is shown in Fig. 4. The top and bottom compartments are separated by a bacterio-

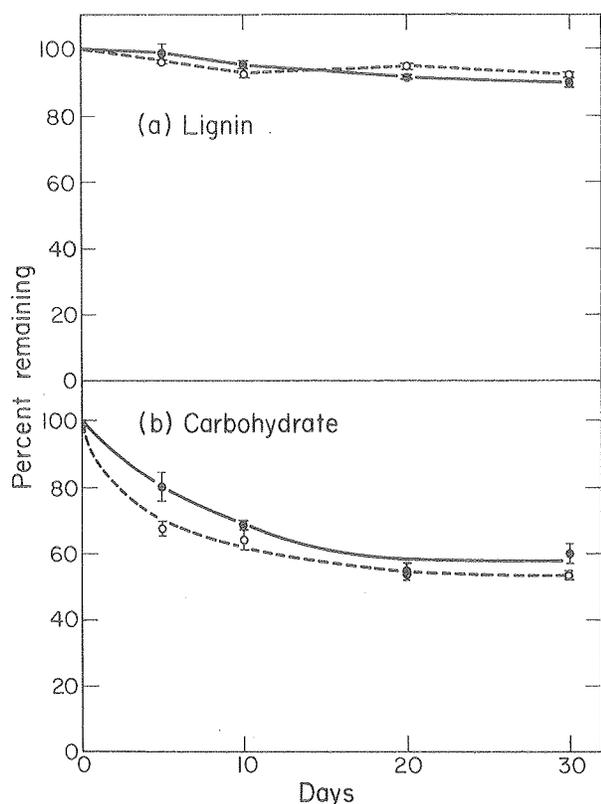


Fig. 1. Lignin and carbohydrate loss in shaking submerged cultures of *C. pruinosa* grown in mineral medium plus manure fiber in the presence of air ●—● or oxygen ○---○. Each data point represents the average of two cultures. (XBL 784-659)

logical membrane filter. Sterile lignocellulose is pressed against the underside of the filter by a sponge plug. The top compartment contains a mold inoculum plus or minus lignocellulose. The presence of diffusible lignin and cellulose-degrading enzyme systems is indicated by the loss of solid lignin and carbohydrate from the bottom compartment.

A number of known lignin-degrading molds was tested in this apparatus, and none gave evidence of producing significant levels of diffusible lignin degrading activity, although many showed diffusible carbohydrate-degrading activity. Data for most of the organisms tested are presented in Fig. 5. The simplest interpretation of the results is that one or more components of the lignin-degrading system produced by these organisms is bound to the cell surface or otherwise immobilized close to the site of production. For some of these organisms this appears to be true of the cellulase enzymes as well. Members of group-1 showed excellent lignocellulose-degrading ability when in contact with the substrate and might be considered for the production of single cell protein from ligno-

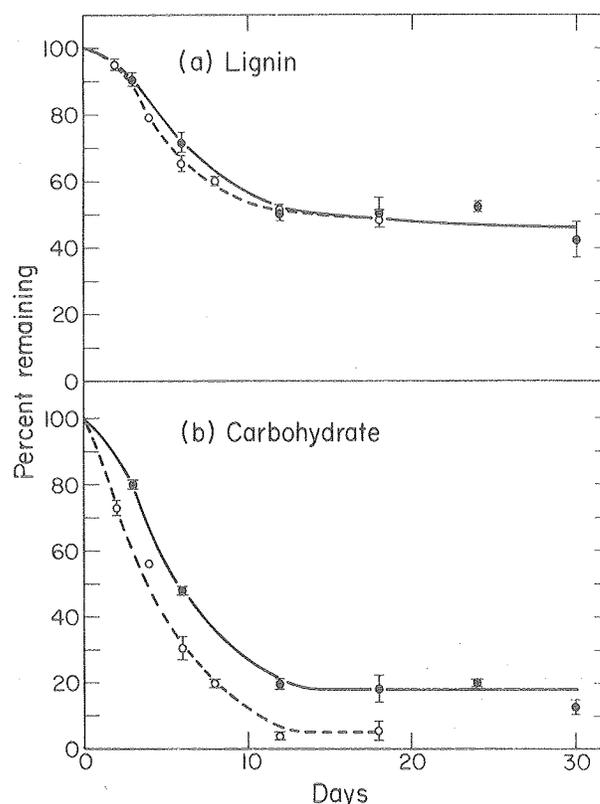


Fig. 2. Lignin and carbohydrate loss in damp manure fiber cultures of *C. pruinosa* grown on the surface of mineral agar plates in the presence of air ●—● or oxygen ○---○. Each data point represents the average of two cultures. (XBL 784-660)

cellulosic wastes. A more complete description of this work can be found in references 1 - 3.

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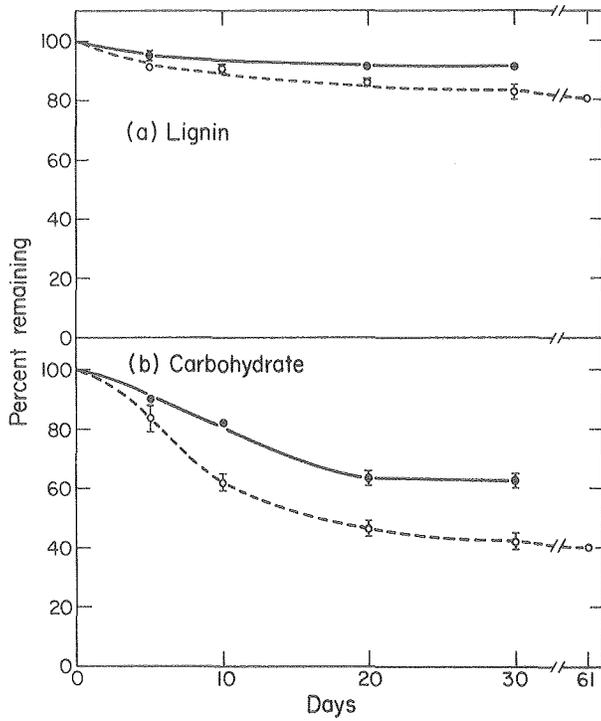


Fig. 3. Lignin and carbohydrate loss in stationary submerged cultures of *C. pruinosa* grown in mineral medium plus manure fiber in the presence of air ●—● or oxygen ○---○. Each data point represents the average of two cultures.
(XBL 784-661)

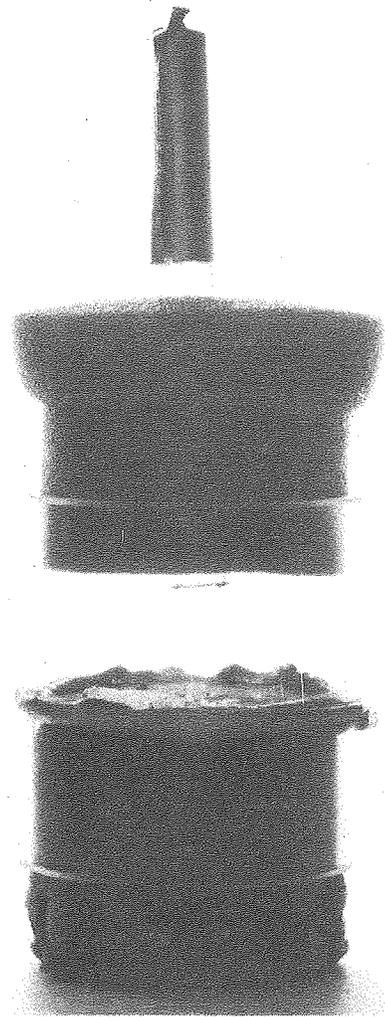


Fig. 4. Diffusion Chamber. Top plug has been raised and bottom foil cover has been removed to show details of construction.
(CBB 783-2637)

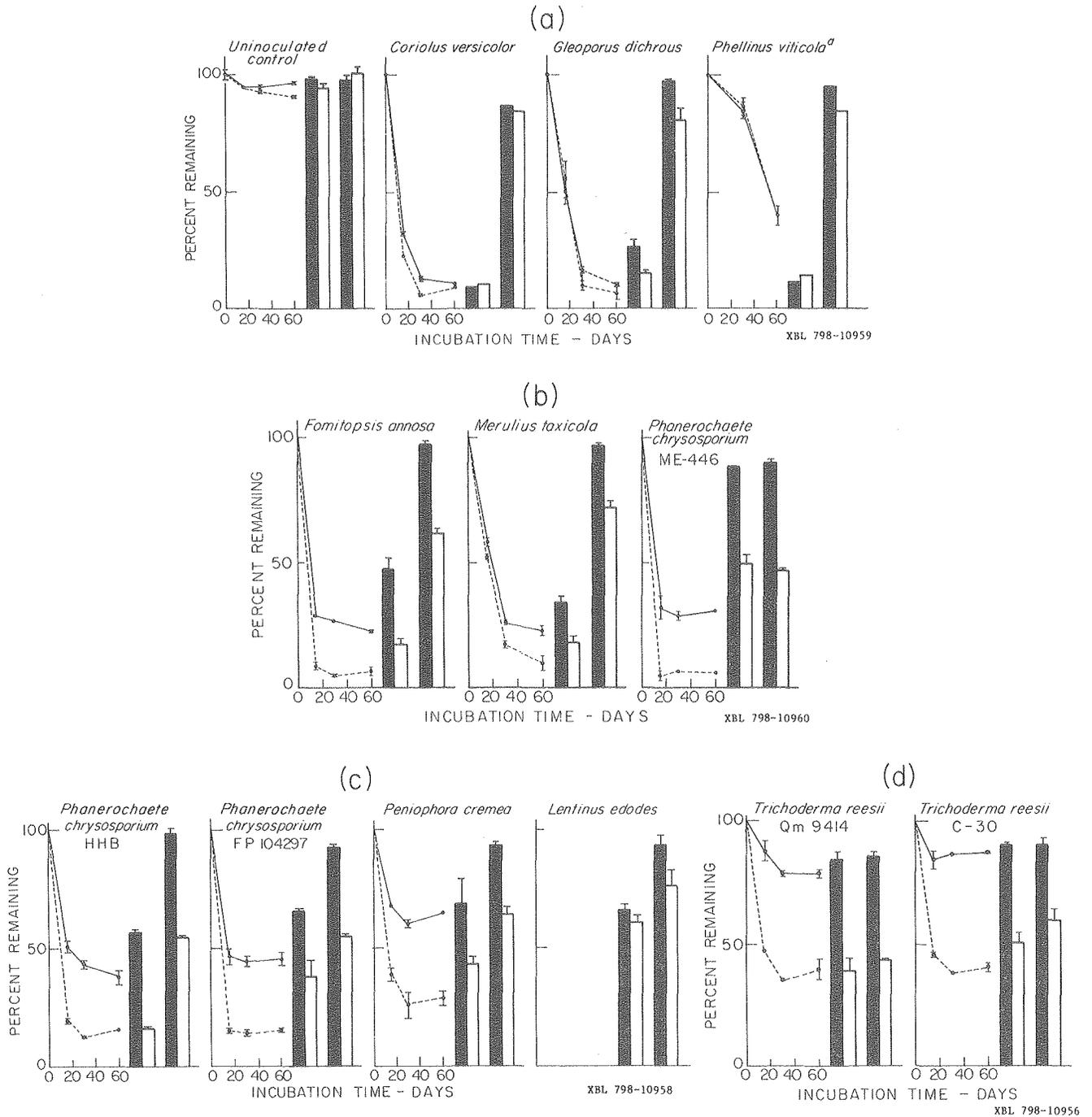
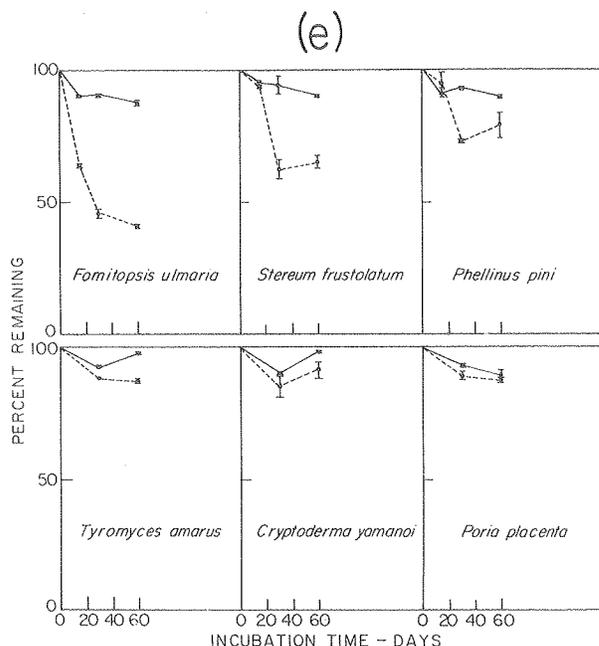


Fig. 5. (a-d) Lignin and carbohydrate remaining in washed manure fiber degraded by cellulolytic and ligninolytic fungi. ———lignin and ----carbohydrate remaining in agar plate cultures. Lignin (dark bar) and carbohydrate (light bar), remaining in diffusion cultures. Left-hand bar pair = residual lignocellulose in top (inoculated) chamber. Right-hand bar pair = residual lignocellulose in bottom (sterile) chamber. Error bars indicate range of variability in replicate samples. No-error bar means only one sample processed. Diffusion cultures were incubated for 30 days except for the *P. viticola* culture which was incubated for 60 days.



XBL 798-10957

Fig. 5(e). See caption on previous page for key.

STATUS OF BIOMASS LIQUEFACTION AT LAWRENCE BERKELEY LABORATORY

S. Ergun

Conversion of biomass into oil or gas is not a new idea, nor is the recognition that synfuels derived from wood wastes or wood grown for such a purpose could meet a substantial portion of America's needs of energy and chemicals. Suffice it to state that there was a genuine interest in the early 1940s for fuels from wood, which was lost upon the discovery of huge oil fields in the Arabian peninsula soon after.

The interest in synthetic fuels from biomass was revived some thirty years later for reasons that need no elaboration. The current biomass liquefaction program of DOE has evolved from the lignite liquefaction program of the Bureau of Mines (BOM) in the late 1960s and early 1970s. Noting the widespread interest in municipal waste disposal,

the Bureau of Mines researchers explored the effectiveness of a process particularly well suited for lignite to liquefy organic municipal waste. They found that organic municipal waste and other biomass wastes such as sawdust and manure, liquefied with greater ease under milder conditions than did lignite.

Encouraged by the results of bench-scale research and economic feasibility analysis, the Bureau of Mines proceeded with the design and construction of a process development unit (PDU) capable of processing 3 tons of wood daily or to yield roughly 5 barrels of oil daily. The plant site chosen was adjacent to the Experimental Metallurgical Station of the Bureau of Mines at Albany, Oregon.

In October 1977, DOE contracted with LBL to monitor both the development program at Albany and the supporting activity, to provide a third-party objectivity in the evaluation of results, to make recommendations regarding the future course of the program, and to provide assistance and appraisal to the operators of the facility.

LBL was also given the responsibility of monitoring the supporting research activity on biomass liquefaction in order to utilize the results in the development program at Albany. Also, LBL has conducted supporting engineering and development studies to provide optional approaches to biomass liquefaction. Accordingly, process modifications and/or new process options had to be researched and a data base provided for testing at Albany.

As lead laboratory for Biomass Liquefaction, LBL has undertaken the following objectives:

1. To provide a continual independent evaluation for the Biomass Energy Systems (BES) Branch of the Department of Energy (DOE) of the technical progress made in biomass liquefaction projects sponsored by DOE.
2. To monitor the operations of the Biomass Liquefaction Facility at Albany, Oregon and to provide technical operating directives for the test runs to be conducted at Albany.
3. To undertake engineering and bench scale experimental studies to enhance the progress of the biomass-to-oil program of DOE.

The following reports summarize LBL's efforts over the past year.

PRETREATMENT OF BIOMASS PRIOR TO LIQUEFACTION*

L. Schaleger, N. Yaghouzadeh, and S. Ergun

INTRODUCTION

The preparation of a concentrated slurry of biomass and its introduction into a high-pressure reaction system are critical operations in the DOE-Albany waste wood-to-oil process. The original Bureau of Mines scheme called for green wood chips to be dried and milled to a flour. The flour was to be blended with a carrier oil and then pumped into the reactor at a solids concentration of 30%. Unfortunately, in practice it has not been possible to pump slurries more concentrated than 10% on a continuous basis. This has had a large negative impact on the economic feasibility of the process since the lower the concentration of biomass in the feed to the reaction system, the larger the plant must be for a given production rate.

Studies at LBL have therefore been directed toward finding alternatives to the Bureau of Mines scheme for injecting biomass into a liquefaction system. Work has centered on chemical pretreatment for the purpose of producing slurries which are pumpable at high concentrations of solids. Physical pretreatment, that is drying and grinding, accounted for 22% of processing costs in the original scheme and has therefore been eliminated from the LBL process development concept. The most promising method of chemical pretreatment found was hydrolysis promoted by mild aqueous acid. The major objectives of the FY 79 research program in pretreatment were: (1) to provide an engineering data base for hydrolytic pretreatment through bench-scale research; (2) to evaluate the resulting slurries of hydrolyzed wood as to liquefiability; and (3) to investigate means of integrating chemical pretreatment and catalytic liquefaction in a continuous manner.

This subproject was begun in October, 1978, using the facilities of the UC Forest Products Laboratory at the Richmond Field Station. After 1 June 1979, research was conducted in the group's permanent facility in Bldg. 934.

ACCOMPLISHMENTS DURING 1979

A series of bench-scale experiments on the hydrolysis of green wood chips were conducted and a set of conditions which resulted in the production of a slurry having superior rheological properties was established. After appropriate procedural and equipment modifications were made, these results were duplicated on a 200-gal scale by Rust Engineering Corp., operators of the DOE-Albany facility. A subsequent liquefaction run at Albany succeeded in producing 6 bbls of purely wood-derived oil from prehydrolyzed wood slurry. Thus the chemical feasibility of the LBL approach was demonstrated. In this report the studies on pretreatment which culminated in the successful production of oil at Albany are detailed.

Chemistry of Pretreatment

Wood is composed of carbohydrate, which includes cellulose (about 40%) and hemicellulose (25-30%), and lignin (25-30%). When treated with aqueous acid at elevated temperatures and pressures, the carbohydrate fraction is broken down to its constituent monosaccharides, cellulose yielding glucose and hemicellulose yielding a mixture of mannose, glucose, xylose, galactose, and arabinose. Hemicellulose undergoes hydrolysis much more rapidly than cellulose. Continued exposure to hot, aqueous acid causes the degradation of monomeric sugars to fur-

fural derivatives. Hydrolysis also liberates small amounts of acetic acid, uronic acids, fatty acids, and resinous substances. These are the facts concerning hydrolysis which were taken into account in the design of a suitable pretreatment option.

Data Base for Hydrolysis

Initially we found that the reaction of green Douglas Fir wood chips with water at 250°C gave a char unsuited for pumping or liquefaction. However, the fact that extensive size reduction of the wood chips had occurred by means of chemical action encouraged further efforts along these lines. It was found that the addition of dilute sulfuric acid to the aqueous phase permitted the use of milder conditions for the same degree of size reduction. Approximately a dozen experiments were conducted; the conditions shown in Table 1 were found to be optimal.

Table 1. Data Base for hydrolysis.

Wood/Water Ratio	23/77
Heat-up Time	12 min.
Temperature	180°C
Acid	650 ppm H ₂ SO ₄
pH	2.0
Retention Time	45 min.

Under the conditions specified, the hemicellulose portion is nearly completely hydrolyzed with minimal degradation of the liberated sugars. The reaction mixture is vigorously agitated in order to enhance particle size reduction. This combination of chemical and physical action results in the reduction of the major fraction of wood chips to fine, non-fibrous particles having a bulk density of about 1.4 g/mL. Approximately 30% of wood solids become solubilized so that the concentration of insoluble solids is reduced from 23 to a more manageable 16% during the course of the reaction.

The resulting slurries are quite fluid and appear to be pumpable. However it was found that a minor fraction of partially hydrolyzed wood chips always remain. These could be removed by screening. However, since they are easily crumbled between the fingers, further mechanical treatment such as disc refining may suffice to prepare the slurry for injection into a liquefaction loop.

Ferric chloride and hydriodic acid have also been found to be suitable pretreatment catalysts

provided that the initial pH is 2.0. Material, carbon, hydrogen and energy balances have been found to be 85% or greater.

Several experiments designed to test the liquefiability of prehydrolyzed wood slurries were performed. Under identical conditions prehydrolyzed wood was found to give a slightly higher yield of oil than wood flour.

The results indicate that acid pretreatment affords a promising option to drying and grinding as a method for preparing wood for catalytic liquefaction. Further work will be necessary to establish the technical feasibility of incorporating acid pretreatment into an integrated biomass liquefaction process.

PLANNED ACTIVITIES FOR 1980

A major fraction of the FY 80 effort will be devoted to process development considerations. One major task will be to undertake an investigation of the rheological properties of prehydrolyzed wood slurries. These will be characterized as to viscosities, settling rates, concentration limits and other factors pertinent to the question of their pumpability. Pumpability tests will be conducted in a laboratory scale pumping loop under construction.

Neutralization presents another difficulty. The current liquefaction scheme calls for acid pretreatment slurry to be neutralized with sodium carbonate prior to liquefaction. While neutralization is not a problem technically, it is wasteful and adds expense. Pretreatment and liquefaction could be more economically integrated if either a satisfactory basic pretreatment catalyst or an acidic liquefaction catalyst could be found. Exploratory research along these lines will be continued.

FOOTNOTE AND REFERENCE

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CATALYTIC LIQUEFACTION OF BIOMASS*

*M. Seth, R. Djafar, G. Yu, S. Ergun,
and T. Vermeulen*

INTRODUCTION

Work on this project began in November 1978. We reviewed the literature on the hydrogenation and hydrogenolysis of wood, cellulose, lignin, and sugars. Based on this review, 20 potential catalysts were screened. Both the review and the results of the screening experiments have been reported.¹ These experiments led to the identification of ferric chloride as an effective reagent for wood liquefaction.

The objectives of this project are:

- To undertake bench-scale studies leading to improvements in the present liquefaction process.
- To formulate and conduct exploratory research for the identification and development of new, integrated processes for biomass liquefaction.
- To investigate the characteristics and stability of biomass liquids.
- To explore and develop options for the upgrading and utilization of liquids from biomass.

The selection and development of integrated process concepts generally proceeds in three phases. The first phase involves exploratory catalyst screening. Several potential catalysts are screened at standard conditions based on the chemical approach being pursued. The effect of process variables is then investigated for the most promising catalytic systems. Finally, changes that could result in improved process economics or process operation are tested and evaluated. Two related aspects of the project are concerned with the analysis and characterization of products and with product upgrading and utilization.

ACCOMPLISHMENTS DURING 1979

Exploratory Research on Catalysis

In the task of exploring new catalysts, two chemical approaches are being tested for their application to wood liquefaction. The first relies on the solvolytic depolymerization of cellulose and/or lignin using acidic mixtures of water and wood-derived organic solvents. Hydrogen transfer from partially hydrogenated lignin-derived solvents is the second approach being tested. In this approach tests are being run to see if hydrogen can be added to wood by the acid catalyzed hydride transfer reaction. We will also test the use of organometallic catalysts and other hydrogenations and decarboxylation catalysts.

Solvolytic Degradation/Hydrogenation System

Several hydrogenation catalysts have been tested for the production of liquids from wood, cellulose, lignin and sugars.^{2,3,4} In order to hydrogenate wood over a solid catalyst, the wood must first be depolymerized to fine particles or to material soluble in a carrier solvent. The depolymerization and hydrogenation steps could be integrated if a fraction of the products of wood hydrogenation could be used as the carrier solvent. Solvolysis in an acidic medium could be used for the depolymerization of cellulose (and lignin). If the carrier liquid is also a good solvent for the products of solvolysis, a substantial fraction of the wood could be put into solution.

Methanol, ethanol, propanol, ethylene glycol and glycerol were screened in order to test the effectiveness of alcohols as recycled solvents for the solvolytic degradation of wood. Phenol and catachol were selected as representative lower molecular weight lignin-derived solvents for testing.

All screening experiments were run in a 300 mL Parr reactor. About 15g of wood, 30g of acid and 30g of the organic solvent were weighed into a glass liner. The liner was then placed in the reactor and the reactor sealed. The reactor was charged with 200 psig hydrogen and 200 psig carbon monoxide. The reactor was then heated to temperature and held there for one hour. At the end of the run the reactor was quickly quenched to room temperature.

Products were separated into fractions soluble in toluene, acetone, reaction liquor (i.e., the acidic-solvent medium), and the remaining insoluble residue. Toluene solubles ranged from about 1% of dry wood for hydrolysis (in a pH of 2.5), to 22% for propanol. With most other organic solvents the toluene soluble material ranged between 2 and 10%. Acetone solubles ranged about 5% for solvolysis with propanol to about 36% with catachol. Up to 60% of the wood was converted to material soluble in the reaction medium at room temperature. Catachol and phenol gave the lowest yields of insoluble material (2% and 9% of the wood, respectively). Ethylene glycol was the solvent that resulted in the lowest yield of insoluble residue amongst the alcohols (18%).

Hydride Transfer

Hydrogenation of solid hydrocarbons such as coal can occur by the donation of hydrogen from organic liquid molecules. Thermal cleavage of bonds followed by hydrogen abstraction from the solvent is the basis of SRC-type coal liquefaction processes. It may be possible to catalytically transfer hydrogen from hydrogen-rich solvents and so effect the reduction of hydrocarbonaceous feeds at lower temperatures.

Two representative solvents, cyclohexadiene and α -phellandrene (5-isopropyl - 2-methyl - 1,3 cyclohexadiene), were selected for testing. Each solvent was run at 250°C for one hour with aqueous sulfuric acid pH of about 2.5 and 3. The reaction procedures used were exactly the same as those for the solvolytic degradation experiment.

In the experiments, about 75-80% of the wood was solubilized. Acetone soluble yields were between 30 and 35% with cyclohexadiene and 22% with α -phellandrene within the range of our tests acid pH seemed to make little difference to yield and atomic H/C and O/C of product fractions for both solvents. Extensive alkylation of products occurred when α -phellandrene was used as the solvent.

During the next year we will extend the study to other potential hydride transfer solvents. The effect of acid pH, reaction time and reaction temperature on the yield and quality of products will be explored. Spent solvents will be analyzed to determine the extent of hydrogen transfer.

Investigation of Process Variables

The effect of process variables are being studied for three catalytic systems. Sodium carbonate catalyzed liquefaction in an aqueous medium (LBL process) is the first catalytic system undergoing tests. The effect of catalyst concentration, reaction time, and slurry concentration are being determined at a reaction temperature of 360°C. In the second catalytic system, the effects of catalyst concentration, slurrying solvent, and reaction time are being tested for the ferric chloride at reaction temperatures of 250 and 360°C. We expect to begin testing the hydrogen iodide system, our third catalytic system in the near future.

Aqueous Sodium Carbonate System

The Bureau of Mines (BOM) process uses a mixture of aqueous sodium carbonate and recycled oil as the carrier solvent for wood liquefaction, whereas the LBL option relies on the acidic hydrolysis of wood chips followed by sodium carbonate catalyzed liquefaction in an aqueous medium. The effect of process variables on the aqueous (LBL) system has, however, never been systematically evaluated. We have recently begun to determine the effect of catalyst concentration, slurry concentration and reaction time on the yield and quality of the products obtained during aqueous sodium carbonate catalyzed liquefaction.

All sodium carbonate experiments were run in a one-liter autoclave reactor. About 50g of wood flour and 220g of aqueous sodium carbonate solution was used for each run. The autoclave was charged with 300 psig of H₂ and 300 psig of CO. The reactor and its contents were heated to 360°C in 40-55 min and held there for the desired reaction time. At the end of the run the autoclave was cooled and the products removed.

Total water solubles (i.e., material soluble in the reaction liquor plus material obtained by water extraction) were determined for selected

experiments. In each case between 17 and 19% of the starting wood appeared as water-solubles. In the absence of sodium carbonate only 4% of the products dissolved in water.

Insoluble residue ranged from 2 to 8% of the wood and generally increased with decreasing sodium carbonate concentration. When no sodium carbonate was present about 25% of the wood was obtained as an insoluble residue.

Between 42 and 47% of the original wood was accounted for in each run where catalyst was present, and about 50% of the original wood was recovered in the absence of a catalyst.

To characterize product fractions, ultimate analysis was done for each fraction of products obtained. Among the soluble fractions, the toluene solubles contained the least amount of oxygen per carbon atom (O/C = 0.11). Atomic O/C ratios of the acetone solubles were comparable to those of the toluene soluble material. The toluene soluble fraction had an atomic H/C of 1.25 which was significantly higher than that of the acetone soluble fraction (H/C = 0.18). Fractions soluble in water had similar O/C ratios (about 0.66), whereas product soluble in the reaction liquor had a considerably higher H/C ratio than product obtained by extraction with water. About 67% of the initial carbon was recovered in the various product fractions.

Average molecular weights and spectroscopic analysis of different product fractions is underway. More conclusive comments on the nature of the products may be possible when additional information becomes available.

Ferric Chloride System

In the LBL modification of the BOM process, wood chips are hydrolyzed with dilute acid to form a pumpable slurry which is then liquefied using a basic catalyst (sodium carbonate). Another option would be to use an acidic catalyst effective both for hydrolysis and liquefaction. Initial screening experiments¹ indicated that ferric chloride may be a good reagent for liquefaction. Dilute solutions of ferric chloride may be a good reagent for liquefaction. Dilute solutions of ferric chloride were also found to hydrolyze wood chips. The ferric chloride system is being further evaluated by testing for the effect of process variables on the yield and quality of the products.

The effect of ferric chloride concentration, reaction time and reducing gases on the yield of product fractions were determined both for wood flour and pre-hydrolyzed slurries at 180 and 250°C. Products were fractionated into acetone and toluene solubles.

The insoluble residue obtained usually varied between about 28 and 45% of the starting wood. Within this range an increase in ferric chloride concentration led to a small reduction in insoluble solids at 180°C. Ferric chloride concentrations higher than 1.2% appeared to have little effect on the yield of insoluble solid at 250°C for reaction times of 1 hour or more.

Where no reducing gases were used, the toluene-soluble fractions of the product appeared to depend on reaction time and ferric chloride solution concentration at 180 and 250°C. At the lower temperature an increase in residence time from 1 to 2 hrs resulted in a decline in toluene solubility from about 14 to 0.4%.

Our research on the Ferric Chloride System indicates the following:

- Presence of reducing gases (CO/H) is beneficial for liquefaction with ferric chloride.
- A complex set of reaction occur where toluene-soluble materials are further converted to products soluble in either water or acetone.
- Reaction conditions could be tailored to obtain any of a wide span of products (as indicated by their solubility characteristics)
- In order to be of possible commercial use, the ferric-chloride system must be modified so as to convert the large fraction of insoluble material to more desirable products.

We plan to continue studying the ferric chloride system in the future. The feasibility of using co-catalysts that enhance the yield of liquids and the use of non-aqueous slurries will be explored.

Product Characterization and Stability Studies

So far the major effort in this task was geared toward developing adequate separation procedures. Methods for separation of products for each catalytic system have been discussed in the appropriate sections.

We have also begun spectrometric analysis and molecular weight determinations of selected product fractions, which will enable us, we hope, to better understand possible chemical structures in product fractions.

During the next year we plan to test a variety of methods for the characterization of wood-derived liquids. Thermal and oxidative stabilities of liquid products will also be evaluated.

PLANNED ACTIVITIES FOR 1980

Activities planned for 1980 have been mentioned above. Other work, to begin in March 1980, is briefly summarized below.

Investigation of Process Improvement Options

The objective of this task will be to test and evaluate modifications that could lead to improved process economics. In particular, changes that could result in higher slurry concentrations, better product quality, higher oil yield, and reduced heat transfer and separation costs will be identified and tested. As a first step, we plan to evaluate changes in slurry solvent composition and the use of co-catalysts. As more information is collected other areas of interest may become apparent, and these will be further evaluated if necessary.

Product Upgrading Utilization Options

The objective of this task will be to screen several potential methods for upgrading the utilization of products obtained from biomass liquefaction. Potential uses for biomass liquids will be suggested once sufficient chemical and physical characterization has been completed. Several solid hydrogenation, hydrogenolysis, and decarboxylation catalysts will be tested for their effectiveness in further upgrading biomass liquids so as to obtain a wider range of liquid fuels.

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MONITORING THE BIOMASS LIQUEFACTION PROCESS DEVELOPMENT UNIT AT ALBANY, OREGON*

S. Ergun, C. Figueroa, and C. Karatas

INTRODUCTION

Serious efforts to convert biomass to oil were initiated by the Bureau of Mines, Department of Interior, during the late 1960s. The Bureau's efforts were culminated by the design and construction start-up of a process development unit (PDU) at Albany, Oregon early in 1974. It was expected that the construction of the facility would be completed during the third quarter of 1975 and supporting research and analytical work necessary for the development activity would be provided by the Pittsburgh Energy Research Center and Albany Metallurgical Research Center of the Bureau of Mines.

During 1974, the Energy Research and Development Agency (ERDA) was established and the biomass liquefaction program was transferred to ERDA's Solar Energy Division. During the transition period, ERDA authorized a number of reevaluation studies regarding the economics of producing oil from biomass, best use of the facility under construction, options for modifying the PDU and experimental programs that could be undertaken. In all of these studies construction completion and a genuine effort for process development were recommended.

The construction of the PDU was completed at the end of December 1976. Bechtel National, Inc. was awarded the contract to commission the facility, affect the modifications indicated in the earlier ERDA studies and to conduct some test runs. The Bechtel contract was for one year; it was extended for another six months (on a monthly basis) pending the responses to an RFP issued by ERDA for a two year development program. The Rust Engineering Company was awarded the contract to operate the facility for two years starting July 1978.

The following is a brief account of the results of the monitoring efforts undertaken by LBL in biomass liquefaction.

ACCOMPLISHMENTS DURING 1979

LBL monitored the Albany operations through an independent analysis of the raw data obtained, and plant modifications proposed and planned. LBL stationed a chemical engineer at Albany for a period of three months in order to become fully familiar with equipment, operating procedures, and data acquisition.

Analysis of production difficulties, coupled with in-house research, led LBL researchers to seek alternative processes. A literature survey by LBL revealed that catalysts other than sodium carbonate had been utilized by researchers in converting wood and wood components (especially lignin and cellulose) into oil and chemicals (phenols, high boiling alcohols, etc.). Promising catalysts were evaluated.

An LBL analysis of all of the data obtained at Albany led to the following conclusions regarding the involuntary termination of all of the runs conducted during 1977 and 1978:

- 1) Remedy for operational problems is not likely to be found by altering the operating conditions (wood/oil ratio, catalyst/wood ratio, temperature, pressure, residence time, agitation levels, etc.).
- 2) The cause of the difficulty is likely to be related to the process chemistry.
- 3) It could be pinpointed by investigating the performances of the various process units one by one, by isolation if possible.

Researchers conducted a comprehensive test run that established the following conclusions about the existing process:

- 1) A major portion of sodium salts remained in the solid residue, and not in the aqueous phase.
- 2) The centrifuge was not designed properly to separate relatively small amounts (<10%) of aqueous phase from an oil phase.
- 3) Densities of oil and salt-laden solid residue being about the same, neither the available three-phase centrifuge or a rented sludger could separate the solid phase.

In April, 1979, after consultation with Rust Engineering Company (the plant operators), LBL issued an operating directive to test the chemical and technical feasibility of a modified process that appeared promising on the basis of results obtained at LBL. This test run was conducted during the first week of May, 1979, and for the first time an oil derived from wood was obtained in large quantities.

Noting that the number of tests that can be conducted at Albany are limited and would be insufficient for a systematic investigation of the influences of the various process variables to arrive at optimum conditions, LBL proposed the construction of a continuous process evaluation unit that would simulate the Albany Facility and incorporate a tubular reactor that is lacking at Albany. During FY 79, LBL designed, fabricated and procured the necessary equipment for the continuous unit shown schematically in Fig. 1. The objectives of this engineering effort are:

- 1) To screen the influences of process variables and provide a data base for

the test runs that can be conducted at Albany.

- 2) To provide engineering data regarding heat, momentum transfer, and reaction rates for the design of a reactor and other process units that may be (or has to be) incorporated into the Albany facility.
- 3) To screen, under continuous flow conditions, promising process concepts that may come from bench-scale batchwise experiments being conducted at participating laboratories and to provide firm data base for pilot scale reactor design.

The construction of this unit will be completed in December 1979. It is anticipated that the unit will be operational during February, 1980. The expected oil production rate is between 2.5 to 5 gallons per day if operated on a 24 hour basis.

In summary, the PDU monitoring effort by LBL consisted of the following efforts:

- 1) To overcome the mechanical and operational difficulties of the existing facility.
- 2) To examine the chemical, technical, and economic feasibility of the Bureau of Mines Liquefaction Process.
- 3) To develop and evaluate the feasibility of an alternative process.
- 4) To undertake supporting research.

PLANNED ACTIVITIES FOR 1980

Project Evaluations and Novel Process Concepts

Various research institutions are conducting research solely dedicated to biomass liquefaction. LBL will provide DOE with an independent evaluation of the technical progress made in the projects authorized by DOE based on reviews of reports issued and analyses of data provided. As in FY 79, LBL

will provide DOE with evaluation of projects that may have produced promising results or may have been brought to the attention of DOE because of attractive claims or discoveries. The technical approach by LBL for the evaluation and enhancement of such results and/or claims will be the same as in FY 79.

In FY 80, it is anticipated that LBL will follow a process scheme advanced by SRI that involves molybdate salts as a catalyst. The preliminary results reported indicate the synthesis of a high quality oil (toluene soluble) with reasonable large yields (57%). Another scheme worthy of following is the biomass thermolysis advanced by Wright-Malta and Pacific Northwest Laboratory.

The third promising scheme planned for investigation concerns dissolution of wood by chemicals derived from hydrogenation followed by catalytic hydrogenation of dissolved wood. It is now under scrutiny.

Monitoring

In FY 80, LBL formulated and issued an operating directive to remedy or correct the short-cuts or improvisations made at Albany in producing six barrels of oil using the LBL process, because they concern the technical and economic feasibility of the process in question. If this operating directive is successfully carried out, LBL will issue an operating directive to test the new process option under the condition that assures its technical feasibility.

Research and Engineering Studies

This task is the core of the LBL in-house program. It consists of:

Prehydrolysis and Slurrying Studies

The objectives of this task are 1) to find conditions that maximize wood/water ratio and 2) to provide a data base for design of a continuous prehydrolyzer. The base-line water/wood ratio in

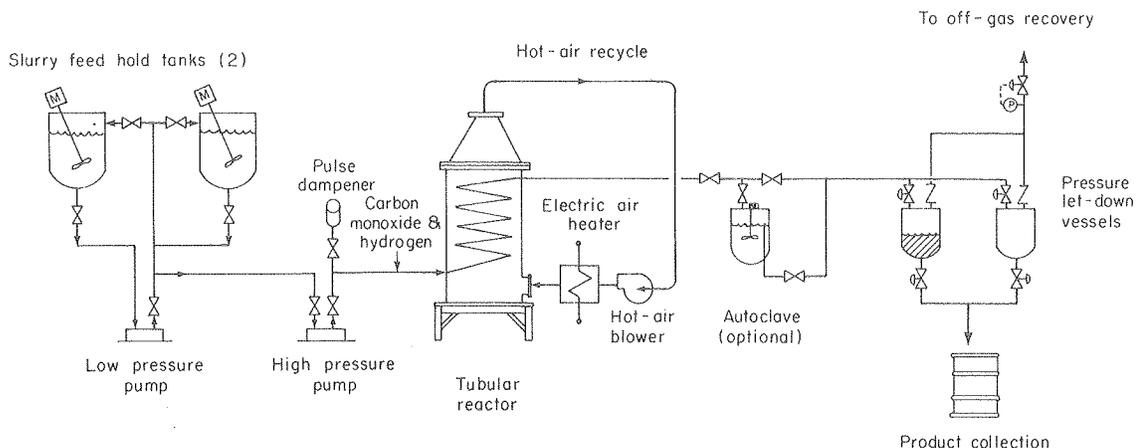


Fig. 1. Biomass liquefaction process evaluation unit LBL process. (XBL 7910-4293)

the LBL process (based on estimates from batchwise experiments) was $77/23 = 3.35$. Recirculation studies already conducted (during October–November, 1979) showed that this base-line condition is technically feasible in a continuous mode of injection. If this ratio can be reduced to $69/31 = 2.23$, it would result in 35% increase in oil production per unit reactor and, at the same time, a 34% decrease in reactor heat input requirement, i.e., the economics of the wood liquefaction process would improve tremendously. For this reason LBL will explore the influences of pH, temperature, time on prehydrolysis. This effort requires tedious analytical work and physical experimentation.

Catalysis Studies

The objective of this subtask is to provide a database for the chemistry and kinetics of liquefaction, product upgrading, etc. This will be accomplished through exploratory research on catalysis, investigation of the influence of process variables and process improvement options, and catalytic hydrogenation of product oil.

Engineering Development

The scope of the engineering development progress is given below:

Continuous Process Evaluation Experiments

- Installation of process evaluation unit (PEU)
- Calibration and shakedown tests

- PEU performance evaluation
 - Evaluation of process variables
 - Database for design
- Exploratory Design Investigations
- Definition of design parameters
 - Acquisition of data required
- Integrated Plant Concepts
- Process flowsheet developments
 - Comparative economic feasibility assessments

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LBL CONTINUOUS BIOMASS LIQUEFACTION PROCESS ENGINEERING UNIT (PEU)*

S. Ergun, C. Figueroa, C. Karatas, and J. Wrathall

INTRODUCTION

Ever since the commissioning and subsequent operation of the Albany, Oregon Biomass Liquefaction Process Development Unit (PDU) in 1977, it became very evident that the PDU would be unable to provide basic reactor design data for a commercial-sized plant. Beginning in 1977, LBL was contracted to provide technical monitoring followed in 1978 by supporting research. LBL research efforts were divided into three areas:

- 1) Biomass liquefaction catalysis
- 2) Biomass pretreatment-hydrolysis
- 3) Construction of a continuous biomass liquefaction PDU.

Discussion centers on the latter of these three areas.

ACCOMPLISHMENTS DURING 1979

The intent of the PEU was to provide engineering support to the Albany, Oregon PDU. However, it later became clear that basic engineering design data for slurry pumping and the reactor would be the final product. Undertaking this task meant long-term planning as high-pressure equipment generally have long delivery times. By January 1979, a detailed schematic for the PEU was finalized as shown in Fig. 1. Major or minor equipment investigations, specifications, and procurement commenced and proceeded into late 1979.

Completion of major piping, electrical, and instrumentation is expected by December 1979. Preliminary shakedown testing will continue for three months, after which a preliminary liquefaction run is expected by March 1980.

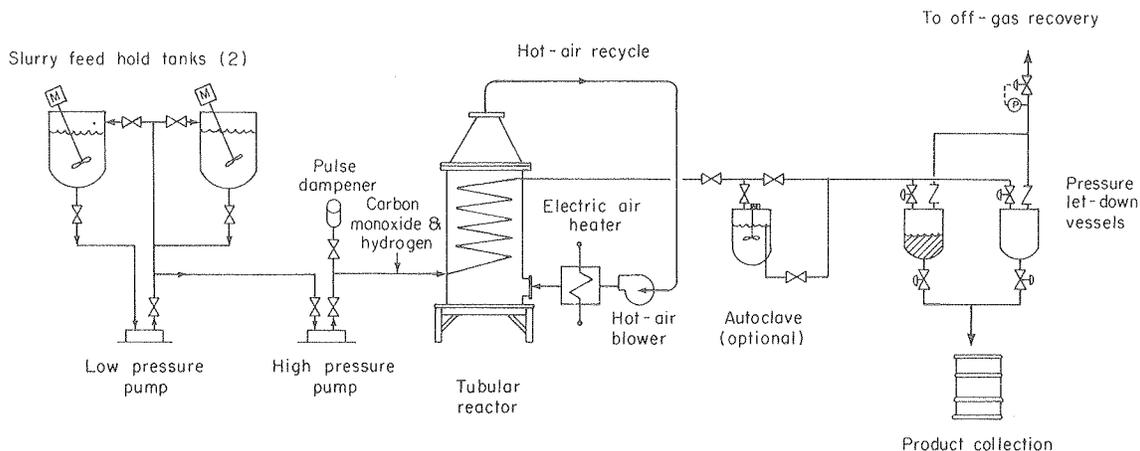


Fig. 1. Biomass liquefaction process evaluation unit LBL process. (XBL 7910-4293)

During the months of October and November, 1979, extensive testing of the PEU slurry pumping capabilities took place and is the subject of an unpublished report.¹ Findings from this study indicate that hydrolyzed biomass slurries of 20% can be easily pumped without any difficulties. The key to this capability apparently lies with the slurry ability to uptake gas (approximately 10% by volume).

FOOTNOTE AND REFERENCE

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SELECTIVE HYDROGENATION OF COAL*

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INTRODUCTION

Coal liquefaction processes currently under development operate by thermal decomposition (pyrolysis) of the coal in a hydrocarbon 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 hydrogen consumption while the latter require special processing (e.g., gasification) for their utilization. The coal pyrolysis is required because pyrolysis temperatures, and solid catalysts can not promote the reaction of the solid coal material.

The objective of this project is to convert coal to liquid products by the use of homogeneous catalysts that promote selective scission of certain bonds in the coal structure below coal pyrolysis temperature. The bonds to be attacked are those

linking conjugated hydroaromatic groups in the coal, including aliphatic bridges and oxygen links (e.g., ether bridges). The catalysts are dissolved in, or constitute, a liquid reaction medium and have 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 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 hydrogen gas are considered to determine the extent to which these processes may limit conversion rates.

This project was initiated in January 1974, and during its first three years concentrated on

studies of the action of organic and inorganic reaction media on sub-bituminous coal and on model compounds. The inorganic melts examined as catalysts include phosphoric acid, sodium hydroxide, and zinc chloride. In 1977, the studies began to focus on use of mixed organic-inorganic treatment media, in particular zinc chloride 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 and single medium under the same temperature conditions.

ACCOMPLISHMENTS DURING 1979

The project activities planned for 1979 were directed mainly to investigation of the effect of treatment parameters on the conversions of coal in zinc chloride/organic mixed media. The work utilized sub-bituminous coal because of its high reactivity under these treatments. The reaction paths were explored by successive treatments at different temperatures and of fractionated intermediate reaction products. Product analyses and characterization were emphasized to provide insight into the manner by which treatment parameters influence conversion, and proposed reaction mechanisms were treated through model compound studies. Reaction rate studies were also conducted for coal-solvent and coal-melt-solvent interactions.

Interaction of Coal with Organic Solvents

(Grens, Zieminski)

The rate of dissolution of coal in hydroaromatic organic solvents was studied over the temperature range 200-300°C in specially designed apparatus having a time resolution of about 30 s (heating, cooling, and sampling times of the order 10 s). The rates of such interactions are important because these solvents serve to promote access of reactive species and catalysts to the coal interior structure and to remove reaction products from the coal.¹ Studies of Wyodak coal in tetralin show relatively slow overall dissolution kinetics (70% of ultimate in 20 minutes) with modest influence of coal particle size. The initial extraction rates for -100 mesh coal significantly exceeded those for -30 mesh, but after 10 minutes the rates were comparable. Stirring rates beyond those required to achieve uniform coal mixing in the solvent had no significant effect. The initial dissolution reaction shows an apparent activation energy of around 8 kcal/gmole, and apparently is both reaction and pore diffusion controlled. The dissolution mechanisms will be further examined in the coming year.

Coal Conversion in Zinc Chloride/Tetralin Mixtures

(Grens, Edwards, Hershkowitz, Maienschein)

During the past year, our investigations of coal conversion in mixed organic-inorganic media have been primarily on one two-phase system, zinc chloride/tetralin, and one single-phase system, zinc chloride/methanol. In both cases detailed investigations of reaction conditions and product properties have been undertaken.

The treatment of coal in zinc chloride, tetralin media has usually involved 50 g of Wyodak sub-bituminous coal with 300 g of ZnCl₂ melt (10% H₂O) and 50 g of tetralin.² The rates of conversion to oils (cyclohexane solubles), asphaltenes (incremental toluene solubles), and preasphaltenes (incremental pyridine solubles), have been determined in the 200-300°C temperature range (initial coal pyrolysis is at about 325°C). As shown in Fig. 1, for 300°C treatment, the conversion to preasphaltenes is quite rapid, with subsequent slower conversions to asphaltenes and oils. Experiments in which products were fractionated (into oils, asphaltenes, preasphaltenes, and residue) after short reaction time, and then separately treated for additional time, establish that conversion proceeds through preasphaltenes and asphaltenes to oils, as well as directly from preasphaltenes to oils.

It has been previously noted that conversion of Wyodak coal by this procedure is accompanied by large reductions of the oxygen content of the coal, and certainly involves catalytic scission of oxygen linkages in the coal. We have examined this phenomenon in more detail by chemical analyses of the coal and coal products, for hydroxyl and carbonyl oxygen, and by difference for other (largely ether) oxygen content. These studies have established that the conversion of coal to preasphaltenes involves major reductions in ether oxygen (the carbonyl oxygen content is small), while the conversion of preasphaltenes to oils involves removal of hydroxyl oxygen.

The analysis of soluble products from the reactions indicates a relatively uniform decrease in molar H/C ratios of these products with increasing extent of conversion, as illustrated in Fig. 2, extending over a wide range of treatment media and temperatures. The products of more complete conversion have lower H/C ratios than the original coal (1.0 in the coal). Examination of residues as well as extracts indicates significant internal hydrogen transfer in the processes.³ The molecular-weight distribution in the products is characterized by gel-permeation chromatography in pyridine and (for oils) in tetrahydrofuran. Representative

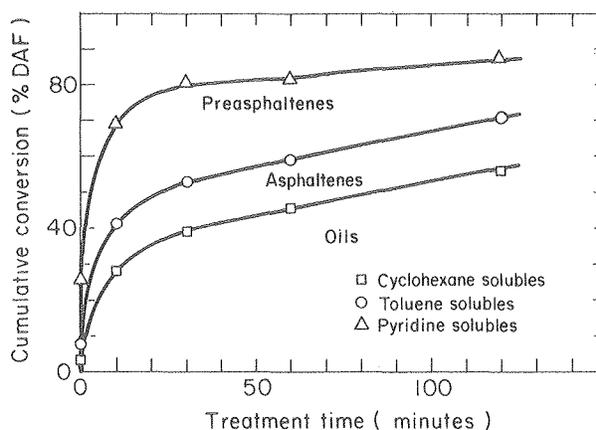


Fig. 1. Effect of treatment time at 300°C. 50 g Wyodak coal + 275 g ZnCl₂ + 50 g tetralin + 35 bar H₂. (XBL 801-75)

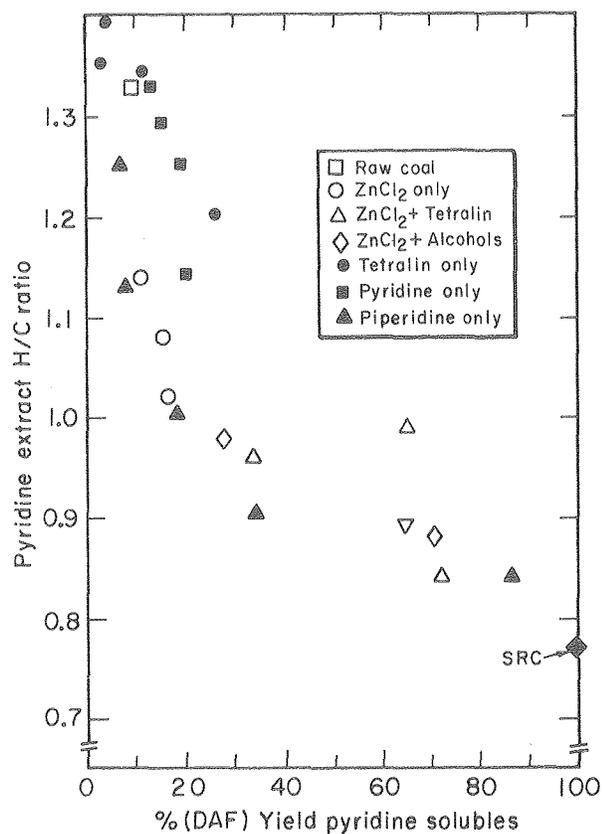


Fig. 2. Wyodak coal extracts after treatments in various media at 200 to 300°C. (XBL 7811-3698)

chromatograms are given in Fig. 3; the high-MW peak for preasphaltenes represents colloidal material that slowly precipitates in the pyridine solution. The wide molecular-weight ranges, and large degrees of overlap, of these fractions is apparent. Although the characterization into oils, etc., by fractional solubility is a standard procedure in coal research, its validity as a measure of meaningful product characteristics is extremely limited, and alternate characterizations are being investigated.

The coal conversion products also are examined by proton NMR spectrography for the aromaticity of their hydrogen content and, indirectly, of their carbon structure. Typically the oils produced have aliphatic-to-aromatic hydrogen ratios of about 1.7, and Brown-Ladner carbon aromaticities of about 0.7; these are far less aromatic materials than those produced by higher temperature conversion methods such as the solvent-refined coal process.

The zinc chloride/tetralin treatment studies are now being extended to determine the effect of inorganic melt acidity and water content on product yields and properties. The treatments are also being applied to model compounds, including those with hydroaromatic and aromatic nuclei linked by ether and aliphatic bridges, to investigate the mechanisms and kinetics of action on specific bond types.

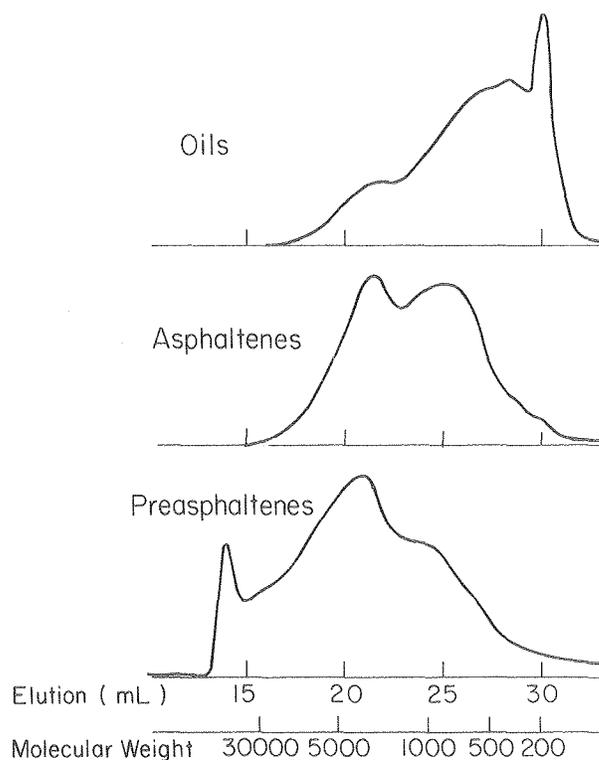


Fig. 3. Gel permeation chromatogram of products Wyodak coal with ZnCl₂ + tetralin 300 C and 25 bar H₂ for 1 hour. Pyridine carrier - 1 mL/min 100A + 500A + 1000A styragel 313 nm UV detector. (XBL 801-74)

Coal Conversion in a Zinc Chloride/Methanol Melt

(Vermeulen, Onu)

When methanol addition is used in zinc chloride melt treatment of sub-bituminous coal (serving to depress the ZnCl₂ melting point), relatively high conversions to solvent-soluble products are obtained. Total-conversion levels approaching 90% at 250°C, and 95% or better at 275°C, were reported for 1978.^{3,4}

Efforts to extract the products from the melt-coal suspension at 250°C with decalin or other high-boiling solvents have been only partially successful, suggesting that the preasphaltene fraction is strongly complexed with the zinc chloride. This finding has focused special attention on the need to obtain a high conversion of preasphaltenes to lower-molecular-weight products.

Two effects have been utilized to reduce the preasphaltene content of the products--addition of zinc metal to the ZnCl₂ melt, and staged increases in processing temperature.

Higher molar hydrogen-carbon ratios appear to correlate with increased production of oils. The addition of metallic zinc to the zinc chloride/

Table 1. Effect of zinc metal addition to $ZnCl_2$ melt, in treatment of Wyodak coal at 275°C (or 300°C) for 30 minutes (50 g coal with 30 g melt).

Run No.	Pressure of H_2 (bar)	Additives	Extractibles, daf Basis %			Atomic H/C
			Oil	Asph.	Preasph.	
5	35	10% CH_3OH , 10% $CaCl_2$	17	14	57	0.89
2	35	same + 1.5% Zn	28	.11	35	1.02
43	55	14% CH_3OH	22	15	63	1.01
44	55	14% CH_3OH , 1.5% Zn	30	16	54	1.03
51	55	14% CH_3OH , 3% Zn	32	15	53	1.05 est.
54 ^a	55	10% CH_3OH	17	14	61	0.88
77 ^a	55	14% CH_3OH , 3% Zn	33	17	50	1.04

^a300°C

Table 2. Effect of temperature staging in treatment of Wyodak coal at 55 bars hydrogen, with 3% Zn and 14% CH_3OH (50 g coal with 300 g melt).

Run No.	Temp (°C)	Time (min)	Extractibles, daf Basis, %			Atomic H/C
			Oil	Asph.	Preasph.	
70	275	15	31	14	54	1.00
51	275	30	32	15	53	1.05 est
63	275	45	35	15	48	1.09
76	{ 275 300 }	{ 15 15 }	37	18	45	1.10
69	{ 275 300 325 }	{ 15 15 15 }	46	10	44	1.10
73	{ 275 300 325 }	{ 15 15 30 }	54	10	36	1.19
74	{ 275 300 325 340 }	{ 15 15 15 15 }	51	9	40	1.13
79 (without Zn)	{ 250 275 300 325 }	{ 10 10 10 10 }	27	10	63	1.09
78 with Zn)	{ 250 275 300 325 }	{ 10 10 10 10 }	40	15	45	1.06

methanol melt appears to increase the yield of oils and also to prevent low H/C values, as is shown in Table 1. It appears possible that the zinc dissolves into the melt to form catalytically active monovalent-zinc ions such as Zn_2^{++} .

The question of time-temperature relations and the selection of optimum temperatures sequences has been studied in several comparative runs for the $ZnCl_2$ /methanol treatment. It has appeared likely that different types of bonds have different thresholds for $ZnCl_2$ -catalyzed scission, as well as for thermal pyrolysis, and hence that higher-temperature treatment will give more complete conversion.

In Table 1, comparison between run 51 at 275°C and run 77 at 300°C shows almost no advantage for the higher temperature. However, in Table 2, run 76 at 275°C and 300°C in succession is clearly superior to run 51 entirely at 275°C (both for 30 minutes). Adding 15 minutes at 325°C (run 69) or 30 minutes at 325°C (run 73) produces highly significant improvement. The results for run 77 may show that treatment at 300°C or above should be preceded by treatment at 275°C.

Pushing the reaction mixture of 340°C for 15 minutes (run 74) appears to reverse the beneficial effect of 325°C, possibly by fostering coke-forming reactions. Run 78 can be considered kinetically similar to 15 minutes at 275°C and 15 minutes at 325°C, and indeed comes out between runs 76 and 69. Thus, while pretreatment at 275°C appears beneficial, pretreatment at 250°C seems to impart no further advantage.

The inference from these runs is that a sequence of 275°C briefly and 325°C for a longer period will give the lowest residual preasphaltene in the shortest total time. The possibility remains that tetralin added to the methanolic $ZnCl_2$ will give still better conversion. Comparison of run 73 with the tetralin/aqueous $ZnCl_2$ results (Fig. 1) shows about the same total for preasphaltene plus insoluble residue after 60 minutes of treatment. These combined treatments will be further studied during the coming year.

Slurry-Reactor Development for Coal Conversion by Zinc Chloride Melt

(Vermeulen, Joyce)

In a consideration of large-scale reactor concepts for melt treatment of coal, it has been concluded that a plug-flow type of reactor can be used, with minimum costs for both construction and maintenance. The reactor should operate with downflow of slurry and counterconcurrent (upward) flow of hydrogen. To achieve a relatively uniform gas flow of hydrogen and minimize the excess input of hydrogen, the input hydrogen can be fed at several levels (perhaps five).

Because water is produced from the original oxygen content of the coal, residual hydrogen should be withdrawn near the mid-height of the reactor to insure that water does not accumulate by reflux in the melt and correspondingly lower its catalytic activity.

It is projected that slotted trays could be used to reduce backmixing of the slurry by equalizing the pressure drop throughout each cross section of the reactor. The trays would restrict axial mixing in the slurry, and might also enhance the hydrogen holdup and the interfacial area available for gas-liquid mass transfer.

Exploratory mass-transfer measurements at room temperature have been made (on helium in a nitrogen carrier gas stream) with zinc chloride solutions in water, glycol, and glycerol, to determine whether zinc chloride exerts any special adverse physical effects (such as foam formation) on mass transfer. Slurry viscosities up to 100 centipoise, simulated by viscous solutions, showed an inverse square-root dependence of mass-transfer rate upon viscosity, in agreement with existing correlations. Even at the upper viscosity level, the mass-transfer rate projected for hydrogen under reaction conditions is approximately ten times the anticipated chemical rate of hydrogen consumption by the coal contained in the slurry.

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*This work was supported by the Director, Energy Research, U.S. Dept. of Energy.

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COAL DESULFURIZATION*

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INTRODUCTION

The many coals of the United States were formed under a wide variety of conditions and, as a result, display a wide range in all properties of interest. For example, pyrite weight percent varies from nearly 0 to 20%, while organic sulfur varies from 0 to 10%. These two properties can be used to classify coals for optimum end use.

Coal is most economically used as a direct boiler fuel. However, motor fuel supply cannot drop significantly without serious economic and social disturbance. Thus coal, by necessity, must also serve as a feedstock for liquefaction processes as petroleum availability declines.

Direct Burning of Coal

A combination of environmental and economic considerations dictates the amount of sulfur that can be emitted by coal-fired facilities. This, in turn, sets limits on the amount of sulfur in the coal to be burned. Other properties, such as free-swelling index, mineral matter composition, and volatility determine whether a particular coal can serve as a boiler fuel. Thus, both environmental and technical considerations enter into selection of boiler fuels.

Applicability of Cleaning Processes to U.S. Coals

Since current coal cleaning processes remove only a fraction of the total sulfur,¹ the question arises as to what fraction of U.S. coals can be cleaned to comply with current EPA new source standards (1.2 lb. SO₂ per MBtu). A number of studies have shown the fraction to be encouragingly large. A report on the applicability of the Meyers process² estimates, on the basis of 35 coals sampled, that 40% of the samples could be burned cleanly after some combination of physical separation and chemical leaching.

A report by Ergun³ on coal cleaning gives the higher estimate of cleanability of 56%, based on 455 samples properly weighted between Eastern and Western coals. Beyond this figure, Ergun estimates an additional 17% is cleanable if 30-40% of the organic sulfur is removed, bringing the total cleanable to 73%.

Data from a study by Cavallaro,⁴ with coal reserves taken from a study by Beekers,⁵ give an estimate in agreement with that of Ergun on the amount of coal cleanable by pyrite removal.

In summary, it can be seen that cleanable coal reserves increase by 33% if processes are used which can remove what are probably the more reactive organic sulfur species,⁶ such as aliphatic

mercaptans, sulfides, and disulfides. A process which attacks the refractory thiophenic sulfur could conceivably increase the cleanable coal reserves by another 20 - 30%, assuming roughly equal distribution between reactive and refractory organic sulfur.

History of the Project

Prior work concentrated on developing and evaluating separate methods for removing both inorganic and organic sulfur from coal. A kinetic study of reductive desulfurization of heteroaromatic coal subunits (organic sulfur) was extended to the upgrading of a heavy residuum produced by solvent refining of coal.⁷ Exploratory work on combustion of coals with sulfur-trapping salts indicated the possibility of a technically and economically feasible method of coal utilization that could be implemented with a minimum of process development.⁸

Sodium sulfides were found to attack pyrite (inorganic sulfur) with limited success,⁹ while preliminary research into oxidative pyrite leaching showed that a concentrated ferric acid solution (Fe₂(SO₄)₃ + H₂SO₄) offered both kinetic and by-product recovery advantages over a similar process developed elsewhere.¹⁰

ACCOMPLISHMENTS DURING 1979

LBL is involved in five aspects of research on pretreatment of coal prior to combustion to decrease sulfur emissions.

The first aspect is development of an acidic oxidative leach process involving H₂SO₄, (a cheap and readily available bulk chemical) in combination with Fe₂(SO₄)₃ and O₂ or possibly H₂O₂. Pyrite oxidation is complete under mild conditions (160°C, 30 atm oxygen pressure). These process conditions have the advantages of recycling the reaction by-products, making it possible to remove the surplus byproducts in a relatively concentrated form that will permit economic recovery, minimizing the costs of chemical feeds for neutralization and of waste disposal, minimizing the raw-water requirements for such a process, and avoiding the formation of elemental sulfur, which requires an additional extraction step in similar presently available processes. As yet, the effect of the acid solution on organic sulfur is minor.

The second aspect involves development of techniques for independent analysis of sulfur forms other than pyrite or sulfate. The first has been directed toward spectrophotometric identification of elemental sulfur, which may be an unwanted by-product of pyrite oxidation, and also a component of raw coals. Both sulfur analysis and pyrite

oxidation are discussed in more detail in Lawrence Berkeley Laboratory Report LBL-9963.¹⁰

Another study has dealt with direct identification of organic sulfur, using x-ray fluorescence. Hitherto, this component has been determined as a difference between inorganic sulfur (pyrite, sulfate, elemental) and total sulfur.

The third aspect considers the question of whether the organic sulfur species in coal can be effectively converted to water-soluble products without serious loss in the coal's calorific value.

The fourth aspect is reductive desulfurization of primary conversion products from raw coal, for example high-sulfur forms of solvent-refined coal. The catalytic action of pyrite in hydrodesulfurization and the physical and chemical factors affecting that catalyses have been an area of study.

The fifth aspect is combustion of coal that has been treated with a "trapping agent," notably an alkali metal base or salt. Chemical costs for such treatment will probably be comparable to those for alkaline or neutral desulfurization, or lower if the cost of oxidizing agent (O₂, air, H₂O₂) is included.

The last three activities and the x-ray analysis technique are discussed in Lawrence Berkeley Laboratory Report LBL-10118.¹¹

PLANNED ACTIVITIES FOR 1980

Prior to any studies of reductive or oxidative coal desulfurization processes in the continuous units at the Coal and Biomass Laboratory at LBL, flow modeling of coal or related slurries will be carried out in order to determine the operating conditions necessary to overcome such problems as settling, channeling, slug flow, and solids holdup.

Several reactor heat exchange systems will be evaluated to determine which is most applicable to the processes being considered. Preliminary kinetic parameters will be developed for the ferric acid pyrite leach, as well as rough cost estimates for any new permutations of the process. A mathematical treatment of the sulfation reaction will be developed and tested with data from either a single-particle or fluid bed flow furnace, in order to obtain a better understanding of sulfur-trapping during coal combustion.

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PROCESSING OF CONDENSATE WATERS FROM SOLID-FUEL CONVERSION

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INTRODUCTION

Nearly all approaches for converting solid fuels (coal, oil shale, biomass) to gaseous or liquid fuels produce substantial amounts of process-condensate water. This water is formed by condensation from the reactor effluent as it is cooled. It typically contains large amounts of ammonia, carbon dioxide and dissolved organics. In some cases there are also substantial quantities of nonvolatile salts and sulfur-containing compounds. There are also toxic substances, such as polynuclear aromatics, nitrogen heterocyclics, and cyanides. Water supply, environmental considerations and process economics dictate that such waters be purified sufficiently to allow a high degree of recycle.

Conventional biological treatment has often given poor results for these condensate waters. Also, biological-treatment processes are highly sensitive to upsets in feed concentration and are of questionable value for various refractory substances, such as trihydric phenols (trihydroxybenzenes). Consequently, the thrust of this project is process research directed toward physico-chemical treatment methods, such as combinations of solvent extraction and stripping, followed by carbon adsorption if necessary, to provide sufficient removal of organics and ammonia to allow recycle as cooling-tower make-up.

Process condensates from coal conversion contain large amounts of phenols. Among these, the di- and trihydric phenols are the most difficult to remove. They are also strong precursors of color. Hence the project is directed toward development of effective extraction solvents for these compounds. Another area of concern is innovative and effective combination of stripping and extraction processes to reduce the large energy (steam) requirement for stripping of ammonia. Ammonia is difficult to strip because of chemical interaction of the basic ammonia with CO₂, H₂S and carboxylic acids in aqueous solution.

The project was started in October 1977. Through 1978, accomplishments included characterization of phenolic compounds present in process condensates from the SRC liquefaction process and the Synthane gasification process, using flame-ionization gas chromatography, mass spectrometry and high-performance liquid chromatography.¹ It was confirmed that darkening of the waters is associated with pyrocatechol, resorcinol, and possibly other polyhydric phenols as well. Initial explorations were made of the effect of pH on equilibrium distribution coefficients for extraction of phenolics. This question is of importance since the pH of condensate waters tends to be in the range 8.0 to 9.5, where applicable fractions of the phenolics can be ionized.

ACCOMPLISHMENTS DURING 1979

Analysis of Water Samples

The analyses by gas chromatography and liquid chromatography (HPLC) described in the 1978 report were extended to demonstrate the existence of 610 ppm of a trihydric phenol, phloroglucinol (1,3,5-trihydroxybenzene), in an aged sample of condensate water from the SRC coal-liquefaction demonstration plant in Ft. Lewis, Washington.¹ This is the first quantitative report of a trihydric phenol and is significant since nearly all previous analyses of coal-conversion condensate waters have been conducted in ways that would not reveal trihydric phenols, and since the trihydric phenols are quite resistant to biological oxidation.

Extraction of Phenols

Measurements of equilibrium distribution coefficients for solvent extraction of various phenols from synthetic aqueous solutions were made for several purposes--(1) to assess the relative capacities of different solvents, (2) to determine the relative distribution coefficients for different mono-, di-, and tri-hydric phenols, (3) to quantify the effect of pH on the equilibrium distribution coefficients for different phenols in various physical solvents, and (4) to determine the effect of temperature on the equilibrium distribution coefficient.

Effect of pH

Figure 1 shows equilibrium distribution coefficients for extraction of resorcinol (1,3-dihydroxybenzene) from water into diisopropyl ether (DIPE) as a function of aqueous-phase pH.¹ DIPE is the solvent in the Lurgi Phenosolvan process. The solid curve represents the prediction of a model based upon the assumption that the non-ionized portion of the resorcinol distributes between phases in accord with the distribution coefficient at low pH, while the ionized portion is totally non-extracted:

$$K_D = \frac{K_{D, \text{low pH}}}{(K_a/[H^+]) + 1} \quad (1)$$

Here, K_D is the equilibrium distribution coefficient (wt. fraction in solvent phase/wt. fraction in aqueous phase), and K_a is the acid dissociation constant for resorcinol. $K_{D, \text{low pH}}$ is a fitted parameter, and K_a is taken from the literature. Similar results for extraction of other phenols into DIPE and MIBK also confirm the applicability of Eq. 1, based upon literature values of K_a .

Table 1 gives values of $K_{D, \text{low pH}}$ determined for different phenols extracted from water into DIPE and methyl isobutyl ketone (MIBK), along with

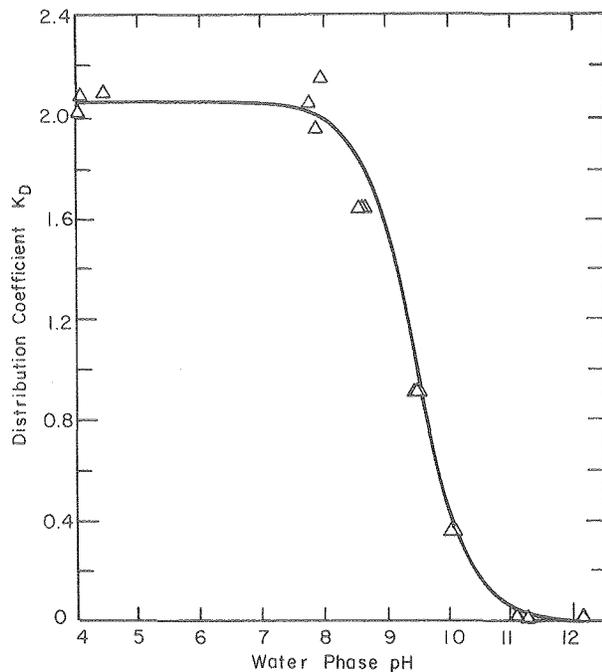


Fig. 1. Equilibrium distribution coefficient of resorcinol at high dilution between DIPE and water vs. pH at 298 K. Solid curve is based upon Eq. 1, with $K_{D, \text{low pH}} = 2.06$ and $K_a = 3.36 \times 10^{-10}$. (XBL 795-6299)

values of K_a determined from the literature.¹ Since condensate waters from solid-fuel conversion processes typically fall in the pH range between 8 and 9.5, one can see from Eq. 1, Fig. 1 and Table 1 that ionization of the different phenols can substantially reduce K_D below the low-pH values.

Polyhydric Phenols

From Table 1 it is apparent that the dihydric phenols are much less extracted than phenol itself, and that the trihydric phenols are even less extracted than the dihydric. This is a direct result of the very low activity coefficients of the polyhydric phenols in water; adding more -OH groups increases water compatibility. Since the polyhydric phenols are known to be present in substantial quantities in coal-conversion condensate waters, they will be substantially more difficult to extract than phenol, cresols, xylenols, etc.

MIBK vs. DIPE

Table 1 also shows that MIBK is much more effective than DIPE for removing polyhydric phenols. An extraction process requires that $K_D S/W$ be 1.5 or more for good removal, where S = solvent flow and W = water flow. Therefore, very high solvent-to-water ratios ($S/W = 1.5$ or more) would be required to remove the dihydric phenols using DIPE, even at low pH, while S/F of 8 or more would be required to remove trihydric. Such large solvent flows would pose a great economic penalty.

Table 1. Equilibrium distribution coefficients determined at low pH (3.8 - 5.8) for different phenols, along with literature values of pK_a . * All values are for 298 K.

Solute	$K_D, \text{low pH}$		pK_a
	DIPE	MIBK	
Phenol	36.5	(90)**	9.98
Pyrocatechol (1,2-dihydroxybenzene)	4.9	18.7	9.48
Resorcinol (1,3-dihydroxybenzene)	2.1	17.9	9.47
Hydroquinone (1,4-dihydroxybenzene)	1.03	9.9	10.1
Pyrogallol (1,2,3-trihydroxybenzene)	ND	3.6	9.01
Hydroxyquinol (1,2,4-trihydroxybenzene)	0.18	5.0	NA
Phloroglucinol (1,3,5-trihydroxybenzene)	ND	3.9	8.44

* - $pK_a = \log_{10} [(K_a)^{-1}]$. The value of pK_a is also the value of pH at which the solute is exactly half ionized.

** - 303 K (Reference 2)

ND - not determined

NA - not available

Effect of Temperature

Since condensate waters are available at temperatures above ambient, extraction at the source temperature would be attractive from the standpoint of minimizing heat exchange. K_D for phenol from water into MIBK was measured as a function of temperature, with the result that K_D decreases as temperature increases, dropping from 90 at 303K to 37 at 348K.² Thus the operating temperature for extraction should represent a compromise between lower K_D at higher temperatures and less cost for heat exchange at lower temperatures.

Stripping of Residual Solvent

Solvents such as DIPE and MIBK have solubilities in waters of order 1%. Hence it is necessary to remove residual solvent before recycle of the water to a cooling tower. Alternatives include atmospheric and vacuum steam stripping, inert-gas stripping, and extraction with a hydrocarbon, such as isobutane. Conceptual-design studies were made for recovery of butyl acetate, DIPE or MIBK by vacuum steam stripping, operating at a pressure near the vapor pressure of water at the feed-water temperature. It was shown that the properties of MIBK are particularly well suited to this sort of recovery process, and that the vacuum steam-stripping approach is economically attractive for recovery of MIBK. This lends further incentive to the use of MIBK as a physical solvent for removal of phenols.

Chemically Complexing Solvents

DIPE and MIBK are solvents which should interact with phenols through simple hydrogen bonding. Solvents which complex chemically in other ways were explored in a search for substances which would give higher K_D values for di- and tri-hydric phenols. Tertiary amines in the tri-C₈ to C₁₀ range have been found to be very effective for extraction of acetic acid, when mixed with a suitable diluent or co-solvent.³ A commercial mixture of such amines (Alamine 336, General Mills, Inc.) was therefore tested as an extractant for the more weakly acidic phenolics.

For resorcinol, K_D was measured for Alamine 336 with four diluents (1/1 volume ratio, amine/diluent) -- 2-ethyl-1-hexanol (2EH), diisobutyl ketone (DIBK), Chevron Solvent 25 (a mixture similar to butylbenzene), and kerosene. Of these, Alamine 336 in 2EH gave the highest K_D , which was 5.0. However, 2EH by itself gave $K_D = 3.7$, so the effect of the amine was not large. For pyrogallol, K_D was 0.9 in 1/1 Alamine 336/2EH, and was 0.7 in pure 2EH. There were also problems of material-balance non-closure for resorcinol and of darkening, suggesting an undesirable loss of the amine as well.

In related EPA-sponsored research, tricresyl phosphate (TCP) was studied as an extractant for phenolics. K_D for phenol into undiluted TCP was 72, and K_D for phenol extracted into mixtures of TCP with MIBK, 2EH, and Chevron Solvent 25 was approximately what would be expected from a simple linear blend of the K_D values for TCP and for the pure diluents. Resorcinol and pyrogallol gave K_D values of 12 and 1.5, respectively, in pure TCP.

Phosphine oxides are stronger bases than phosphates, because of the greater electronegativity imparted to the phosphoryl oxygen by the presence of R- groups rather than RO- groups. Tri-n-octyl phosphine oxide (TOPO) [(C₈H₁₇)₃PO], diluted in DIBK (1 part TOPO to 3 parts DIBK, by volume), was tested as a solvent for pyrogallol, giving a strikingly high K_D value of 110. Some unanswered questions still surround this result, however. Although commercial TOPO has a rather high cost--around \$10/lb--it is obviously worthy of further study as an extractant for polyhydric phenols.

Stripping of NH₃ and CO₂

We have assembled a batch, one-stage nitrogen-stripping apparatus for investigating removal of ammonia and carbon dioxide from condensate waters. We have also implemented and confirmed ion-selective electrodes as means of monitoring these two substances in solution. Initial tests have been carried out with synthetic solutions of NH₄HCO₃ and (NH₄)₂CO₃ in water, with results for ammonia stripping which agree well with predictions from the equilibrium data of van Krevelen, et al.⁴

Wastewater Workshop

Participants from the project organized and conducted a workshop on processing of waters from coal-conversion, shale-retorting and biomass-pyrolysis processes held at DOE headquarters in Germantown in June 1979. The proceedings are in press.⁵

PLANNED ACTIVITIES FOR 1980

A short conceptual-design study will be made to assess the potential for fully physico-chemical, as opposed to biological, processing of condensate waters as a roughing treatment to enable recycle to a cooling tower. This will also identify the more critical questions and opportunities associated with bulk reduction of chemical oxygen demand (COD) by extraction, coupled with NH₃ stripping. Experimental studies of solvent extraction will be directed toward (1) identifying the most effective extraction solvent(s) and processing scheme for bulk COD reduction, and (2) development of improved extractants for polyhydric phenols. TOPO will be examined further as a solvent for phenols, as will any other substance identified as having comparable promise.

These efforts will be supported as needed by analytical studies of condensate waters from demonstration plants. One or more new samples of condensate water from the SRC demonstration plant at Ft. Lewis, Washington will be used to confirm and extend identifications of polyhydric phenols and to make a specific comparison of measured COD with the theoretical oxygen demand (TOD) predicted by adding contributions from individually identified constituents.

The apparatus for batch, one-stage stripping will be used to monitor rates of stripping of NH₃ and CO₂ from water samples from actual processes. These rates will then be interpreted in terms of the equilibrium data of van Krevelen, et al.,⁴ as implemented by Edwards, et al.⁶ and modified to allow for the presence of non-volatile anions and

cations. We shall also initiate experimental and conceptual design studies to assess the potential of an approach which uses two separation processes (e.g., stripping and extraction) simultaneously to remove both acid and basic substances, at a steam consumption less than that required for stripping alone.⁷

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APPLIED BATTERY AND ELECTROCHEMICAL RESEARCH PROGRAM

E. J. Cairns and F. R. McLarnon

INTRODUCTION

LBL, together with the San Francisco Operations Office (SAN), has assumed field management responsibility for the contracts comprising the Applied Battery and Electrochemical Research Program supported by the Energy Storage Systems Division (STOR) of the Department of Energy (DOE). This program provides the applied research base which supports all of the Electrochemical Systems missions in STOR, and the general objective of the program is to help provide electrochemical systems that 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 scale-up. The LBL participants in the program are: E. J. Cairns, L. C. DeJonghe,* J. W. Evans,* F. R. McLarnon, R. H. Muller,* J. S. Newman,* P. N. Ross,* and C. W. Tobias.*

ACCOMPLISHMENTS DURING 1979

This program started during July 1979, and an implementation plan has been prepared, describing how LBL, in cooperation with SAN, will conduct the management responsibilities, delineating appropriate managerial controls to meet the program objectives. LBL is contracting with and directing the activities of project participants. LBL is overseeing the technical status, costs and schedules of the technical projects, providing reports of same to STOR, and establishing appropriate project modifications. LBL maintains overall accountability for successful field management of the program.

PLANNED ACTIVITIES FOR 1980

The technical direction of the Applied Battery and Electrochemical Research Program for FY 1980 and beyond is described in the implementation plan and is designed to support the DOE Electrochemical Systems missions: electric vehicles, solar electricity, dispersed electric load-leveling, and energy and resource conservation. General problem areas addressed by the program 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 STOR, and the establishment of engineering principles applicable to batteries and electrochemical processes. Major emphasis will be on 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 R&D, Engineering Science Research, and Materials Research.

The Exploratory Battery R&D area provides for the study of new electrochemical couples, or of new approaches to known battery systems, and offers the prospect of developing better-performing, simpler, longer-life, safer, and/or lower-cost batteries. Research on the calcium/metal sulfide cell will progress toward the technology transfer stage, and exploratory work on such systems as solid electrolyte, organic electrolyte, and molten-salt cells will be pursued.

Engineering-Science Research will include morphological studies that address problems hindering the timely development of near-term batteries (lead/lead dioxide, iron/nickel oxide, and/or zinc/nickel oxide); phenomenological studies to provide basic information needed for the rational design, operation and control of electrochemical processes; studies on physiochemical methods for electrochemical research to aid the development of such advanced tools as ellipsometry and spectrometry for the detailed study of battery materials and processes; and modeling studies aimed at quantitative prediction of the dynamic behavior of cells, cell components and batteries.

Materials Research seeks to identify, characterize, and improve the materials and components to be used in batteries and electrochemical processes. Investigations of solid electrolytes, including those of ceramic (beta-alumina, NASICON), glass, and polymeric compositions, will continue, and advanced liquid electrolytes, such as low-temperature molten-salt mixtures and ionizing organic liquids, will be studied.

FOOTNOTE

*Materials and Molecular Research Division of Lawrence Berkeley Laboratory.

BATTERY ELECTRODE STUDIES*

E. J. Cairns and F. R. McLarnon

INTRODUCTION

The purpose of this work is to study the behavior of electrodes for rechargeable batteries, and to investigate means for improving their performance and lifetime. For example, some aqueous electrolyte batteries exhibit a redistribution of active material over the face of one or both electrodes, causing a significant loss in the cell's capability of storing energy. In cases such as this (e.g., Zn), the purpose of the work will be to investigate the mechanism(s) by which the redistribution of active material takes place, and to evaluate means of minimizing or eliminating the redistribution and thereby increase the electrode life. Other related purposes include the investigation of morphology changes, nucleation, and current density distribution. In the case of batteries with molten salt electrolytes, the purpose of this work will be to investigate the mechanisms of capacity loss of the electrodes and means for eliminating this loss.

The goal of this research program is to aid the development of rechargeable batteries for vehicle propulsion and energy storage applications, an area beset with significant problems in achieving adequate performance and lifetime at an acceptable cost. There are electrodes available with acceptable performance and potentially acceptable cost, but inadequate lifetime. In some cases, inadequate information is available concerning the precise cause(s) of short lifetime.

In the case of the zinc electrode, there are many theories concerning the cause(s) of active material redistribution over the face of the electrode, but none is recognized as being correct, or even in good agreement with observations. This is a significant problem because the cycle life of cells with zinc electrodes is inadequate for many applications, but the performance and projected cost are both acceptable. Furthermore, there are

several important cells that use zinc electrodes, and therefore could benefit from added knowledge about the zinc electrode. Examples of cells with zinc electrodes are: Zn/NiOOH, Zn/AgO, Zn/Br₂, ZnCl₂, Zn/Air, and Zn/MnO₂.

High-temperature cells with molten salt electrolytes have been under investigation for at least two decades. During this period, a number of electrodes have been investigated for use as either the positive or negative electrode. The early work was concentrated on active materials which were liquid under cell operating conditions. These early cells (e.g., Li/S, Li/Se, Li/Te) demonstrated very high performance, but inadequate lifetime. Gradually, efforts have shifted to solid electrodes of more complex geometry and composition. At the same time, the cell performance was decreased, and the cell lifetime has increased. Present cell lifetimes are in the neighborhood of 10,000 h, with the goal being 3 to 10 times that, depending upon application. Cell performance is presently about 2/3 of the minimum goal. Examples of molten-salt cells of current interest are Li-Al/FeS, Li-Al/FeS₂, Li-Si/FeS, Li-Si/FeS₂, and Na/β-Al₂O₃/NaCl-AlCl₃-SCl₄.

The approach used in these investigations will be to study the problems discussed above under realistic cell operating conditions, with modern instrumental techniques for monitoring the behavior of the electrodes during operation. Post-test examination and analysis will also be carried out. The results will then be analyzed and used to test theories and candidate explanations for the behavior of the electrode. Using the results and compatible theories, improvements in the electrodes will be proposed and investigated.

ACCOMPLISHMENTS DURING 1979

This is a new project starting in FY 1980.

PLANNED ACTIVITIES FOR 1980

Equipment for the characterization and cycle life testing of electrodes will be designed, ordered and set up. Details of the first phase of experimentation will be planned, and investigations will be initiated.

FOOTNOTE

*This project is part of a larger effort, "Electrochemical Synthesis and Energy Storage," the remainder of which is reported in the Materials and Molecular Research Division 1979 Annual Report. This work was supported by the Energy Storage Systems Division of the Department of Energy.

