ALTERNATIVE ANODIC REACTIONS IN WATER SPLITTING

FINAL REPORT

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TABLE OF CONTENTS

	<u>Page</u>
BNL PERSPECTIVE.....	iv
ABSTRACT.....	vi
SUMMARY.....	1
1. INTRODUCTION.....	10
2. EXPERIMENTAL.....	14
2.1 Electrochemical Cell.....	14
2.2 Electrodes.....	14
2.3 Removal of Trapped Iron Species in Coal Samples....	15
2.4 Preparation of Lignite, Grass and Household Waste Slurries.....	17
2.5 Electrolyte Solutions.....	18
2.6 Electrochemical and Analytical Equipment.....	18
2.7 Extraction of Coal-Derived Organic Liquids in Aqueous Phases.....	19
3. RESULTS.....	23
3.1 Elemental Analysis of Texas Lignite.....	23
3.2 Voltammetric Behavior of Carbonaceous Slurries.....	24
3.2.1 Current/Potential Curves for Unwashed Lignite Slurries in Sulphuric Acid Solution.....	24
3.2.2 Current/Potential Behavior of Washed Lignite Slurries in Sulphuric Acid Solutions.....	25
3.2.3 Effect of Temperature.....	25
3.2.4 Effect of Solution pH on Washed Lignite Slurries.....	26
3.2.5 Current/Potential Behavior of Washed Lignite as Compared to the Filtrate.....	26
3.2.6 Amount of Current Consumed by the Oxida- tion of Dissolved Fe^{2+} Ions for Washed Lignite Slurries and the Filtrate Derived from it.....	27
3.2.7 Effect of Added Redox Couples on the Electrochemical Oxidation Rate of Lignite Slurries.....	27

3.2.8.	Electrocatalysis in the Electrochemical Oxidation of Washed Lignite Coal Slurries.....	28
3.3.	The Carbon in the Filtrate from Lignite Slurries Prior to, and After, Electrolysis.....	28
3.4.	Current/Potential Curves for Biomass Slurries in Sulphuric Acid Solutions.....	29
3.5.	Identification and Analysis of Organic Com- pounds Produced by the Electrolysis of Lig- nite and Biomass Slurries.....	29
3.5.1.	Sep-pack Separation of Organic Com- pounds in Electrolyzed Aqueous Acidic Lignite Slurries in Conjunction with GC/MS Analysis.....	30
3.5.2.	Further Investigations of the Appro- priateness of Sep-pack Cartridges for the Separation of Organic Compounds from Aqueous Acidic Lignite Slurries....	32
3.5.3.	Sep-pack Separation of Organic Com- pounds from Electrolyzed Aqueous Acidic Biomass Slurries in Conjun- ction with GC/MS Analysis and Compu- ter Identification of Components Present.....	35
3.5.4.	Alternate Method of Analysis: GC/MS Analysis and Semi-Quantification of Organic Compounds Obtained from Liquid-Liquid Extractions of Lignite Slurry Filtrates.....	36
3.6.	Mass-Charge Balance on Electrolyzing Washed Lignite Slurries.....	41
3.7.	Summary of Analysis Results of New Compounds Introduced into Carbonaceous Slurries as a Result of Electrolysis.....	42
4.	DISCUSSION.....	43
4.1.	Situation of the Washed Lignite Slurry Before Electrolysis.....	43
4.2.	Characteristics of the Voltammetric Curves Pertaining to Lignite Slurries.....	44

4.3.	Mechanism of Electrochemical Oxidation of Washed Lignite Slurries.....	46
4.4.	Electrochemical Oxidation of Washed Lignite Slurries for Extended Times.....	51
4.5.	Maximum Current Density Obtainable from the Electrolysis of Lignite Slurries.....	52
4.6.	Separation and Identification of Organic Compounds Produced by the Electrolysis of Washed Lignite Slurries.....	52
4.7.	On the Anodic Liquefaction of Coal.....	55
	References.....	59
	Tables.....	61
	Figure Captions.....	81
	Figures.....	88

BNL PERSPECTIVE

Exploratory investigations reported by Texas A&M represent the far-term orientation of current R&D thrusts within the DOE/BNL Chemical/Hydrogen Energy Systems Program. The program seeks to develop a technology base which will be applicable to future considerations for converting, storing and transporting inexhaustible primary resources using low-cost and abundant materials. Water splitting to produce hydrogen as an energy carrier and storage medium can be accomplished by heat dissociation, chemical dissociation and electrolysis. Of these processes, electrolysis is farthest along in development; however, incentives remain to improve process efficiencies and the economics of conversion. It has been recognized that electrochemical dissociation of water is inefficient due to Carnot-limits of steam cycles to produce high-grade electric energy. Among the options being considered for reducing electric energy requirements is the introduction of low-cost depolarizing agents which would suppress the evolution of oxygen such that hydrogen would be produced at voltages substantially below the oxidation potential of water. Further cost/economic benefits would accrue if the oxidized products at the anode have commercial value.

Performance trends identified at Texas A&M must be considered in a very preliminary sense. Although energy efficiency improvements via anode depolarization mechanisms have been clearly demonstrated, the reaction kinetics observed from these preliminary investigations fall short of projected practical requirements. The semi-quantitative analyses of anodic products point to possibilities of their commercial value subject to achieving greatly improved kinetics without cost or energy penalties for effecting product separation. The prospects for developing a viable electrochemical water dissociation process using low-cost depolarizing agents, such as coal, grass, household wastes, etc., rely on overriding the current limiting factors. It is not clear whether such systems are inherently poor from the standpoint of achieving practical current densities; although it is suggested that agitation or stirring would have resulted in improvement by as much as 50 fold. Brief reference is made to work at Chevron Corporation (Clark et al) indicating organic oxidation rates of the order of 250-500 A/ft².

BNL has obtained an abstract of the paper, "The High Rate of Aqueous Anodic Oxidation of Carbonaceous Crude Fuels," by Clark, Folter, Vaughn of Chevron Research Company. The paper describes the use of ferrous/ferric redox catalysis as the means for achieving current densities of 200 A/ft² when operating at temperatures of 180°C at 10 BAR. Uncertainties remain regarding the ability to sustain these current densities as well as with life and stability of electrochemical components.

BNL field management value judgments suggest that the prospects for developing a viable concept along the lines of the Texas A&M investigations are highly speculative at this time. It is recommended that further activities be limited to tracking investigations ongoing elsewhere (i.e., Chevron) to firmly establish the relevance of those findings to the anode depolarization investigations at Texas A&M. In the interim, consistent with the broadbased exploratory research nature of the C/HES Program, other approaches such as the use of redox couples and subsequent selective oxidation of organics as well as the direct oxidation of alkanes to alcohols should be brought to a similar level of concept definition. The comparative merits of the several approaches to anode depolarization processes should permit firm programmatic direction. It should be noted that the assignment of project priorities is necessitated by budgetary constraints. If these constraints were relaxed, BNL would strongly recommend parallel pursuits.

Abstract

An anodic depolarization path to hydrogen production through water electrolysis has been examined, using lignite, grass and household wastes. Iron was removed from lignite by extensive washing.

Several institutions were used to carry out parallel analyses of organic compounds formed on electrolyzing carbonaceous slurries. Methods utilized included Sep-pack cartridges and liquid-liquid extractions for extraction of compounds from the aqueous electrolyte in conjunction with GC/MS analytical techniques. Identifications of compound types were made by computer pattern recognition and matching of chromatogram retention times, as well as mass spectral patterns with those of pure test compounds.

The degree of dissolution of lignite in 5 M H_2SO_4 at 100°C is ca. 0.1 wt %. Washed lignite dissolves less than unwashed material.

Cyclic voltammograms showed peaks arising from dissolved organics. Increase of temperature produced more peaks. In alkaline solution, peaks disappeared. Oxidation currents were three times greater if the lignite particles were in contact with the electrode compared with their absence from solution. Platinum anodes oxidized lignite better than PbO_2 . Redox systems, added to the electrolyte, helped compound formation. Grass and household wastes gave similar results but lower oxidation currents.

Sep-pack cartridges produced contaminants which did not prevent detection of changes in compounds created by electrolysis. Compounds produced by electrolysis are hydrocarbons with $\text{C}_8\text{-C}_{18}$ carbon skeletons.

Mass-charge balance agreed with quantitative analyses obtained from two organizations but not with that of a third. Conversely, qualitative analyses from all three institutions agreed that saturated hydrocarbons ($\text{C}_8\text{-C}_{18}$) were the principal compounds formed on electrolyzing lignite slurries.

SUMMARY

The kind of approach to hydrogen generation described in this report was conceived by Juda and Moulton in 1972. These workers were the first to show that injection of SO_2 into the anode compartment of a cell evolving hydrogen caused a considerable fall in the net cell potential, and the production of sulfuric acid. From that time onwards a class of work in hydrogen electrolysis had been concerned with the attempt to eliminate the high overvoltage oxygen electrode and to use experiments aimed at making other electrode reactions occur at the anode.

The electrolysis of coal with special attention to this effect was carried out by Coughlin and Farooque and they reported current densities of up to 50 mAcm^{-2} and a current efficiency of CO_2 evolution of about 80 percent. However, repetition of the work by Okada, Guruswamy and Bockris showed only qualitative agreement; the high currents were shown to be due to an anodic reaction of the oxidation of ferrous material which had come from the coal and which faded after 10 hours in certain lignite samples to give a lower current density of about 5 to 10 mAcm^{-2} . At the same time it was found that the CO_2 evolved was only about 10 percent of what was to be expected from the coulombs passed and the validity of this measurement was confirmed when it was found that 90% of the expected amount of CO_2 could be obtained so long as the carbon used was a pure carbon and not coal.

It was thought that the key to obtaining cheap hydrogen from the so-called coal-slurry electrolysis would be to obtain commercially useful materials in the anode compartment with the 90% of the current which was not going to form CO_2 . The net cost of hydrogen would be reduced below that predicted by Coughlin and Farooque (and also more recently Clarke from Chevron).

The orientation of the work therefore veered towards the difficult task of analyzing what compounds were in the anode compartment.

EXPERIMENTAL

The electrochemical cell used contained a platinized platinum cylinder with an area of about 70 square centimeters. The cathode was a platinum electrode of 1 cm². The coal was sieved and the 38 to 45 micron section selected. It was washed in two ways to remove the iron. In the less demanding way it was washed in sulfuric acid in 5 molar H₂SO₄ solution keeping the temperature between 80 and 100° and the time of this washing with agitation was between 12 and 300 hours. The average time of washing was 24 hours. The coal was centrifuged and finally collected and dried in nitrogen at 90°C. In the second method of drying the ASTM procedure D2492 was followed. This consists essentially of washing in nitric acid and hydrochloric acid and drying as above.

The dried lignite was slurried and introduced in the solution at 0.6 grams per milliliter. The electrolyte usually used was 5 M H₂SO₄. However, 5 M KOH and phosphoric acid were utilized in addition.

The coal was divided into two parts and one was maintained in the electrolyte for a given time and the other was maintained for the same time in the same electrolyte but for the second sample current was passed.

Electrochemical experiments were of two types. Essentially, they were investigations of the current potential relations which were carried out by potential sweep techniques using a sweep rate of about 1 millivolt per second. However, when it had been established that there were certain peaks in the anodic region, the potentiostat was set to cycle between these peaks and electrolysis carried out for various times, the shortest one which was 3 hours.

ANALYSIS

By far the greatest time in this investigation was spent in carrying out the analysis in various ways. First, the inductively coupled plasma device was used to measure the total carbon

dissolved in the solution. Secondly, a number of methods were used to obtain information about the organic compounds present.

To obtain these, the coal slurry in solution of both currents, unelectrolyzed and electrolyzed, were filtered through sensor glass filters. The problem of removing the organic material from the aqueous phase was then faced.

Extensive advice was sought and it was universally the opinion that a SEP-PAK filter would be the best thing to use. The SEP-PAK filter consists of a silicious base on the top of which a C₁₆ alkane has been introduced in the manufacture of the filter. The solution passes through here and the alkane is supposed to remove nonpolar organics.

After the filtrate had been taken from this and extracted with ether, the samples were then subjected to two kinds of procedures.

In one, a GC/MS approach was used and this was carried out largely at the University of Texas in Austin. However, two samples were sent to the Radian Corporation; and finally to the Pacific Northwest Laboratories.

In a second approach to analysis, a liquid-liquid extraction with benzene was used.

Five milliliters of filtrate were used. The cartridges were washed three times in water and then in ether and dried in nitrogen. It was then washed with ether. Blanks were used to test the SEP-PAK itself for impurities.

When the GC/MS data had been obtained at the University of Texas, the results were subject to the INCOS Data Program at the University of Cornell. Comparison was then made with the patterns of 46,000 organic compounds and in this way an analysis was made based on a percentage of overlap of properties both with the gas chromatograph heights and the mass spectroscopic data. The data was returned from the computer where the matching compound characteristics were 90% or more.

About 80% of the analytical work was done in this way. When definite compounds were indicated, they were added from the

shelf. About 10% of the compounds were verified in this way and in all cases it was found that when the INCOS Program indicated that the probability of a substance being there was 90%, it was indeed verified by the identical GC/MS pattern being obtained when the compound itself was added. The Radian Corporation was used to verify 2 to 3% of the results and the identity of results was excellent. Radian did not use the INCOS Program but direct comparison of typical GC patterns with data which they had themselves on the compounds which they suspected were there. Battelle-Northwest used the latter technique in respect to their GC/MS analysis but in addition used a benzene liquid-liquid extraction together with GC/MS work. The varying results obtained will be discussed below.

RESULTS

The first results were current-potential curves with unwashed coal as the suspended material in the anode compartment. The type of curve which was obtained here showed no peaks, i.e., indicated that no organic compounds would be oxidized as a principal source of the current but they showed normal limiting currents as though a single substance (obviously ferrous ions) were the source of the current. Experiments were made in varying the coal concentration and analyses were made of the ion present and it was ascertained that when the coal was present about 0.6 grams per milliliter the ion was present at about 2,000 parts per million.

With coal washed in the first manner (24 hours in sulfuric acid) the iron was reduced to 300 parts per million (from 2200 parts per million) and the shapes of the curve changed. A typical example of such curves is given in Figure 3 of the longer report. Two peaks can be seen; one at approximately 0.9 volts and one at approximately 1.2 volts on the NHS. The peak current, however, is only about 5 mAcm^{-2} . Other electrolytes gave lesser peaks. Phosphoric acid gave a peak at about 4 mAcm^{-2} but with

sodium hydroxide the peaks were changed radically so that they were indistinct.

Another result of interest was obtained with the thoroughly washed coal. Here, results are shown which indicate the effect of contact with the electrode. It was found that the current density was about 3 times higher if contact of solid coal with the electrode was made during the electrolysis (in the alternate procedure, the filtrate from a coal-slurry saturated solution was contacted to the electrode).

Three more variables were investigated. Addition of the ceric-cerrous couple was found to increase the current considerably.

Electrocatalysis was examined by utilizing lead dioxides instead of platinum and it was found that lead dioxide gave a less high peak but at the same position as that which had been obtained with platinum. Biomass and lignite were examined. They gave the same kinds of patterns though the currents were somewhat less.

ANALYSIS WITH SPECIAL REFERENCE TO SEP-PAK

To explain and discuss the validity of the analysis, it is important to see as a model one particular chromatogram and this is shown in Figure 10 which contrasts a situation without the electrolysis and the situation with the electrolysis. It is seen that the pattern is somewhat changed after electrolysis. The graph given is only one part of an extensive gas chromatograph analysis of the products. In this case, the electrolysis has taken place for 3 hours and the detailed substances which arise after electrolysis--and were not there before--are given in Table 4 of the longer paper. In general, they consist of alkanes and they are of carbon numbers C₈-C₁₉. The ones up to C₁₅ would probably be liquid oils.

Considerable time was spent in examining the degree to which the SEP-PAK filter contributed to the lines observed. At first

it had been thought that no lines arose from the SEP-PAK filter but later on it was found that the SEP-PAK filter did contribute some lines to the situation and although these acted confusingly, they should not alter the situation because no more lines would be added after electrolysis than before from this source. In Figure 11, the first slide shows the lines obtained after electrolysis of lignite and the second diagram shows SEP-PAK filter lines obtained with blank sulfuric acid. The third diagram shows the lines obtained with ether washing and the last diagram shows the diagram obtained with ether only, without any contact with the SEP-PAK.

Such observations were made by Pacific Northwest Laboratories, but were found to a much lesser extent in the analysis made by the University of Texas and by Radian. Note that many of the results obtained by the Northwest Laboratory were similar to those obtained by the University of Texas and Radian. For example, they obtained a similar chain of numbers in concentration of compounds with the slurry touching the electrode and for samples in which the electrolysis was carried out without the coal being in contact with the electrode. Again, the change with time of electrolysis was shown (see Figure 13) in the same way with the analysis from the Northwest Labs as from the University of Texas. But the difference between the Northwest Labs and the University of Texas and Radian comes out in the concentration of the alkanes found, about 1/10th for the Northwest Labs. In fact, the Northwest Labs found overwhelmingly one compound, namely butyrolactone.

To throw light on this matter it is possible to make a charge balance. In this respect we are fortunate in knowing the total amount of carbon present in the electrolyte without any ambiguity because of the plasma analysis. Utilizing this and the assumption that the hydrocarbons are produced by a Kolbe synthesis for alcohols with an average chain length of 5, one gets a calculated 63% current efficiency which is consistent with the 83% which one would expect from the CO_2 . Now on the other hand,

if one compares this with the hydrocarbon content obtained by Northwest, then the current efficiency is only 0.1%.

Although the matter of the analysis remains not totally resolved, there does seem to be a considerable case for favoring the agreeing results between the University of Texas and that of the Radian Corporation. For one thing, these measurements were accompanied by tests and matching of the compounds concerned. They matched the total coulombs balance much better than those of the Northwest Laboratories.

They also seem more in agreement with what one would expect. In fact, it is obvious that one would not expect to have no compounds present in coal in the unelectrolyzed samples (as stated by the Northwest Laboratories) and indeed one would not expect to have one compound (butyrolactone) dominating the results after electrolysis.

The discussion will therefore proceed on the assumption that the University of Texas results are correct: of course, this must be verified by further work.

DISCUSSION

The first thing to be discussed is the model for what is happening here--how do the compounds arise from the coal in the solution? It is easy to make a model of the coal particles concerned and this is given in detail in the paper. If one assumes that the coal is porous and that the solution penetrates to all parts of the pores of the coal it is easy to come out with a net concentration which corresponds approximately to that observed (about 10^{-3} moles per liter) for the total organic material present after electrolysis.

The identical peak values of the voltammograms obtained both on lead oxide and on platinum is consistent with the fact that the peaks are due to organic compounds and not due to, e.g., the oxidation of platinum.

The classes of compounds in the solution before electrolysis tend indeed to be alcohols and this is what is needed for a Kolbe reaction. The formation of the hydrocarbons therefore occurs in this way though there are uncertainties because the Kolbe reaction is examined with respect to room temperature at a higher anode potential, about 2.2 volts, and here we are talking about 1.1 volts at 100°. However, the situation is not inconsistent because the actual reversible potential for Kolbe is about -0.2 (volts) so that most of the excess potential is overpotential and this would be rapidly decreased by an increase in concentration.

As far as the difference between results obtained if the coal contacted the electrode, or simply the solution containing substances from coal, we made various attempts to explain them. In particular, we thought that we could explain them in terms of direct electrolysis upon contact with electrons passing between the electrode and the first layers of the coal, but calculations showed this to be an unfeasible proposition and we want to suggest that the most reasonable explanation is simply one of erosion: when the electrode is present the coal particles have a much greater area to collide with the platinum and to erode some of the coal off of the platinum and to increase the area available for dissolution.

Finally, we would like to make a speculation. It has been shown that by increasing the pressure to 10 atmospheres and the temperature to 180°C a current density of 500 mAcm⁻² can be attained. Clarke's temperature and the length of his electrolysis lead to the destruction of all the organic compounds, but it seems very feasible to assume that with the vigorous stirring methods used by Clarke, utilizing a lower temperature, the current density can be increased 10 to 20 times, i.e., to about 100 mA per square centimeter and the organic compounds can be retained. Within a time of about 10 hours it would then be possible to increase the concentration of the organic compounds to more than 10 times and they would become insoluble and begin to come out of solution. The speculation is that under these

conditions, oil will float on the electrode and thus oil recovery would become practical.

Under these circumstances one comes--and taking reasonable figures for the cost of coal, etc.--to the conclusion that the sale of crude oil at about half the market price gives rise to negative or very low prices for hydrogen.

FUTURE WORK

The most important thing about the future work is to decide which of the two analyses is correct. This is not an easy matter because the analysis of coal samples of this type costs about \$10,000 and as the apparatus now no longer functions and the trained co-worker concerned has left due to the cut off of funding, a minimum project could not be mounted for less than \$25,000 (i.e., \$10,000 for the analysis and say \$15,000 for a half year's employment of the co-worker).

Once the point of the analysis has been decided, there are a large number of things which can, and should be done (if the result is positive). These include use of a fluidized bed to increase contact between the electrode and the coal; use of enhanced temperatures, and stirring conditions; use of redox compounds to enhance the current; use of different types of coal (e.g., conducting anthracine could be used as an electrode itself).

The conclusion to this work is that it has been shown that hydrogen could be obtained at about half the potential at which it normally is obtained by the use of coal and the currents of 500 mAcm⁻² are obtainable. There is also some indication that it may be possible to obtain very interesting organic compounds or by-products and, indeed, an anodic liquefaction of coal.

1. INTRODUCTION

Peak production of liquid and gaseous fossil fuels has been accepted to occur in the 1990-2000 time frame.¹ Thus, cheap hydrogen from the electrolysis of water could play a central role in future energy scenarios, either in the manufacture of synfuels from coal or as a fuel itself.

In the electrochemical decomposition of water, electrical energy losses are associated with the sluggish oxygen evolution reaction.² Attempts are made to reduce these losses by the use of electrocatalytic coatings on the anode³ and by electrolysis of steam⁴ at temperatures in the region of 1000°C. In the latter approach, it will be difficult to lower cell voltage below a value of ca. 1.5 V. However, larger reductions in the use of electrical energy may arise, if the anodic product is not oxygen gas but another product from an alternative reaction.

Early work on anode depolarization associated with cheap hydrogen production involved the anodic oxidation of SO₂ to H₂SO₄, with the coproduction of hydrogen gas at voltages which were ca. 0.8 V lower than that required in the absence of SO₂.⁵ Recent research work at Westinghouse Electric Corporation on SO₂-depolarized water electrolysis^{6,7} has brought

about hydrogen production rates of ca. 400 mA cm^{-2} at a cell voltage of 1.0 V, facilitating a reduction in electrical energy consumption of over 50%, compared to normal water electrolyzers,⁸ operating at the same hydrogen production rates.

Anode depolarizers suitable for suppression of the oxygen evolution reaction in water electrolysis should possess the following characteristics:⁸ (i) the material should possess a thermodynamic oxidation potential less than that for water [1.23 V (NHE)]; (ii) the material should be readily available and sufficiently cheap, so that economic savings associated with the production of hydrogen, arising from the depolarizer, would be greater than its cost; (iii) ideally, the anodic product derived from the depolarizer should have commercial value. If not, the waste product must be non-polluting and easily discharged.

Thus, carbonaceous materials, such as coal, peat, oil shale, biomass, industrial and household wastes, are prime candidates as anode depolarizers in the electrochemical splitting of water. An early attempt in the utilization of carbonaceous material as an anode depolarizer was that made by Coughlin and Farooque,⁹⁻¹¹ who used a coal slurry in the anode compartment of an electrolysis cell. Oxygen gas was not evolved, the anodic gas stream, 10-20% of the anodic products on a current efficiency basis, being composed main-

ly of CO_2 , and the overall cell voltage for the decomposition of water was about 50% of that required in normal electrolysis. No attention was paid to anodic processes associated with the oxidation of coal beyond that of monitoring the formation of CO_2 and CO .

A re-examination of the former work by Okada, et al.,¹² revealed that the anode depolarization by coal observed by Coughlin and Farooque⁹⁻¹¹ was associated mainly with iron leached out of the coal in the form of Fe^{2+} ions. The facile electrochemical oxidation of ferrous to ferric ions was observed to last for a time duration of ca. 10 hours, after which the oxidation current decreased, eventually levelling out at about 5 mA cm^{-2} . It was also found that the amount of CO and CO_2 produced during the electrolysis of coal was not more than 10%,[†] thus, indicating the participation of other organic reactions in the oxidation of coal.

A cyclic voltammetric study of coal in aqueous solutions by Baldwin, et al.,¹³ confirmed the findings of the latter researchers, that the initial oxidation currents of coal were due to impurities present, mainly iron as Fe^{2+} . Recent work

[†]It is noteworthy that when pure carbon was used as a depolarizer, the CO_2 yield reached ca. 90%.

by Park, et al.,¹⁴⁻¹⁶ indicated, however, the occurrence of a homogeneous oxidation reaction, namely the oxidation of coal particles by electrochemically produced Fe^{3+} ions in solution, the Fe^{2+} ions produced in this reaction being subsequently oxidized to Fe^{3+} ions at the electrode surface.

The substantial reduction in the cell voltage obtained¹² for the evolution of hydrogen by utilizing coal as an anode depolarizer is favorable, but it must be placed in perspective with the fact that it is necessary to pay for the coal (or other carbonaceous materials) which are added to the anode compartment. Since the situation at the anode is multi-determined, in this report the nature of the anodic products associated with the electrochemical oxidation of coal has been investigated with respect to electrode potential, temperature, electrocatalysis, slurry pH, nature of electrolyte, effect of added redox couples and the nature of the coal (washed or unwashed lignite). An assessment has been made of the feasibility of using coal as an anode depolarizer in the commercial production of hydrogen by the electrolysis of water, paying particular attention to the anode products and their possible influence on the net cost of the hydrogen.

2. EXPERIMENTAL

2.1. Electrochemical Cell

The cell used was similar to that described earlier¹² and consisted of three separate compartments for the working, counter and reference electrodes. The anode compartment was separated by a fritted glass disc from the cathode compartment and by a salt bridge from the reference electrode compartment (cf., Fig. 1). Two built-in water-cooled condensers were located on top of the cathode and anode compartments to prevent the loss of volatile components, originating from the electrolysis of coal at the temperatures employed. The cell was suitable for the collection of coal-derived organic compounds and for the analysis of gaseous components, e.g., CO₂, which is expelled in the anodic gas stream.

All glass containers, including the electrochemical cell, were thoroughly washed, involving overnight immersion in chromic acid, followed by copious rinsing with triply distilled water.

2.2. Electrodes

Working electrodes were made of platinum and were of the following type: Pt plate of area 1.5 cm², Pt foil of area

6.3 cm², or a Pt cylinder, in gauze form, of area 39.3 cm². The counter electrode was, again, a Pt cylinder, fashioned out of gauze and of area 39.3 cm². The reference electrode was a commercially available saturated calomel electrode.

Platinum electrodes were cleaned by immersing in boiling aqua regia for ca. 10 minutes, followed by rinsing with triply distilled water.

2.3. Removal of Trapped Iron Species in Coal Samples

Lignite coal samples used in this work were received in powder form, of particle dimension 297 microns (50 mesh). The samples were from a batch reported in earlier work.¹² The coal particles were crushed further and sieved down to the 38-45 micron fraction.

Two procedures were utilized in washing coal to remove the unwanted iron content. In the first procedure, a finely ground coal sample was introduced into aqueous sulphuric acid (either 1 M or 5 M) and the ensemble heated for various times in the time interval of 5-310 hours, at temperatures between 80°C and 100°C. During this time, the glass vessel containing the coal/sulphuric acid suspension was vigorously agitated mechanically. On cooling, the coal suspension was centrifuged, separating the coal particles from the solution, thus, facili-

tating the rate of subsequent filtration. On completion of the filtration process, the coal was washed with triply distilled water, while maintaining a vigorous agitation of the coal particles. After washing, the coal was again centrifuged, filtered, and this last step repeated a second time. Finally, warm nitrogen gas (90°C) was passed through the coal particles to dry them.

In the second procedure, coal was washed in accordance with ASTM Method D2492. Lignite previously subjected to the first washing procedure was boiled in aqueous HCl (two parts concentrated HCl to three parts water) for 90 minutes, left overnight, filtered and washed with small increments of triply distilled water to get rid of all non-pyritic iron. The coal sample was then introduced into an aqueous HNO_3 solution (one part concentrated HNO_3 to seven parts water), boiled for 90 minutes, while stirring, and left overnight at room temperature to get the particles free of pyritic iron. The suspension was afterward filtered, washed copiously with triply distilled water and dried, using a warm pure nitrogen gas stream.

2.4. Preparation of Lignite, Grass and Household Waste Slurries

Dried lignite, prepared as described above, was introduced into the electrochemical cell at a slurry suspension concentration of 0.6 g/ml of solution. Acid solutions used were either 5 M H_2SO_4 or 85% H_3PO_4 . In the case of the former acid, coal suspensions were heated at temperatures between 80°C and 100°C , while, for the latter acid, the temperature range was 80°C to 130°C . Slurry suspensions consisting of 0.33 g/ml of lignite in 5 M KOH were also used. In this case, suspensions were heated to temperatures in the interval of 90°C and 100°C .

In the formulation of grass slurries, ground and minced grass was weighed (with moisture) and placed in 5 M H_2SO_4 at a slurry concentration of 0.3 g/ml. Concentrations higher than the latter were too thick for agitation. Household waste slurries were also made up in 5 M H_2SO_4 at a slurry concentration of 1.0 g/ml.

For each particular experiment, carbonaceous slurries were divided into two parts; one part was used for electrolysis, and the other part as a blank sample which was treated under identical conditions with regard to temperature, stirring and length of time of heating as for the electrolyzed

part. Prior to electrochemical treatments, the cell containing carbonaceous slurries was deaerated overnight by bubbling pure nitrogen gas through the slurry.

2.5. Electrolyte Solutions

Solutions were made up using triply distilled water, once from permanganate, and analytical-grade chemicals, H_2SO_4 , H_3PO_4 and KOH.

2.6. Electrochemical and Analytical Equipment

Cyclic voltammetry and controlled potential electrolysis were performed by means of a PAR potentiostat (model 363), programmed by a PAR universal programmer (model 175). Current/voltage curves were recorded on a Houston Instruments Omnigraphic X-Y recorder (model 100).

Elemental analysis (carbon, hydrogen, sulphur and nitrogen) of dried virgin lignite was determined by means of a Perkin-Elmer elemental analyzer (model 240). For identical lignite samples, the total amount of iron and oxygen was measured using fast neutron activation analysis. The neutron source was a Kaman 710 sealed-tube neutron generator. For iron, the product of the (n,p) reaction was detected using a Canberra Ge(Li) gamma detector and Nuclear Data ND66 pulse

light analyzer. For oxygen, two NaI(Tl) gamma detectors were used to detect the reaction product.

Quantitative analyses of various elements in a pre-treated lignite sample were obtained by means of an ARL (model 3400) simultaneous inductively coupled argon plasma emission spectrometer. The total amount of carbon in the filtrate derived from coal samples prior to, and after, electrolysis was determined quantitatively by means of a Horiba PIR 2000 infrared instrument, in conjunction with a persulfate oxidation-CO₂ trapping technique.

Dissolved iron in coal slurry solutions was analyzed using a Perkin-Elmer atomic absorption spectrometer (model 306).

2.7. Extraction of Coal-Derived Organic Liquids in Aqueous Phases

On completion of electrolysis, the coal slurry was drained from the anode compartment of the cell into a cleaned glass container, and the coal particles were allowed to settle. The slurry was then centrifuged and filtered through either Whitman sulphuric acid-resisting filter papers or through a fine-grade sintered glass-based glass funnel.

Two approaches were used for separating coal-derived

organic liquids from the aqueous electrolyte phase. The first involved the use of commercial Sep-pack cartridges and was performed at three different institutions: the University of Texas, Austin, Texas; Radian Corporation, Austin, Texas, and Battelle, Pacific Northwest Laboratory, Richland, Washington. In the second approach, a classical liquid-liquid extraction method, utilizing benzene as a solvent, was applied. This extraction procedure of coal-derived organic liquids was also carried out at Battelle, Pacific Northwest Laboratory, Richland, Washington.

In the case of the Sep-pack method, a typical procedure involved the passage of 5 mls of the aqueous filtrate phase from an electrolyzed lignite slurry through a Sep-pack cartridge for three to six times. The cartridge was then washed with 3 x 10 ml volumes of triply distilled water and dried with a flow of compressed nitrogen gas to remove residual water. Finally, the Sep-pack cartridge was eluted with 3 mls of ACS-grade diethylether, the volume of the ether being later reduced under a stream of nitrogen gas to approximately 100 μ l for gas chromatographic analysis. Several blank analyses of the Sep-pack cartridges were also performed to determine the extent of organic contamination from this procedure.

A typical procedure used for the organic-aqueous liquid-

liquid extraction method consisted of diluting 1-5 mls of the coal slurry filtrate to 25 mls with triply distilled water and extracting this aqueous phase with 3 x 50 ml volumes of nanograde benzene (Burdick and Jackson Solvents). The combined organic phases from this liquid-liquid separation were reduced in volume to 25 μ l or less with nitrogen. Caution was exercised in reducing sample volumes to ensure minimal sample component loss. In this method, all samples were extracted at an acidic pH of approximately 1.0. However, sample 1 (to be discussed later) was also extracted at a neutral pH ($\sim$ 7.0) and a basic pH ($\sim$ 14), the pH of the aqueous phase being adjusted in these cases by addition of appropriate volumes of 5 N NaOH. Appropriate liquid extraction blanks of the acid/water phase at each pH level were also analyzed to check for accumulation of organic constituents from either the organic solvents or aqueous reagents employed.

At Battelle, Pacific Northwest Laboratory, a Hewlett-Packard (HP) gas chromatograph (model 5880), equipped with a 30 m x 0.25 mm internal diameter fused silica DB-5 capillary column (0.25 μ m film thickness; J&W Scientific, Inc.) was used for the high-resolution gas chromatographic analyses. The gas chromatograph was operated from 50°C to 260°C, with a temperature program rate of 4°C/min. A flame ionization

detector (FID) was used for the analyses of the coal slurry isolates. Semiquantitative gas chromatography was performed on the HP 5880 computerized integrator by the standard addition method with commercially available 2-chloroanthracene, which was added to each sample (Aldrich Chemical Company). Qualitative analysis of each isolate was also performed on a HP 5982A capillary column gas chromatograph/mass spectrometer system (GC/MS) operated in the electron impact mode (70 eV). Identifications were made by comparison of sample component and reference mass spectra from either the "Eight Peak Index of Mass Spectra" or mass spectra acquired from authentic standard compounds.

At the University of Texas and Radian Corporation, a Finnigan 4023 coupled gas chromatograph/mass spectrometer system, furnished with a column identical to that employed in the Battelle system, was used for organic analyses. Operating conditions were similar to those adopted at Battelle. In the University of Texas, data collected from GC/MS analyses were interpreted, by means of a computer program employing the INCOS data system, on a pattern recognition basis.

3. RESULTS

3.1. Elemental Analysis of Texas Lignite

Finely crushed unwashed lignite samples (38-45 μm range), dried at 110°C in a flowing dry nitrogen gas atmosphere, gave on analysis an indication for carbon, hydrogen, nitrogen, oxygen, sulphur and iron (Table I). The value for carbon obtained from the Texas lignite used (Table I) is slightly higher than that found for North Dakota lignite,¹⁷ while that for iron is low (ca. 1% for North Dakota lignite¹⁷).

Results of an analysis pertaining to the filtrate of a lignite slurry (0.6 g/ml, 5 M H_2SO_4) is given in Table II; iron, sodium, silicon and magnesium were found. When lignite undergoes extended washing, the metal content in the filtrate declines with increase of time.

Utilizing the carbon content in lignite (56%, Table I), and taking into account the total amount of carbon in a lignite filtrate (Table II), the degree of dissolution of washed lignite in 5 M H_2SO_4 at 100°C is ca. 0.1 wt %.

3.2. Voltammetric Behavior of Carbonaceous Slurries

3.2.1. Current/Potential Curves for Unwashed Lignite Slurries in Sulphuric Acid Solution

A cyclic voltammogram obtained from a solution of an unwashed lignite slurry (0.6 g/ml, 5 M H_2SO_4) is shown in Figure 2(a). The limiting current density, i_L , is ca. 9 mA cm^{-2} . Similar voltammetric behavior was observed for temperatures in the range 65^o-110^oC and for scan rates in the interval 10-50 mV s^{-1} .

Variation of the measured limiting current density in the case of aqueous FeSO_4 solutions at the same temperature and scan rate [Fig. 2(b)] indicates that the concentration of dissolved Fe^{2+} in the unwashed lignite slurry was ca. 4.2×10^{-2} M (2,346 PPM).[†]

3.2.2. Current/Potential Behavior of Washed Lignite Slurries in Sulphuric Acid Solutions

A typical cyclic voltammogram for a prewashed lignite

[†]The various values given for the iron concentration in lignite slurry filtrates depend on whether the lignite has been washed or not and, in the case of washed lignite samples, on the method of washing, as well as the extent of washing for a given method.

slurry* (0.6 g/ml, 5 M H₂SO₄) is given in Figure 3(a).

The dissolved iron content in the slurry of the washed lignite, as measured by atomic absorption spectroscopy, was found to be ca. 6×10^{-3} M (335 PPM).[†]

Peaks are present [Figs. 3(a) and (b)]. The i_L for washed lignite slurries associated with the oxidation of lignite organic species are about 50% lower than that for unwashed samples at a potential of 1.15 V. This comparison may be misleading. In the case of unwashed lignite, the current contains contributions from the Fe²⁺ oxidation reaction.

3.2.3. Effect of Temperature

The current/potential curves pertaining to a prewashed lignite slurry* (0.6 g/ml, 5 M H₂SO₄) for two different temperatures, 80°C and 100°C, at the same scan rate are shown in Figure 4. At 100°C, a new peak appears at 0.9 V, compared to the original at 1.15 V.

* Finely crushed virgin lignite (38-45 μ m) was introduced into 5 M H₂SO₄ solution and heated at ca. 100°C for 200 hours while being constantly agitated.

3.2.4. Effect of Solution pH on Washed Lignite Slurries*

The effect of pH is shown in Figure 5. Current/potential curves for a lignite slurry (0.6 g/ml, 85% H_3PO_4) at temperatures of 80°C, 100°C and 130°C are given in Figure 5(a). Peaks are similar (but less than) those observed in sulphuric acid (Figs. 3 and 4).

A current/potential curve for acid-washed lignite in potassium hydroxide solution (0.33 g/ml, 5 M KOH) at 100°C is presented in Figure 5(b). No peaks are observed. The current density increase at ca. 0.8 V corresponds to oxygen evolution.

3.2.5. Current/Potential Behavior of Washed Lignite (ASTM Method, See Section 2.3) as Compared to the Filtrate Derived from It

A cyclic voltammogram for a thoroughly washed lignite slurry (0.6 g/ml, 5 M H_2SO_4) is shown in Figure 6(a). Voltammetric behavior similar to that of Figure 4 is observed. A voltammogram for the filtrate derived from a similarly prepared lignite slurry is given in Figure 6(b). At 1.15 V, the current density is ca. three times greater for the system in which coal particles contact the electrode, compared with the result obtained when the filtrate of a slurry system is

electrolyzed.

The iron in the solution obtained from the thoroughly washed lignite slurry and the filtrate therefrom was determined by atomic absorption spectroscopy to be ca. 8.2×10^{-4} M (46 PPM).[†]

3.2.6. Amount of Current Consumed by the Oxidation of Dissolved Fe^{2+} Ions for Washed Lignite Slurries (ASTM Method) and the Filtrate Derived from It

To determine how much of the current in the case of the washed lignite slurry and filtrate solution [Figs. 6(a) and (b), respectively] was consumed by the iron present in the solution, cyclic voltammetry was carried out in various solutions containing only 8.2×10^{-4} M FeSO_4 . The voltammetric curves are shown in Figure 7. Comparison of these curves with those obtained for the thoroughly washed lignite slurry [Fig. 6(a)] and for the filtrate solution [Fig. 6(b)] reveals that about 3% of the current is due to the Fe^{2+} content in the lignite slurry and about 10% in the case of the filtrate solution.

3.2.7. Effect of Added Redox Couples on the Electrochemical Oxidation Rate of Lignite Slurries

Addition of Ce^{4+} ions to a well-washed lignite slurry

(ASTM method) gave rise to a substantial increase in lignite oxidation currents over the whole potential range, corresponding to lignite oxidation [Fig. 8(a)] when compared with the situations for lignite in the absence of Ce^{4+} or for Ce^{4+} ions alone in 5 M H_2SO_4 .

3.2.8. Electrocatalysis in the Electrochemical Oxidation of Washed Lignite Coal Slurries

A current/potential curve for a washed lignite slurry* (0.6 g/ml, 5 M H_2SO_4) utilizing a PbO_2 electrode is given in Figure 8(b). At 1.1 V, the oxidation rate using a PbO_2 anode is ca. 1% of that obtained on Pt. Similar behavior to that presented in Figure 8(b) was obtained for scan rates in the range 2-50 mV s^{-1} , and for temperatures in the interval 100°-120°C. The anodic peak at ca. 1.1 V indicates that the same lignite oxidation process is taking place in the case of both electrode materials.

3.3. The Carbon in the Filtrate from Lignite Slurries Prior to, and After, Electrolysis

The carbon in the filtrates of lignite slurries (0.6 g/ml, 5 M H_2SO_4), derived from lignite washed by the ASTM D2492 procedure, and either subjected to electrolysis at 1.1 V for three hours at 100°C or not electrolyzed but heated at 100°C

for three hours, is presented in Table III. The carbon in the filtrate after electrolysis (the lignite particles having been in contact with the electrode) was three times higher than the sample not electrolyzed.

3.4. Current/Potential Curves for Biomass (Grass and Household Wastes) Slurries in Sulphuric Acid Solutions

The potential sweep relation for a grass slurry (0.3 g/ml, 5 M H_2SO_4) is shown in Figure 9(a). Two peaks at 0.8-0.9 V and at 1.1-1.2 V compare well with peaks found for lignite slurries (Fig. 3).

A voltammogram for a household waste slurry (1.0 g/ml, 5 M H_2SO_4) is given in Figure 9(b). Peaks at 0.8-0.9 V, 1.15 V and at 1.3-1.4 V, respectively, are similar to those found for grass and lignite [Figs. 9(a) and 3, respectively]. However, the current densities at 1.15 V for grass slurries [Fig. 9(a)] is 0.75 mA cm^{-2} and even lower for household waste slurries, 0.3 mA cm^{-2} {lignite gave $7-15 \text{ mA cm}^{-2}$ [Figs. 3 and 6(a)]}.

3.5. Identification and Analysis of Organic Compounds Produced by the Electrolysis of Lignite and Biomass Slurries

Two methods were employed for extracting organic liquids from the aqueous filtrate of both electrolyzed and non-electrolyzed slurries. These involved the use of Sep-pack car-

tridges, as well as the application of a conventional liquid-liquid extraction procedure.

3.5.1. Sep-pack Separation of Organic Compounds in Electrolyzed Aqueous Acidic Lignite Slurries in Conjunction with GC/MS Analysis (University of Texas and Radian Corporation)

Typical gas chromatograms of the organic compounds separated by the Sep-pack method and analyzed by gas chromatography for a washed lignite slurry* (0.6 g/ml, 85% H_3PO_4) electrolyzed by means of sweeping the electrode potential anodically from 0.6-1.1 V (NHE) at a sweep rate of 1 mV s^{-1} for 10.5 hours (no cathodic return sweep) at a temperature of 130°C , as well as for an identically treated but non-electrolyzed slurry, are given in Figure 10. Mass spectra for each component were also recorded at appropriate retention times. Similar data was obtained in the case of lignite slurries electrolyzed in 5 M H_2SO_4 .

As part of the analysis work performed at the University of Texas, retention times, peak intensities and mass spectral patterns were submitted to a computer program using the INCOS data system and compared on a pattern recognition basis with patterns for 25,000 organic compounds. Mass spectra data were also interpreted and compounds identified at Texas A&M,

using Cornell's computer programs of PBM and STIRS. Only compounds designated as having greater than 90% probability of being present have been accepted here.

Compounds identified as arising only from the electrolysis of a washed lignite slurry (0.6 g/ml, 5 M H_2SO_4) at 1.15 V (NHE) for three hours at a temperature of 100°C , using a platinum anode, are given in Table IV. The compounds are almost exclusively hydrocarbons, the predominant proportion having a $\text{C}_8\text{-C}_{19}$ carbon skeletal structure. An indication of alcohol formation is also to be noted. The concentrations of the individual compounds are also given in Table IV and are in the 10^{-3} to 10^{-4} moles per liter range. An almost identical product yield was obtained with a lead dioxide anode for the same electrolysis conditions.

A lignite slurry filtrate (filtered solution from a lignite slurry heated in 5 M H_2SO_4 for three hours at 100°C) electrolyzed under identical conditions gave rise to the compounds shown in Table V. Again, the organics produced are almost exclusively hydrocarbons in the $\text{C}_{10}\text{-C}_{21}$ carbon content interval, with a trace of alcohol (C_{14}) and carboxylic acid (C_{16}) formation. However, the organic concentrations are now in the 10^{-4} to 10^{-5} moles per liter range.

It can be seen (Tables IV and V) that compounds present

as a result of contact between the filtrate solution and the electrode are also present when the coal particles contact the electrode. However, coal contacting the electrode gives 12 additional compounds. The concentration of compounds common to both situations is about five times greater in the case in which coal particles contacted the electrode.

Compounds arising from the electrolysis of an unwashed lignite slurry (0.6 g/ml, 5 M H_2SO_4) at 1.15 V (NHE) for three hours at 100°C are presented in Table VI; similar type compounds, alkanes with C_{10} and C_{21} frameworks and a C_{16} containing carboxylic acid (although less of them, in the case of unwashed slurries), are evidently formed from washed and unwashed lignite (cf., Tables IV and VI).

3.5.2. Further Investigations of the Appropriateness of Sep-pack Cartridges for the Separation of Organic Compounds from Aqueous Acidic Lignite Slurries

In the earlier analysis performed at the University of Texas and Radian Corporation, complications arose in compound identification, due to the presence of components which appeared to have their origin in the Sep-pack cartridges. In all cases, these foreign components were taken into account to the greatest extent by the analysis of suitable blank samples. However, it was felt that a further investigation

of the Sep-pack separation method in the lignite slurry application was desirable. This work was performed at Battelle, Pacific Northwest Laboratory.

A chromatogram of the organic material separated by the Sep-pack method and analyzed by gas chromatography for a sample of washed lignite* electrolyzed at 1.1 V (NHE) in 5 M H_2SO_4 (0.6 g/ml) at 100°C for three hours (sample 1, Table VII) is shown in Figure 11(a). Peak identifications were achieved by capillary GC/MS and are listed in Table VIII. The compounds observed are almost exclusively hydrocarbons possessing a C_{13} - C_{18} carbon skeletal structure. Typical mass spectra for components 3 and 4 in Figure 11(a) are presented in Figure 12.

In Figure 11(b), a capillary column gas chromatogram is shown concerning the organic material present in a Sep-pack blank sample, prepared by first eluting the Sep-pack cartridge with 3 x 10 ml volumes of 5 M H_2SO_4 , not containing a coal slurry, followed by eluting with 3 x 10 ml volumes of triply distilled water, drying with a flow of compressed nitrogen gas and finally eluting with 3 mls of ACS-grade diethylether, the latter volume of ether being reduced under a stream of nitrogen to approximately 100 μl prior to sample injection into the gas chromatograph (sample 2, Table VII). Thus, for

analyses performed at Battelle, this chromatogram is almost identical to that presented in Figure 11(a), indicating, in this particular instance, that the compounds observed in the latter chromatogram are mostly contaminants from either the Sep-pack cartridge, the H_2SO_4 or the ether employed. This is in disagreement with similar analyses performed at both the University of Texas and Radian Corporation, where a large number of compounds were observed to arise only after the electrolysis of a lignite slurry (see Table IV). Peak identifications were obtained as for sample 1 and are again presented in Table VIII.

To determine if the Sep-pack cartridge itself contributed any organic contaminants which may give rise to peaks observed in Figure 11(a), a cartridge was eluted with only diethylether; the sulphuric acid and water elutions were not performed (sample 3, Table VII). A capillary column gas chromatogram of the ether elution (3 ml) of a Sep-pack cartridge is shown in Figure 11(c) (peak assignments are given in Table VIII). The close similarity of the chromatograms in Figure 11(a)-(c), as obtained in Battelle, points to the source of contaminants, which give most of the peaks in the chromatograms, in total disagreement with similar work performed at the University of Texas and Radian Corporation, to the Sep-pack cartridges or

to the ether used.

In Figure 11(d) is a gas chromatogram of the ether solvent blank without sample or without passage through a Sep-pack cartridge (sample 4, Table VII). Therefore, it would appear from the analyses performed at Battelle that most of the compounds detected in the filtrate of an electrolyzed lignite slurry, as separated by the Sep-pack method [Fig. 11(a)], are contaminants arising from the Sep-pack cartridge itself, contrary to that found for identical analyses at the University of Texas and Radian Corporation (see Table IV).

3.5.3. Sep-pack Separation of Organic Compounds from Electrolyzed Aqueous Acidic Biomass Slurries in Conjunction with GC/MS Analysis and Computer Identification of Components Present (University of Texas)

Compounds identified after electrolyzing a grass slurry (0.3 g/ml, 5 M H_2SO_4) by means of sweeping the potential anodically from 0.8-1.25 V (NHE) at a sweep rate of 1 mV s^{-1} for seven hours (no cathodic return sweep) at 110°C are given in Table IX. Only compounds produced as a result of electrolyzing the slurry are given in Table IX; compounds observed without electrolysis are not included. The principal organics produced were a diether functional group containing compound (C_7) and an alcohol with a C_6 skeletal structure.

3.5.4. Alternate Method of Analysis: GC/MS Analysis and Semi-Quantification of Organic Compounds Obtained from Liquid-Liquid Extractions of Lignite Slurry Filtrates (No Use of Sep-pack Filter)

A number of uncertainties associated with the Sep-pack method of separation of organic compounds from acidic aqueous electrolytes can arise, e.g., sample contamination from organic components of Sep-pack cartridges, or the lack of complete separation of all the organics produced. Thus, an alternate method, namely liquid-liquid extraction, was employed to separate the organic compounds from the aqueous electrolyte. This also provides a means of checking the results of the Sep-pack method of analysis performed at the three analytical institutions.

Aqueous filtrates of lignite slurries (samples 1, 5-10, Table VII) were extracted with benzene and the resulting organic phase analyzed by GC and GC/MS for organic compounds in the aqueous acidic phases.

(i) Organic Compounds in the Filtrate of a Washed* Electrolyzed Lignite Slurry. A capillary column gas chromatogram of the organic extract for a washed lignite slurry made up in aqueous 5 M H_2SO_4 and electrolyzed at 1.1 V (NHE) for three hours at 100°C (sample 1, Table VII) is presented in Figure 13(a). The identity of the numbered peaks, as obtained by

GC retention times and mass spectra data, is given in Table X. The semi-quantitative concentrations of components detected in this sample are also listed in Table X and are of the order of 10^{-6} moles per liter.

The major compound detected was butyrolactone ($C_4H_6O_2$)[§] by comparison of the GC retention time and mass spectrum of the authentic standard compound, while the predominant class of compounds were hydrocarbons, typically C_{14} , C_{15} alkanes. An indication of aliphatic aldehydes and carboxylic acids was also obtained. Mass spectra data for components 1 and 5 are given in Figure 14. The sample was also extracted at both a neutral and basic pH, to insure that analysis of all extractable compounds was achieved. GC analyses of these extracts showed no further extractable constituents as compared to the blank extracts of the aqueous phases. Consequently, the remaining samples were extracted only at an acidic pH level.

The GC chromatograms of similarly treated washed lignite slurries, except that the time of electrolysis was lengthened considerably (for a period of eight days and thir-

[§]This compound was also detected by GC/MS on washing the surface of lignite particles ($\sim 40 \mu m$) with THF, which had previously been washed in 1 M H_2SO_4 at ca. $100^\circ C$ for 60 hours.

teen days, samples 5 and 6 in Table VII, respectively) are presented in Figures 13(b) and (c), respectively. Comparison of Figures 13(b) and (c) with that of 13(a) reveals complete loss of organic compound formation for the longer times of electrolysis (~ ten days, compared with a few hours). A similar observation was found in the case of the Sep-pack separation method performed at the University of Texas.

(ii) Organic Compounds Produced by the Electrolysis of a Washed Lignite Slurry Filtrate. The GC chromatogram associated with the organic compounds formed on electrolyzing a washed lignite slurry filtrate (no coal particles touching the electrodes, sample 7 in Table VII) at 1.1 V (NHE) for three hours at 100°C is shown in Figure 13(d). Identification of the numbered peaks (pattern recognition approach) is given in Table X. Comparison of the chromatograms in Figures 13(a) and (d), which correspond to situations in which lignite particles were, and were not, in contact with the electrodes, respectively, reveals that the concentration and extent of organic compound formation as a result of electrolysis is increased by particle-electrode collision. Similar observations were found using the Sep-pack separation method (3.5.1).

(iii) Organic Compounds from an Unwashed Electrolyzed

Lignite Slurry. A GC chromatogram, derived from an unwashed lignite slurry in 5 M H_2SO_4 electrolyzed at 1.1 V (NHE) for three hours at 100°C (sample 8, Table VII), is shown in Figure 15(a). Numbered peaks are identified (pattern recognition) in Table X. The GC chromatograms in Figures 15(a) and 13(a) correspond to similarly treated lignite slurries, except that for Figure 15(a), the lignite slurry used was unwashed; it is seen that organic compound formation is negligible for the unwashed slurry compared to the washed one. Butyrolactone and an unidentified organic acid (component E), as well as some other unidentified components, were detected. This result is in agreement with that found when the Sep-pack method of extraction was used. In the case of the latter method, a significant reduction in organic compound formation was observed on electrolyzing unwashed lignite slurries (see section 3.5.1), as compared with washed slurries.

(iv) Organic Compounds Detected in an Unwashed Non-Electrolyzed Lignite Slurry. The GC chromatogram obtained from the benzene extraction of the filtrate of an unwashed non-electrolyzed lignite slurry in 5 M H_2SO_4 , heated for three hours at 100°C (sample 9, Table VII) is given in Figure 15(b). The numbered peaks (pattern recognition) are presented in Table X. Comparison of the GC chromatogram for an unwashed

non-electrolyzed lignite slurry [Fig. 15(b)] with that for an unwashed electrolyzed lignite slurry [Fig. 15(a)] shows less compound formation for the non-electrolyzed slurry [Fig. 15(b)] compared with the electrolyzed one [Fig. 15(a)].

(v) Organic Compound Production in a Washed Non-Electrolyzed Lignite Slurry. The chromatogram pertaining to the extracted filtrate of a washed non-electrolyzed lignite slurry in 5 M H_2SO_4 , heated for three hours at 100°C (sample 10, Table VII), is shown in Figure 16(a). The numbered peaks are given in Table X. Like the unwashed non-electrolyzed lignite slurry [Fig. 15(b)], the washed non-electrolyzed slurry [Fig. 16(a)] gives an insignificant amount of organic chemicals, as obtained from the liquid-liquid extraction procedure at Battelle. These analyses are unreasonable, in view of the well-known dissolution chemistry of coal under similar conditions¹⁸ and from Sep-pack results performed at the University of Texas in the present study for identical lignite slurries.

(vi) Organic Contaminants in 5 M H_2SO_4 Electrolyte. In Figure 16(b), a GC trace of the organic fraction obtained on extraction of the 5 M H_2SO_4 electrolyte (sample 11, Table VII), without coal sample, is presented. This electrolyte blank extract was analyzed by GC at three to four times the

concentration of the lignite slurry filtrates to facilitate identification and highlight trace components in this blank sample. Four primary contaminants [peaks 9, 12, 15 and 17 in Fig. 16(b)] were observed in this blank, which were also present in each of the seven extracts from the lignite slurry samples. Peak identifications are presented in Table X. Other contaminants of this electrolyte blank sample were not observable at the concentration levels at which the lignite slurry extracts were analyzed.

3.6. Mass-Charge Balance on Electrolyzing Washed Lignite Slurries

To estimate the mass-charge balance, it is assumed that on average the formation of an organic compound from a lignite slurry requires a 4-electron transfer. Using the electrolysis parameters: cell current, 1.2×10^{-1} A, and electrolysis time, three hours, gives rise to the production of 3.4×10^{-3} moles of organic compounds.

The total concentration of organic compounds[¶] (almost

[¶] This excludes polar compounds (carboxylic acids, alcohols, etc.), which would not be extracted by Sep-pack cartridges or by a benzene liquid-liquid extraction procedure.

exclusively hydrocarbons) produced on electrolyzing a washed lignite slurry, as determined by Sep-pack cartridges in association with GC/MS analysis, yields 2.6×10^{-3} moles l^{-1} (see Table IV). The current efficiency for hydrocarbon formation is, therefore, 76%, using the Sep-pack extraction method.

From the liquid-liquid extraction procedure, coupled with GC/MS analysis of a similarly electrolyzed washed lignite slurry, a total of 1.6×10^{-3} moles l^{-1} of organics[¶] were formed (Table X). This latter figure is made up by only one compound which was present at a significant concentration, namely, butyrolactone. Using this value, the current efficiency for the formation of organic compounds from lignite slurries becomes 47%.

3.7. Summary of Analysis Results of New Compounds Introduced into Carbonaceous Slurries as a Result of Electrolysis

In Table XI, a summary of the main compounds formed, using various analysis procedures, as a result of electrolyzing carbonaceous slurries, is presented.

4. DISCUSSION

4.1. Situation of the Washed Lignite Slurry Before Electrolysis

Coal is a complex substance which differs widely in its properties.¹⁹ The carbon content increases from less than 60 wt % in the less mature brown coals, such as lignite (cf., Table I), to greater than 92 wt % in anthracite. Coal contains other elements in low concentrations, in particular, sulphur, traces of metals, oxygen and nitrogen (cf., Tables I and II).

The aqueous sulphuric acid lignite slurry contains several lignite-derived constituents, in particular, ferrous and sulphide ions (cf., Table II). Unwashed lignite dissolves more readily than washed lignite and extended washing reduces the iron content (cf., Table II) to an extent that the oxidation current comes about 90% from organic compounds (cf., Figs. 6 and 7).

A reasonable model to correspond to these facts is that the dissolution of lignite is associated with the removal of monolayers at the surface. Coal, in general, consists of porous networks.²⁰ Washed powdered lignite dissolves in solution to an extent of ca. 0.1% (cf., Table III). It seems

likely that surface compounds dissolve from the large surface area of porous lignite particles which come in contact with aqueous solution. It is possible to show by a simple argument that this is reasonable.

Assume that the lignite particles are cubic, having the actual particle dimension used (4.0×10^{-3} cm), and consist of pores of diameter 10^{-5} cm, which extend from one side of the cube to the other parallel side, with a tortuosity factor of two. If it is also assumed that 50% of the area of one cube side corresponds to pore aperture area and that 10^{-12} moles of organic compounds (1% of the number of moles of H_2 per cm^2 corresponding to a monolayer) dissolve per cm^2 of particle real surface area; then taking the experimentally determined value of the number of lignite particles per liter of lignite slurry used (7.7×10^9), yields a value of 0.6×10^{-3} moles per liter of dissolved organic compounds.

This is to be compared with the experimentally obtained value, 231 PPM of carbon (cf., Table III), which, on taking an average dissolved molecular species to contain a C_{15} skeleton, translates to 1.3×10^{-3} moles per liter of organics.

4.2. Characteristics of the Voltammetric Curves Pertaining to Lignite Slurries

In respect to the cyclic voltammograms pertaining to

lignite slurries (Figs. 3, 4, 5, 6 and 8), characteristic peaks at 0.9 V (NHE) and at 1.1 V (NHE) appear. For a lead dioxide electrode, a peak, less well developed, appears at 1.1 V (NHE) also, so that there is little doubt that these peaks are connected with the oxidation of materials from lignite, rather than from oxide film formation or oxide film transformation to other oxide species.

Thus, there must be some common groups of organic compounds which are being oxidized at the electrode/lignite solution interface. Since an oxidation process is taking place, it is necessary to take into account a reversible potential, plus a certain amount of overpotential.

To aid in the identification of the classes of compounds, it is necessary to consider the types of organic materials which were present in solution prior to electrochemical oxidation. Since the lignite slurry was heated to ca. 100°C for times of the order of 200 hours in an oxidizing sulphuric acid medium, during the washing stage, the surfaces of lignite particles are likely to be in an oxidized state, with — OH, — CHO, — COOH, etc., functional groups. On subsequent dissolution of the outer layers of these particles in the electrolyte (5 M H₂SO₄, 100°C), molecular species containing alcohol, aldehyde, ketone and carboxylic acid groups will

be formed.

The main classes of compounds present in solution prior to electrolysis, as obtained by Sep-pack[±] separation--GC/MS analysis and computer identification, were alcohols, e.g., 2,6-ditertiary butyl-P-C resol (Ionol, C₁₅H₂₄O), or phenols, e.g., 4-methyl-2,6 ditert butylphenol and 2,6-ditert-butyl-4-methylphenol (C₁₅H₂₄O). The reliability of the identification of these compounds was lower than that normally accepted and typically were in the 60-90% range.

It is likely that the hydrocarbons formed (cf., Table IV) come about through Kolbe reactions, each reaction involving the dimerization of two organic molecules originally in solution containing carboxylic acid groups. The reversible potential for the Kolbe reaction with acetic acid/acetate is ca. -0.40 V (NHE)²¹ and considering the temperature (100°C) and potential used [1.15 V (NHE)], such a scheme is plausible.

4.3. Mechanism of Electrochemical Oxidation of Washed Lignite Slurries

Oxidation currents arising from the situation in which

[±]Sep-pack columns have poor ability to separate polar molecules, i.e., compounds with alcohol or carboxylic acid functional groups (best for hydrocarbons).

lignite particles are in contact with the anode [Fig. 6(a)] are about three times greater than oxidation currents associated with lignite-derived compounds dissolved in solution[#] [Fig. 6(b)], but from which lignite particles have been removed. Thus, it is reasonable to consider a collision mechanism for lignite particles coming in contact with the anode to account for the oxidation rate enhancement.

From classical gas kinetics, an estimate of the number of lignite particles striking the electrode surface per cm^2 per second can be obtained from the expression:²²

$$\text{No. of particles striking the electrode per cm}^2 \text{ per second} = \frac{uc}{4} \quad (1)$$

where u is the average particle velocity in one direction (cm s^{-1}) and c is the number of particles per cm^3 (7.7×10^6). To obtain knowledge with regard to the average particle velocity, u , the Einstein relationship:²³

$$D = kTu \quad (2)$$

can be used (D = diffusion coefficient, $\text{cm}^2 \text{ s}^{-1}$) to yield the

[#]By this is meant lignite-derived compounds dissolved in 5 M H_2SO_4 solution after washed lignite particles had been in contact with the solution for three hours at 100°C and subsequently filtered off.

expression:

$$\frac{D_{\text{gas molecule}}}{D_{\text{lignite particle}}} = \frac{u_{\text{gas molecule}}}{u_{\text{lignite particle}}} \quad (3)$$

However, from the Stokes-Einstein equation:²³

$$D = \frac{kT}{6\pi r\eta} \quad (4)$$

(where r is the particle radius in the system and η is the fluid viscosity), and from this, the relationship:

$$u_{\text{lignite particle}} = \frac{u_{\text{gas molecule}} \times r_{\text{gas molecule}} \times \eta_{\text{gas}}}{r_{\text{lignite particle}} \times \eta_{\text{lignite particle}}} \quad (5)$$

can be obtained. Putting into Equation (5) the appropriate values from Table XII yields a value for $u_{\text{lignite particle}} = 3.0 \times 10^{-3} \text{ cm s}^{-1}$. Taking into account a 100-fold increase, due to the vigorous stirring employed, gives a value of 0.3 cm s^{-1} for the average particle velocity. Using the latter value for $u_{\text{lignite particle}}$, in Equation (1), one finds 5.8×10^5 collisions per cm^2 of electrode surface per second.

The experimentally observed charge consumed per cm^2 of electrode surface per second, 10^{-3} C , shows that per lignite particle collision, $1.7 \times 10^{-9} \text{ C}$ would be passed from the

electrode to a single particle.

If, therefore, the electrode current density is i (approximately 10^{-3} A cm $^{-2}$), and the lignite particle contact area per collision A (1% of the total particle surface area, that is, 4.2×10^{-8} cm 2), and the particle-electrode contact time, τ , is taken to be as high as 10^{-3} s, then the charge passed per collision is given by:

$$\begin{aligned} iA\tau &= C \\ &\sim 4 \times 10^{-14} \text{ coulombs} \end{aligned} \tag{6}$$

This is over four orders of magnitude less than that necessary to maintain the electrode current density at the experimentally observed value. Thus, the contribution to the electrochemical oxidation rate of lignite slurries arising from particle-electrode collisions is negligible.

Can the dissolved concentration of organic compounds support the observed limiting current density?

From Table III, the carbon content associated with dissolved organic compounds, 231 PPM, and taking an average molecular species containing a C $_{15}$ skeleton, transforms to 1.3×10^{-3} moles per liter of organics. Thus, on utilizing the formula:

$$i_L = \frac{nFDc}{\delta} \quad (7)$$

where n , the total number of electrons transferred is taken on average to be 4; D , the average diffusion coefficient for dissolved organic compounds, is taken as $2 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$; c , the concentration of organics per cm^3 , is found to be 1.3×10^{-6} moles, and δ , the diffusion layer thickness, is 0.001 cm for a vigorously stirred lignite slurry, yields a limiting current of ca. 1.0 mA cm^{-2} . Thus, oxidation of dissolved organic compounds in solution can account for the experimentally observed limiting current density in the case of lignite slurries.

A hypothesis for the three-fold increase in oxidation rate when lignite particles are allowed to make contact with the electrode could involve the degradation of lignite particles as a result of the mechanical action of particle-electrode collisions. Such phenomena would give rise to the removal of loosely held microparticles or large lignite macromolecules from the surface of lignite particles, giving rise to an increased amount of dissolved organics and a larger surface area for further dissolution. Such processes would explain the facts presented in Figures 6(a) and (b) without involving electron transfer reactions between lignite particles and the anode surface.

4.4. Electrochemical Oxidation of Washed Lignite Slurries for Extended Times

It has been observed (Tables IV and X) that a series of organic compounds falling into a class of heavy hydrocarbons having a C_{10} - C_{19} carbon skeletal structure, as well as organic alcohols and acids with similar carbon contents, are formed when the electrochemical oxidation of aqueous lignite slurries takes place over a time of three hours. However, after extending the electrolysis time considerably, for example, seven or thirteen days, the organic compounds are greatly diminished in variety and concentration [Figs. 13(a) and (b)] and presumably are oxidized to carbon dioxide gas. It seems, therefore, that a series of reactions took place in which successive oxidations occur, and the final stage is carbon dioxide formation, as would be expected. Thus, there is an optimum time for electrolysis in which the organic compounds formed reach a maximum value.

One may speculate that there may be a stage in the overall reactions in which CO is being produced; this would be valuable in conjunction with the hydrogen gas produced simultaneously at the cathode (e.g., in the synthesis of methanol).

4.5. Maximum Current Density Obtainable from the Electrolysis of Lignite Slurries

In the present work, the highest current density obtained in the case of the electrolysis of thoroughly washed lignite slurries without the addition of any external redox couples was 15 mA cm^{-2} at a potential of ca. 1.1 V (NHE). In the case of unwashed lignite slurries, the current density was about 9 mA cm^{-2} at the latter voltage.

In the present experiments, no attempt was made to increase the stirring rate to a large extent; an increase of about 50 times (i.e., to 750 mA cm^{-2}) would be possible with forced stirring. Reduction of the overvoltage could be achieved by increasing the temperature by, e.g., 50° (although this would be accompanied by a pressure increase to about 5 Atm).

4.6. Separation and Identification of Organic Compounds Produced by the Electrolysis of Washed Lignite Slurries

The analytical results obtained on comparing the results from Radian Corporation and the University of Texas on the one hand (section 3.5.1), with those of Battelle, Pacific Northwest Laboratory, on the other hand (section 3.5.2) are not in agreement. Correspondingly, analytical results ob-

tained at Battelle, using the Sep-pack method, are contradictory with data derived from liquid-liquid extractions at the same laboratory (section 3.5.4). However, the Sep-pack results produced by Radian Corporation and the University of Texas are in qualitative agreement with the liquid-liquid extraction results from Battelle (compare Tables IV and X). The latter fact lends greater credibility to the Sep-pack analyses performed by Radian Corporation and the University of Texas.

In the case of the Sep-pack analyses carried out at the University of Texas and Radian Corporation, reproducibility of the compounds identified (Table IV) was checked by repetition of the experimental work and analyses. Identical samples were sent to both institutions. No computer identification was used at Radian Corporation. Very good agreement was found, for the compounds identified, between results obtained by the two institutions. Further, analyses of authentic samples of materials, identical to those obtained for the unknown coal-derived liquid sample after electrolysis (octadecane, eicosane and dodecane, see Table IV) either as 1% pure solutions or as mixtures in ether solvents were carried out using the same analytical conditions and equipment used for the unknown samples at the University of Texas. By com-

paring peaks due to these real compounds with those obtained from the electrolyzed lignite slurries, the identity of which were under investigation, confirmation of the latter was obtained.

Disparity exists in the quantitative values of organic compounds present in electrolyzed washed lignite slurries analyzed by means of Sep-pack data from the University of Texas and Radian Corporation (see Table IV, approximately 10^{-3} to 10^{-4} molar) and with values derived from the liquid-liquid extraction results from Battelle (see Table X, approximately 10^{-6} molar for all compounds except for one, this having a concentration of approximately 10^{-3} moles per liter). Considering the large number of dissolved organic compounds known to arise from coal in general,¹⁸ and the large variety observed in this work (Table IV), it is likely that, as a result of the electrochemical oxidation of lignite-derived organics, many compounds should be produced having similar concentrations. This is indeed observed in the Sep-pack investigation carried out at the University of Texas and Radian Corporation and agrees well with the electrochemical charge passed. On the other hand, it is unlikely that one compound would be produced at a concentration 1,000 times greater than that of any other compound, as observed in the liquid-liquid

extraction work performed at Battelle. Thus, on the basis of the known dissolution chemistry of coal,¹⁸ and taking into account the charge passed in the electrochemical oxidation reported in this work, the quantitative values derived from the Sep-pack analyses at the University of Texas and Radian Corporation are more credible.

4.7. On the Anodic Liquefaction of Coal

With the limiting current densities obtained here (ca. 10 mA cm^{-2}), the production of organic compounds as a result of the electrochemical oxidation of lignite macromolecules gives rise to concentrations in the millimolar range for overall compound formation. From the carbon content associated with organic compounds after electrolysis, 717 PPM (cf., Table III), and assuming an average molecular structure having a C_{15} carbon skeleton, translates to ca. 4×10^{-3} moles per liter. At such a concentration, the organics would be dissolved in the aqueous electrolyte, and the economic benefits to be derived from them is questionable, due to the costs of separation.

However, at higher temperatures (180°C) than used in the present work (100°C) and pressures of up to 10 atmospheres, limiting currents of the order of $250\text{-}500 \text{ mA cm}^{-2}$ have been

obtained.²⁴ At such an oxidation rate, it would be possible to make oils at more than the saturation solubility of such oils in aqueous electrolytes, and these would then float as a separate phase on the electrolyte. This would eliminate the separation costs. Then, the organics formed may be of economic value and give rise to significant credits to be subtracted from other costs involved in forming hydrogen. Thus, in a zeroeth approximation, separation costs can be neglected, and the organic compounds produced as a result of the electrochemical oxidation of lignite can be taken as crude oil, with an average molecular weight of ca. 212 gm ($C_{15}H_{32}$).

A speculative economic assessment of the cost of hydrogen using lignite depolarization may be carried out (taking established conditions as 500 mA cm^{-2} at a potential of 1.0 V).²⁵ The cost of hydrogen, derived from the electrolysis of water, can be calculated from the equation:[‡]

$$\text{Cost in \$ per GJ of H}_2 = 2.29 E_c + 3 \quad (8)$$

where E is the cell voltage (1.8 V), c is the cost in cents for electrical energy per kWh (4¢), and the factor 3 takes

[‡]The numerical cost value, as given by Equation (8) leaves out profit.

into account amortization of the plant at a 15% interest rate, as well as maintenance, plant depreciation and labor. Utilizing the values stated in Equation (8) yields \$19.50 per GJ of hydrogen. Placing a lignite slurry in the anode compartment would reduce the cell voltage to ca. 1.0 V for current densities of the order of 500 mA cm^{-2} (Clark, et al.).^{24,25} Using the latter cell voltage, the cost per GJ is \$12.00.

One GJ of hydrogen is equivalent to 4,300 moles of hydrogen. To obtain the corresponding number of moles of organic compounds formed, the number of electrons transferred per mole (nF) needs to be known. Since this will vary depending on the nature of the compounds formed, a number of scenarios will be evaluated, corresponding to $n = 4, 6, 8$ and 10 electrons (cf., column two, Table XIII).

Assuming that the average organic compound has a molecular structure containing a C_{15} alkane skeleton, giving rise to an average molecular weight of 212 grams, the total weight of organics formed for each value of n is given in column three, Table XIII.

Taking the cost of a barrel of crude oil (approximately 120 kg) as \$30.00, and assuming that the low quality of the oil produced in the anode compartment would secure a price of about one-half that of crude oil, would give rise to a credit

for the anode products formed as a result of the electrochemical oxidation of lignite as shown in column four of Table XII. However, the anode depolarizer, lignite, is not free, and its cost needs to be taken into account. Taking the cost of a ton of lignite (1,000 kg) as \$30.00, and assuming a 50% conversion of lignite to organic compounds, would yield a cost for the required amount of lignite as presented in column five of Table XIII.

The final cost of the hydrogen produced, using lignite as an anode depolarizer, can be evaluated using a modified form of Equation (8), as follows:

$$\text{Cost in \$ per GJ of H}_2 = [(2.29 E_c) + 3 + \frac{\text{Cost of lignite consumed per GJ of H}_2 \text{ produced}}{\text{of H}_2 \text{ produced}}] - \frac{\text{Credit for organic compounds produced per GJ of H}_2 \text{ produced}}{\text{per GJ of H}_2 \text{ produced}} \quad (9)$$

Thus, the estimated cost of hydrogen per GJ, for each value of n (column 6 of Table XIII), is considerably cheaper than hydrogen produced by the steam reforming of natural gas (ca. \$5 per GJ).

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Table I

ELEMENTAL ANALYSIS OF DRIED LIGNITE SAMPLES

Sample	C(%)	H(%)	N(%)	S(%)	Fe(%)	O(%)
1	55.9	4.3	1.2	2.4	0.33	31.9
2	56.6	4.4	1.1	---	0.34	30.1

Table II

QUANTITATIVE ELEMENTAL ANALYSIS (IN PPM) FOR THE FILTRATE OF A WASHED LIGNITE SLURRY

Sample	Al	C	Ca	Cu	Fe	Mg	Mn	Na	S	Si	Ta	Ti	Zn
Blank 5 M H ₂ SO ₄	0.5	5	0.2	0.02	0.36	0.10	0.01	0.05	2000 ¹	0.36	0.67	0.05	0.01
Previously Washed Lignite (2 Weeks at 100°C in 5 M H ₂ SO ₄) ^a	0.5	103	67	0.7	264	2.4	0.14	10	2000 ¹	2.7	2	20	0.76

^aFinely crushed previously washed and dried lignite (38-45 µm) was introduced into sulphuric acid solution (0.6 g/ml, 5 M H₂SO₄) and heated at 100°C for three hours while being constantly agitated.

¹Sulphur signal arises from sulphur species dissolved out of lignite and from the SO₄⁼ ions pertaining to the electrolyte (5 M H₂SO₄).

Table III

TOTAL AMOUNT OF CARBON IN THE FILTRATE OF LIGNITE SLURRIES
BEFORE AND AFTER ELECTROLYSIS

Sample	Mean Concentration (PPM)
Blank 5 M H_2SO_4	0.4
Before Electrolysis	231
After Electrolysis	717

Table IV

COMPOUNDS IDENTIFIED AFTER ELECTROLYSIS^a OF WASHED LIGNITE IN 5 M H₂SO₄
at 100°C; HELD AT 1.15 V (NHE) FOR THREE HOURS

Compound	Molecular Weight	Molecular Formula	Reliability (%)	Concentration (mol l ⁻¹) x 10 ⁴
Dodecane, 2,6,11-Trimethyl	212	C ₁₅ H ₃₂	93	5.4
Eicosane	282	C ₂₈ H ₄₂	93	4.7
1-Pentanol, 2-Ethyl-4-Methyl	130	C ₈ H ₁₈ O	96	2.2
Dodecane	170	C ₁₂ H ₂₆	94	2.0
1-Hexadecanol, 2-Methyl	256	C ₁₇ H ₃₆ O	94	1.87
Octadecane	254	C ₁₈ H ₃₈	94	1.80
Octane, 2,6-Dimethyl	142	C ₁₀ H ₂₂	92	1.2
Heptane, 2,2,4-Trimethyl	142	C ₁₀ H ₂₂	93	1.1

Table IV. Continued.

Compound	Molecular Weight	Molecular Formula	Reliability (%)	Concentration (mol l ⁻¹) x 10 ⁴
Tridecane, 2-Methyl	198	C ₁₄ H ₃₀	94	0.85
Dodecane, 4,9-Dipropyl	254	C ₁₈ H ₃₈	96	0.8
Tetradecane, 4-Ethyl	226	C ₁₆ H ₃₄	94	0.7
Tridecane, 2,5-Dimethyl	212	C ₁₅ H ₃₂	91	0.5
Tridecane, 7-Hexyl	268	C ₁₉ H ₄₀	91	0.5
Docosane, 11-Decyl	450	C ₃₂ H ₆₆	92	0.46
Heptadecane, 2,6,10,14-Tetramethyl	296	C ₂₁ H ₄₄	90	0.40
Heneicosane, 1-Cyclopentyl	364	C ₂₆ H ₅₂	94	0.30
Octadecane, 6-Methyl	268	C ₁₉ H ₄₀	90	0.23

^aOnly those compounds arising from electrolysis are stated, i.e., compounds originating from thermal and agitation effects have been removed by analyzing appropriately treated blank slurries.

Table V

COMPOUNDS IDENTIFIED AFTER ELECTROLYSIS^a OF A WASHED LIGNITE SOLUTION (NO COAL IN CONTACT WITH ELECTRODE) AT 100°C; HELD AT 1.15 V (NHE) FOR THREE HOURS

Compound	Molecular Weight	Molecular Formula	Reliability (%)	Concentration (mol l ⁻¹) x 10 ⁵
Hexadecane	226	C ₁₆ H ₃₄	98	6.8
Heptadecane, 2,6,10,10-Tetramethyl	296	C ₂₁ H ₄₄	92	5.3
Octadecane	254	C ₁₈ H ₃₈	91	3.5
1-Tetradecanol (Myrlatyl Alcohol)	214	C ₁₄ H ₃₀ O	91	2.8
Hexadecanoic acid	256	C ₁₆ H ₃₂ O ₂	97	2.1
Dodecane, 2,6,11-Trimethyl	212	C ₁₅ H ₃₂	91	1.85
Heptane, 3-Ethyl-2-Methyl	142	C ₁₀ H ₂₂	93	1.6

^aOnly those compounds arising from electrolysis are stated, i.e., compounds originating from thermal and agitation effects have been removed by analyzing appropriately treated blank lignite slurries.

Table VI

COMPOUNDS IDENTIFIED AFTER ELECTROLYSIS^a OF UNWASHED LIGNITE
IN 5 M H₂SO₄ AT 100°C; HELD AT 1.15 V (NHE) FOR THREE HOURS

Compound	Molecular Weight	Molecular Formula	Reliability (%)
Decane	142	C ₁₀ H ₂₂	95
Heptadecane, 2, 6, 10, 15- Tetramethyl	296	C ₂₁ H ₄₄	92
Hexadecanoic Acid	256	C ₁₆ H ₃₂ O ₂	90

^aOnly those compounds arising from electrolysis are stated, i.e., compounds originating from thermal and agitation effects have been removed by analyzing appropriately treated blank lignite slurries.

Table VII

TREATED LIGNITE SLURRY SAMPLES AND APPROPRIATE
BLANK SAMPLES SUBJECTED TO SEP-PACK CARTRIDGES AND/OR
LIQUID-LIQUID EXTRACTIONS AT BATTELLE,
PACIFIC NORTHWEST LABORATORY

Sample No.	Sample Description ^a
1	Washed, electrolyzed 3 hrs
2	Sep-pack cartridge, eluted with 5 M H ₂ SO ₄ , H ₂ O, N ₂ -dried followed by eluting with diethylether
3	Sep-pack cartridge, eluted with diethylether
4	Diethylether solvent blank
5	Washed, electrolyzed 8 days
6	Washed, electrolyzed 13 days
7	Washed, electrolyzed 3 hrs (no coal contacting electrodes)
8	Unwashed, electrolyzed 3 hrs
9	Unwashed, heated, non-electrolyzed
10	Washed, heated, non-electrolyzed
11	Benzene extracted 5 M H ₂ SO ₄ blank

^aWashed: pulverized coal was washed with 5 M H₂SO₄ for
200 hours
Electrolyzed: at 100°C in 5 M H₂SO₄ at 1.1 V (NHE) for
3 hrs
Heated: at 100°C in 5 M H₂SO₄ for 3 hrs

Table VIII

COMPOUNDS IDENTIFIED IN SEP-PACK SEPARATIONS (FIGURE 11)

Peak No. ^a	GC Retention Time (min)	Compound ^b	Comments
1	37.62	Unidentified and/or n-C ₁₉ alkane and/or C ₁₉ alkene isomer	3 Compounds coeluting: (i) base peak mass: 147 amu (probably not molecular ion) (ii) alkane masses: 57,71,85,99 (iii) alkene masses: 55,69,83,97
E 2	22.27	4-Methyl-2:6-Di- <u>tert</u> -Butyl Phenol	Ether preservative and contaminant (220 amu)
3	19.31	n-C ₁₅ alkane	Alkane masses: 57,71,85,99
4	24.36	n-C ₁₆ alkane	Alkane masses: 57,71,85,99
5	38.34	Unidentified	Base peak mass: 147 amu (probably not molecular ion)
6	42.83	Phthalate	Characteristic masses: 167,149
7	24.18	C ₁₆ alkene	Alkene masses: 55,69,83,97
8	28.77	C ₁₇ alkene	Alkene masses: 55,69,83,97

Table VIII. Continued.

Peak No. ^a	GC Retention Time (min)	Compound ^b	Comments
9	28.92	n-C ₁₇ alkane	Alkane masses: 57,71,85,99
10	13.66	n-C ₁₄ alkane	Alkane masses: 57,71,85,99
11	19.09	C ₁₅ alkene	Alkene masses: 55,69,83,97
12	8.75	C ₁₃ alkane isomer	Alkane masses: 57,71,85,99
E 13	36.16	Unidentified	Base peak mass: 147 amu (probably not molecular ion)
E 14	32.27	Unidentified	Base peak mass: 60 amu (characteristic of alcohols, higher, aldehydes, ketones, ethers and some esters)
15	23.59	C ₁₋₂₂₀	Methyl analogue of peak #2
	23.65	C ₁₆ alkane isomer	Alkane masses: 57,71,85,99
16	25.21	C ₁₆ alkane isomer	Alkane masses: 57,71,85,99
17	20.55	C ₁₅ alkene	Alkene masses: 55,69,83,97
18	32.94	C ₁₈ alkene	Alkene masses: 55,69,83,97

Table VIII. Continued.

Peak No. ^a	GC Retention Time (min)	Compound ^b	Comments
19	28.28	C ₁₇ alkane isomer	Alkane masses: 57,71,85,99
20	29.67	C ₁₇ alkane isomer	Alkane masses: 57,71,85,99
21	24.03	C ₁₆ alkene	Alkene masses: 55,69,83,97
22	25.58	C ₁₆ alkene	Alkene masses: 55,69,83,97
	25.85	C ₁₆ alkene	Alkene masses: 55,69,83,97
	26.02	C ₁₆ alkene	Alkene masses: 55,69,83,97
23	33.07	n-C ₁₈ alkane	Alkane masses: 57,71,85,99
24	20.31	C ₁₅ alkane isomer	Alkane masses: 57,71,85,99
25	23.11	C ₁₆ alkane isomer	Alkane masses: 57,71,85,99
26	33.74	C ₁₈ alkane isomer	Alkane masses: 57,71,85,99
27	23.20	C ₁₆ alkene	Alkene masses: 55,69,83,97
28	3.84	n-C ₁₂ alkane	Alkane masses: 57,71,85,99
29	30.13	C ₁₇ alkene	Alkene masses: 55,69,83,97
	30.23	C ₁₇ alkene	Alkene masses: 55,69,83,97

Table VIII. Continued.

Peak No. ^a	GC Retention Time (min)	Compound ^b	Comments
30	34.26	C ₁₈ alkane isomer	Alkane masses: 57,71,85,99
	34.38	C ₁₈ alkene isomer	Alkene masses: 55,69,83,97

^aPeaks listed in decreasing concentration.

^bn-C_{xx} alkanes assigned by GC retention data.

E = ether solvent contaminant

Table IX

COMPOUNDS IDENTIFIED FOR 0.3 gr/ml GRASS SLURRY IN 5 M H₂SO₄
ARISING ONLY FROM ELECTROLYSIS AT 110°C FOR SEVEN HOURS

Compound ^a	Molecular Weight	Molecular Formula	Reliability (%)
Propane, 1-1-Diethoxy (Propylal)	132	C ₇ H ₁₆ O ₂	92
2, Pentanone, 4-hydroxy-4-Methyl (Diacetone alcohol)	116	C ₆ H ₁₂ O ₂	95

^aIn the order of decreasing amount.

Table X

COMPOUNDS IDENTIFIED IN LIQUID-LIQUID EXTRATION OF
SAMPLES 1, 5-10 (TABLE VII), FIGURES 13-16

Peak No. ^a	GC Retention Time (min)	Compound	Approximate ^b Concentration (ng/ml or ppb)	Comments ^c
1	5.49-6.30	Butyrolactone	134,750	Identified by MS using standard compound
2	7.65	Unidentified hydrocarbon	84.8	Unsaturated functional groups
3	9.73	Unidentified hydrocarbon acid or aldehyde	563.5	Base peak mass: 60 amu Characteristic of aliphatic acids and aldehydes
4	9.12	Unidentified hydrocarbon acid or aldehyde	151.8	Base peak mass: 60 amu Characteristic of acids and aldehydes
5	21.22	C ₁₄ alkane	209.6	Alkane masses: 43,57,71
6	14.53	Unidentified hydrocarbon	187.2	Alkane masses: 43,57,71 Strong loss of 28 amu: CO or C ₂ H ₄
7	16.82	Unidentified hydrocarbon	192.6	Strong loss of 28 amu: C ₂ H ₅ Alkene masses: 41,55,70,83

Table X. Continued.

Peak No. ^a	GC Retention Time (min)	Compound	Approximate ^b Concentration (ng/ml or ppb)	Comments ^c
8	20.26	Unidentified hydrocarbon	169.3	Base peak mass: 71 amu
9	24.12	Unidentified hydrocarbon	107.5	Base peak mass: 85 amu CH ₂ analogue of peak #8
A 10	25.47	Unidentified	92.14	Hydrogen contaminated from sulphuric acid
11	28.12	C ₁₅ alkane	31.8	Alkane masses: 43,57,71,85
A 12	37.94	Unidentified	237.9	Hydrocarbon contaminant from sulphuric acid
13	42.73	Unidentified	73.5	Base peak mass: 147 amu (probably not molecular ion)
14	47.90	Unidentified and alkane	---	2 peaks coeluting: (i) alkane masses: 43,57,71,85 (ii) mass: 129
A 15	50.93	Phthalate	995.1	Contaminant from sulphuric acid; characteristic masses of phthalates: 167 and 149 amu

Table X. Continued.

Peak No. ^a	GC Retention Time (min)	Compound	Approximate ^b Concentration (ng/ml or ppb)	Comments ^c
16	42.59	Unidentified	---	GC contaminant
A 17	27.71 27.92 28.13	3 peaks unidentified	---	Hydrocarbon contaminants from sulphuric acid (see Fig. 12) (i) masses at 60 and 73 characteristic of aliphatic acids (ii) Base peak mass: 151 amu (iii) masses at 149 and 167 characteristic of phthalates
18	33.20	Anthracene	---	Base peak mass: 178 amu Impurity from 2-chloroanthracene Internal standard
ISTD	36.84	2-chloroanthracene	---	Internal standard

^aPeak numbers listed in clusters, according to concentration.

^bConcentrations approximated with respect to 2-chloroanthracenes for sample 1 only.

^cComponent characterizations taken from "Interpretation of Mass Spectra," F. W. McLafferty, W. A. Benjamin, Inc., 1973, pp. 265-265.

Table XI

SUMMARY OF RESULTS OF ANALYSES OF NEW COMPOUNDS INTRODUCED
BY ELECTROLYSIS OF CARBONACEOUS SLURRIES

Origin of Compound	Analysis Method	Main Compounds noted
Unwashed lignite slurry	Sep-pack/GC-MS with computer identification	Decane($C_{10}H_{22}$) Heptadecane, 2,6,10,15-Tetramethyl ($C_{21}H_{44}$)
Unwashed lignite slurry	Liquid-liquid extraction/GC-MS with "fingerprint" matching of spectra	Butyrolactone ($C_4H_6O_2$) C_{14} , C_{15} alkanes and carboxylic acids
Washed lignite slurry	Sep-pack/GC-MS with computer identification	Dodecane, 2,6,11-Trimethyl ($C_{15}H_{32}$) Dodecane ($C_{12}H_{26}$) Octane, 2,6-Dimethyl ($C_{10}H_{22}$)
Washed lignite slurry	Liquid-liquid extraction/GC-MS with "fingerprint" matching of spectra	Butyrolactone ($C_4H_6O_2$) C_{14} , C_{15} alkanes and carboxylic acids
Washed lignite slurry filtrate (no lignite particles touching electrode)	Sep-pack/GC-MS with computer identification	Hexadecane ($C_{16}H_{34}$) Octadecane ($C_{18}H_{38}$) 1-Tetradecanol ($C_{14}H_{30}O$)
Washed lignite slurry filtrate (no lignite particles touching electrode)	Liquid-liquid extraction/GC-MS with "fingerprint" matching of spectra	Butyrolactone ($C_4H_6O_2$) C_{14} , C_{15} alkanes and carboxylic acids

Table XI. Continued.

Origin of Compound	Analysis Method	Main Compounds noted
Biomass (grass) slurry	Sep-pack/GC-MS with computer identification	Propane, 1-1-Diethoxy (C ₇ H ₁₆ O ₂) 2-Pentanone, 4-Hydroxy-4-Methyl (C ₆ H ₁₂ O ₂)

Table XII

PHYSICAL CHARACTERISTICS PERTAINING TO OXYGEN GAS
AND LIGNITE SLURRY

Viscosity of oxygen gas at 100°C, $\eta_{O_2} \approx 2.0 \times 10^{-4}$ poise

Velocity of oxygen gas molecules at 100°C, $u_{O_2} = 2.0 \times 10^4$ cm s⁻¹

Radius of an oxygen molecule, $r_{O_2} = 1.5 \times 10^{-8}$ cm

Radius of a lignite particle, $r_{\text{lignite particle}} = 2.0 \times 10^{-3}$ cm

Viscosity of lignite slurry, $\eta_{\text{lignite slurry}} \approx 10^{-2}$ poise

Table XIII

COST OF HYDROGEN PER GJ AFTER TAKING INTO ACCOUNT THE COST OF LIGNITE
AND THE CREDITS FOR ANODIC ORGANIC COMPOUNDS FORMED

Average number of electrons transferred	Number of moles of organics formed per GJ of H ₂	Total weight of organics formed (kg) per GJ of H ₂	Credit for organic products formed per GJ of H ₂	Cost of lignite consumed per GJ of H ₂	Final cost of H ₂ per GJ
4	2,150	456	\$57.0	\$27.4	-\$17.44
6	1,433	304	\$38.0	\$18.2	-\$ 7.64
8	1,075	228	\$28.5	\$13.7	-\$ 2.64
10	860	183	\$22.8	\$11.0	\$ 0.40

FIGURE CAPTIONS

- FIGURE 1. Electrochemical cell for the oxidation of carbonaceous slurries.
- FIGURE 2. (a) Cyclic voltammogram for an unwashed lignite slurry (0.6 g/ml, 5 M H_2SO_4) at 100°C using a platinum electrode. Potential limits: 0.0-1.4 V (NHE). Scan rate: 20 mV s^{-1} .
(b) Variation of the anodic limiting current density as a function of Fe^{2+} concentration from the voltammetric behavior at a platinum electrode in various solutions at 100°C . Potential limits: 0.0-1.4 V (NHE). Scan rate: 20 mV s^{-1} .
- FIGURE 3. (a) Typical cyclic voltammogram for a washed lignite slurry (0.6 g/ml, 5 M H_2SO_4) at 100°C using a platinum electrode. Potential limits: 0.0-1.3 V (NHE). Scan rate: 20 mV s^{-1} .
(b) As for Figure 3(a), except for potential limits of 0.0-2.4 V (NHE).
- FIGURE 4. Cyclic voltammograms for a washed lignite slurry (0.6 g/ml, 5 M H_2SO_4) using a platinum electrode: (—) 80°C ; (-·-·-) 100°C . Potential limits:

0.0-1.3 V (NHE). Scan rate: 20 mV s^{-1} .

FIGURE 5. (a) Cyclic voltammograms for a washed lignite slurry (0.6 g/ml, 85% H_3PO_4) using a platinum electrode: (---) 80°C ; (-·-·-) 100°C ; (—) 130°C . Potential limits: 0.0-1.4 V (NHE). Scan rate: 20 mV s^{-1} .

(b) Cyclic voltammogram for a washed lignite slurry (0.33 g/ml, 5 M KOH) at 100°C using a platinum electrode. Potential limits: 0.0-1.55 V (NHE). Scan rate: 20 mV s^{-1} .

FIGURE 6. (a) Voltammetric behavior of a thoroughly washed lignite slurry, ASTM D2492 method (0.6 g/ml, 5 M H_2SO_4) at 100°C using a platinum electrode. Potential limits: 0.0-1.4 V (NHE). Scan rate: 20 mV s^{-1} .

(b) Cyclic voltammogram pertaining to the filtrate of a thoroughly washed lignite slurry (no lignite particles in contact with the anode) at 100°C using a platinum electrode. Potential limits: 0.0-2.0 V (NHE). Scan rate: 20 mV s^{-1} .

FIGURE 7. (a) Voltammetric behavior of an aqueous 8.2×10^{-4} M FeSO_4 solution at 100°C using a platinum

electrode. Potential limits: 0.0-2.0 V (NHE).

Scan rate: 20 mV s⁻¹.

- (b) As for Figure 7(a), except for an aqueous solution containing 8.2×10^{-4} M FeSO₄ + 5 M H₂SO₄.

FIGURE 8. (a) Anodic potential sweeps pertaining to washed lignite slurries (0.6 g/ml 5 M H₂SO₄) with and without added cerous ions at 100°C using a platinum electrode. Potential limits: 0.0-1.4 V (NHE). Scan rate: 20 mV s⁻¹.

- (b) Cyclic voltammogram for a washed lignite slurry (0.6 g/ml, 5 M H₂SO₄) at 100°C using a lead dioxide electrode. Potential limits: 0.0-1.6 V (NHE). Scan rate: 20 mV s⁻¹.

FIGURE 9. (a) Voltammetric behavior for a grass slurry (0.3 g/ml, 5 M H₂SO₄) at 110°C using a platinum electrode. Potential limits: 0.0-1.5 V (NHE). Scan rate: 20 mV s⁻¹.

- (b) Cyclic voltammogram for a household waste slurry (1.0 g/ml, 5 M H₂SO₄) at 120°C using a platinum electrode. Potential limits: 0.0-2.0 V (NHE). Scan rate: 20 mV s⁻¹.

FIGURE 10. (a) Capillary column gas chromatogram of a washed

lignite slurry (0.6 g/ml 85% H_3PO_4) heated at 130°C for 10.5 hours without electrolysis.

Organic compounds separated by the Sep-pack method.

- (b) Capillary column gas chromatogram of a washed lignite slurry (0.6 g/ml, 85% H_3PO_4) after electrolysis at 130°C for 10.5 hours. Organic compounds separated by the Sep-pack method.

- FIGURE 11. (a) Capillary column gas chromatogram of a washed lignite slurry (0.6 g/ml, 5 M H_2SO_4) after electrolysis at 1.1 V (NHE) for 3 hours at a temperature of 100°C . Organic compounds separated by the Sep-pack method. Injection/sample volume: 0.5 μl /50 μl .
- (b) Capillary column gas chromatogram of a Sep-pack cartridge blank prepared by eluting the cartridge with 5 M $\text{H}_2\text{SO}_4/\text{H}_2\text{O}/\text{Et}_2\text{O}$. Injection/sample volume: 0.5 μl /50 μl .
- (c) Capillary column gas chromatogram of a Sep-pack cartridge blank prepared by eluting the cartridge with Et_2O . Injection/sample volume: 0.5 μl /100 μl .
- (d) Capillary column gas chromatogram of an Et_2O

solvent blank (3 ml ether reduced to 100 μ l;
0.5 μ l injection volume).

FIGURE 12. (a) Mass spectrum for organic component 3 in
Figure 11.

(b) Mass spectrum for organic component 4 in
Figure 11.

FIGURE 13. (a) Capillary column gas chromatogram of a washed
lignite slurry (0.6 g/ml, 5 M H_2SO_4) after
electrolysis at 1.1 V (NHE) for 3 hours at a
temperature of 100°C. Organic compounds
separated by liquid-liquid extraction method.
Injection/sample volume: 0.5 μ l/25 μ l.

(b) As for Figure 13(a), except that time of elec-
trolysis was 8 days. Component A: concen-
tration = 0.27 mg l^{-1} .

(c) As for Figure 13(a), except that time of elec-
trolysis was 13 days.

(d) Capillary column gas chromatogram on electro-
lyzing a washed lignite slurry filtrate (no
lignite particles in contact with anode) at
1.1 V (NHE) for 3 hours at a temperature of
100°C. Organic compounds separated by liquid-
liquid extraction method. Injection/sample

volume: 0.5 μl /12 μl . Lettered component concentrations: B = 5 mg l^{-1} , C = 3 mg l^{-1} , D = 3 mg l^{-1} and component 1 (butyrolactone) = 28 mg l^{-1} .

FIGURE 14. (a) Mass spectrum for organic component 1 in Figure 13.

(b) Mass spectrum for organic component 5 in Figure 13.

FIGURE 15. (a) Capillary column gas chromatogram on electrolyzing an unwashed lignite slurry (0.6 g/ml, 5 M H_2SO_4) at 1.1 V (NHE) for 3 hours at a temperature of 100°C. Organic compounds separated by liquid-liquid extraction method. Injection/sample volume: 0.6 μl /25 μl . Component E concentration = 4 mg l^{-1} .

(b) Capillary column gas chromatogram of the extract of an unwashed non-electrolyzed lignite slurry (0.6 g/ml, 5 M H_2SO_4) heated for 3 hours at 100°C. Organic compounds separated by liquid-liquid extraction method. Injection/sample volume: 0.5 μl /25 μl .

FIGURE 16. (a) Capillary column gas chromatogram of the extract of a washed non-electrolyzed lignite

slurry (0.6 g/ml, 5 M H_2SO_4) heated for 3 hours at 100°C . Organic compounds separated by liquid-liquid extraction method. Injection/sample volume: 0.5 μl /25 μl .

(b) Capillary column gas chromatogram of the liquid-liquid extract of the 5 M H_2SO_4 electrolyte blank. Injection/sample volume: 0.6 μl /10 μl .

FIGURE 1

FIGURE 2

FIGURE 3

FIGURE 4

FIGURE 5

FIGURE 6

FIGURE 7

FIGURE 8

FIGURE 9

FIGURE 10

FIGURE 11

FIGURE 12

FIGURE 13

FIGURE 14

FIGURE 15

Compounds present in solution prior to electrolysis dissolve off the internal surfaces of lignite particles. Increased oxidation currents, caused when lignite particles came in contact with the anode, arose, not because of enhanced electrochemical reactions, but from enhanced lignite dissolution following erosion. The organic compounds eventually form CO_2 ; the presence of heavy oils lasts for ca. ten hours. Current densities up to 750 mA cm^{-2} at ca. 1 V should be obtainable. The hydrocarbons are formed via a Kolbe mechanism from carboxylic acids.

Speculative economic considerations show that the final cost of hydrogen produced, using lignite as an anode depolarizer, is considerably cheaper than that from natural gas: \$0.40 per GJ, or less, compared to \$5 per GJ.

FIGURE 16