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Novel Electrochemical Process for Coal Conversion

Final Report

M. Farooque

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Work Performed Under Contract No.: DE-AC21-87MC23291

For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Morgantown, West Virginia

By
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EXECUTIVE SUMMARY

This report presents the results of an investigation performed under the U.S. Department of Energy Contract No. DE-AC21-87MC23291, by Energy Research Corporation during the period June 1987 to June 1989. The major objective of this investigation was to demonstrate and evaluate processes for electrochemical coal conversion at low severity conditions.

Two electrochemical approaches, utilizing both electro-oxidation and electro-reduction routes, were pursued. The main advantage of electrochemical approaches is that the energy of activation for the conversion reaction is supplied in the form of electricity, possibly allowing low temperature conversion and better control of the product specificity. In the electro-oxidation approach, the coal molecules are oxidized with H_2O molecules leading to conversion of coal to smaller hydrocarbon molecules. In the present study, electro-oxidation of coal produced high purity hydrogen, pure CO_2, as well as small quantities of liquid product. Additional benefits were the complete removal of pyritic sulfur, the partial removal of organic sulfur, and a reduction in the ash content with only a small penalty in heating value and consumption of electricity. A mechanism for the greater than 100% current efficiency of hydrogen production observed in the electro-oxidation of coal was postulated.

The electro-reduction process, which involves reduction of hydrogen ion on the coal surface, leads to saturation of aliphatic and aromatic bonds and reduction of other functional groups. This results in lowering of coal molecular weight through cleavage of oxygen, sulfur and other bonds. The feasibility of electrochemical hydrogenation through the electro-reduction of coal was demonstrated for the first time in this program. With each coal tested, liquid products (but no gaseous products) were obtained. Pyritic sulfur was removed in the electro-reduction reaction as well as in the electro-oxidation. A brief summary of these achievements and areas identified for possible future effort is presented below.

Electro-oxidation

This experimental investigation focused on exploring the potential of electro-oxidation for production of useful products and simultaneous 'upgrading' of the coal. The effect of electro-oxidation process variables has been investigated using eight different coal and pyrite materials leading to several important findings.

The calculated current efficiency for hydrogen production, based on H_2 collected at the cathode, was dependent on coal type and reaction time. In many cases, the current efficiency was observed to be greater than 100%. A mechanism for this observation was postulated in which some of the sulfur in coal is chemically converted to H_2S which is trapped in the electrolyte as dissolved and/or dissociated sulfur species (SH^-,$S^=$) which are oxidized at the cathode to free S and H_2. In this reaction, the H_2 associated with the H_2S evolves at the cathode without requiring electrons to flow in the external circuit, thus producing H_2 in excess of that produced by the current. Support for this mechanism was provided by the experimental identification of dissolved H_2S in the electrolyte and free sulfur in the cathode compartment. Further experiments confirmed that organic sulfur in the coal is the source of the H_2S which is related to the greater than 100% current efficiency.

An essentially complete removal of pyritic sulfur occurred in a 300-hour electro-oxidation test of 53µm particle size Illinois #2 coal. This compares very favorably to the process involving grinding and subsequent electrostatic separation, in which only 60% removal of sulfur from 53µm size coal is obtained. In addition, the electro-oxidation process leads to significant reduction of the ash content while lowering the heating value less than 18%, leaving a coal that is still useful for most conventional applications.

A preliminary economic analysis of the electro-oxidation process indicates that, even without considering the credit for pure CO_2, the economic benefit of pretreating coal by the electro-oxidation process can be significant, approximately $ 8 per ton of Illinois #2 coal.

Electro-Reduction

The electro-reduction behavior of five coals as well as a charcoal and a devolatilized coal were tested. Liquid products were obtained with each sample. Their compositions varied greatly and were dependent upon the parent coal; however, aromatic compounds predominated, with methylated phenols being present in the product from each coal.

The volatile components in the coal appear to play an important role in the electro-reduction process. A comparison of the composition of the volatiles expelled from Illinois #6 by heat-treatment with products of electro-reduction of as-received Illinois #6 demonstrates, however, that the electrochemically produced compounds are not the result of simple devolatilization. The majority of the compounds removed by devolatilization are of much smaller molecular weight than those produced by electro-reduction. The significance of the volatiles in the electro-reduction process can be inferred from the differences in the products obtained from the electro-reduction of the devolatilized and the as-received Illinois #6 coals.

No clearcut relationship between temperature, coal rank, volatile contents, structural origin (as reflected in maceral composition, particularly active components), or applied potential and product quantity or composition was established.

The basic concept of hydrogenation of coal through the electro-reduction process has been proven in this program; however, it was not possible to quantify the reaction rate, quantify the product (except in broad comparative terms) or to determine the current efficiency unequivocally. The cell design utilized in the electro-reduction experiments was not amenable to mass balance determinations which would allow estimation of coal conversions and product quantities. Therefore, because of the absence of sufficient rate and conversion information, an economic analysis of this process was not pursued.

Conclusion

The present study has identified two distinctly different processes for coal conversion. The economic attractiveness of the electro-oxidation approach, which was further developed than the electro-reduction approach, has been identified. Additional development of this process leading to development of a practicable cell design is recommended. The technical feasibility of the electro-reduction route has been successfully demonstrated for the first time in this program. However, further characterization of this process is necessary for a reliable evaluation of its economic potential.

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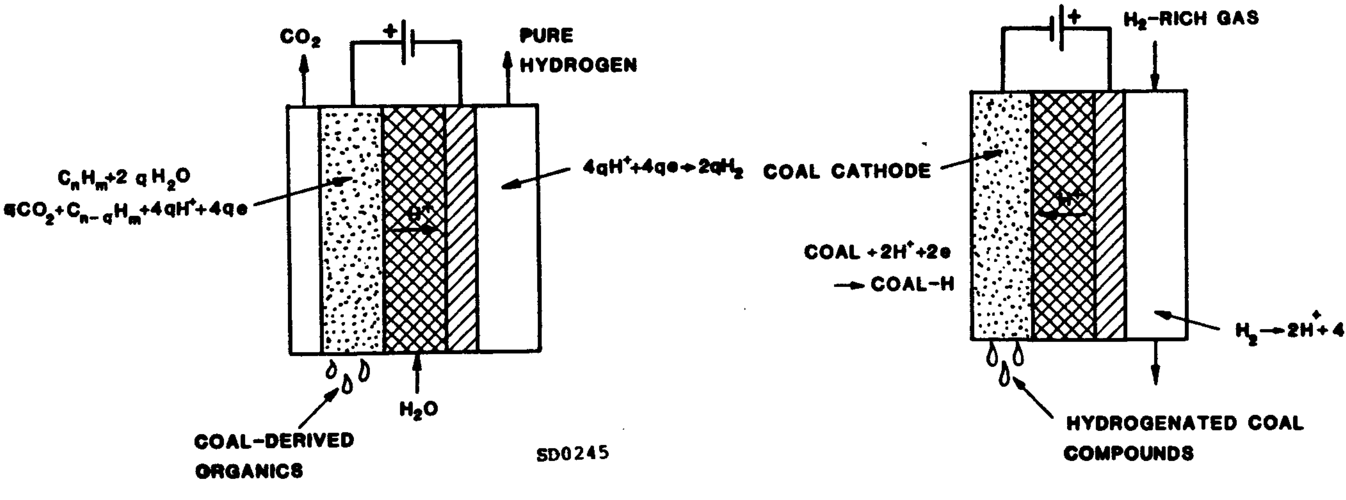
1.0 INTRODUCTION

The United States has an abundant supply of coal. Clean utilization of this domestic coal is a major national energy goal. Conversion of coal to more useful forms of fuel such as H_2 and CO, synthetic natural gas, and liquid fuels (such as gasoline, kerosene and diesel) appears to be the most efficient approach for providing clean fuels from coal and maximizing its utilization.

The coal can be simply modeled as CH_n, where n is ~ 0.8 for bituminous coals. The manufacture of more easily usable fuel from coal involves increasing the number of hydrogen atoms per atom of carbon and can be regarded as a process of 'hydrogenation'. The conventional routes for conversion of coal to more easily usable fuel forms are: (1) gasification, generally involving reactions with steam, (2) direct liquefaction (direct addition of hydrogen), and (3) pyrolysis (thermal decomposition). Coal gasifiers are commonly operated at elevated pressure and in the temperature range of 600-1300°C. Active thermal decomposition of coal begins above 400°C. Direct hydrogenation processes under development are carried out at temperatures from 450 to 475°C and at pressures from 10 to 20 MPa and up to 30 MPa. Pressure favors hydrogenation through (a) inhibiting gas-forming dehydrogenating reactions and (b) increased partial pressures.

The coal-conversion schemes mentioned above are complex and the economic penalties are high because of the severity of the operating conditions. An electrochemical approach to coal conversion has the potential to provide gasification and/or hydrogenation of coal at less severe conditions. In this approach, the energy of activation for the reaction is supplied in the form of electricity at a desired temperature. The controllability of temperature and input energy may allow a broader flexibility over the product selectivity.

Production of coal-derived compounds by both electro-oxidation and electro-reduction routes through cleavage of bonds and hydrogenation are possible. These two electrochemical coal conversion concepts are illustrated in Figure 1.0.



a. ELECTRO-OXIDATION

b. ELECTRO-REDUCTION

FIGURE 1.0 SCHEMATIC OF ELECTRO-CONVERSION OF COAL:

Both Electro-Oxidation and Electro-Reduction of Coal Lead to Cleavage of Coal Molecules.

In the electro-oxidation approach, the coal molecules are oxidized with H_2O molecules leading to conversion of coal to smaller hydrocarbon molecules. The mechanistic and kinetic aspects of this reaction have been investigated extensively [1-22]; however, only limited attention has been focused on defining optimum operating conditions. The electro-reduction process, which involves hydrogenation of coal molecules similar to conventional coal liquefaction, leads to saturation of aliphatic and aromatic bonds and reduction of other functional groups. This is expected to result in the lowering of coal molecular weight through cleavage of oxygen, sulfur and other bonds. Some limited attempts were made to investigate coal electro-reduction in organic electrolytes [23-27, 29 and 32]. Coal electro-reduction in aqueous media had not been investigated.

The present study was conducted to investigate both the electro-oxidation and electro-reduction processes for coal conversion. The objective of the electro-oxidation approach was to demonstrate the possible benefits of this coal treatment process and provide a preliminary economic evaluation of this process. This investigation has identified an electrochemical coal pretreatment process leading to production of pure hydrogen and simultaneous upgrading of coal. This preliminary evaluation also established economic attractiveness for this process. Details of the electro-oxidation study are discussed in Section 2.0 of this report. The electro-oxidation experiments were conducted under the supervision of Prof. Dimitri Gidaspow of Illinois Institute of Technology (IIT) in Chicago. The major goal of the electro-reduction study was to provide a proof-of-concept demonstration of coal hydrogenation by this process, leading to production of useful liquid products. Liquid products were produced by electro-reduction of each of the different coal types tested in this study. The details of this investigation are discussed in Section 3.0. An overall assessment of the coal electrochemical conversion process is presented in Section 4.0.

2.0 COAL ELECTRO-OXIDATION

Electrochemical oxidation of coal provides a unique process for the coal conversion. Early coal electro-oxidation investigations were carried out in alkaline media reporting humic acid and CO_2 as major products. Lynch and Collet reported in 1932 [1] an extensive study on the electrolytic oxidation of Pittsburgh coal in NaOH solution, detecting these products along with small quantities of hydrocarbon products. Farooque and Coughlin [2-8] pioneered acid media electro-oxidation work, proposing an electrochemical method to produce pure hydrogen and other useful products, such as hydrocarbons and pure CO_2, with simultaneous 'upgrading' of the coal. These studies sparked numerous publications [9-23] on the electrochemical oxidation of coal in aqueous electrolytes. An excellent review on coal electrochemistry is available [9]. Murphy et al. [22] have reported production of C_8-C_{18} hydrocarbons by electro-oxidation of lignite. The thermodynamic aspects of coal electro-oxidation are well understood and were summarized by Coughlin and Farooque [6]. Most of the mechanistic understanding for the electrolytic oxidation of coal was developed by Dhooge and Park (13-15) suggesting that iron present with coal has a catalytic effect. Works by Kreysa and Kochanek (23) and by Clarke and Wasson (10) concluded the second order nature, with respect to reactants, of the reaction between ferric ions and coal.

After the work of Dhooge and Park, it was quite clear that the electrolytic oxidation of coal actually involves the oxidation of pyrites and the oxidation of carbon with Fe^{+3} as a catalyst. Because pyrites are involved in the reaction, Lalvani and Coughlin (20 and 21) presented this as a possible process for the removal of sulfur from coal. Their reported results of pyrite removal, however, were $< 50\%$.

The present study was undertaken to establish the potential of coal conversion via an electro-oxidation route for production of useful products and simultaneous 'upgrading' of the coal. Initially, the effect of operating parameters, such as coal particle size, coal concentration, electrolyte type, cell voltage, stirring rate, and temperature, were investigated to establish the preferred operating condition. A long term test was then performed to conduct mass and energy balance. Finally, the results of this analysis were used to determine the commercial attractiveness of the coal conversion process. The results and the significant findings of this study are discussed below.

2.1 EXPERIMENTAL

The coal electro-oxidation experiments were conducted at 1 atm at a temperature of 110°C and at anodic potentials of 0.5 to 1.9V (WRT calomel electrode) in H_3PO_4, HCl, Na_2CO_3, H_2SO_4, and CH_3COOH electrolytes. Sulfuric acid was determined to be the best choice for enhancing the electro-oxidation rate of coal. Pulverized coal slurried with electrolyte in a 0.1 g/ml loading comprised the reactant which was oxidized at the anode to gaseous and liquid products. Hydrogen was produced at the cathode. The gases and liquid products were identified and the effects of the process variables on the kinetics of the electro-oxidation reaction and on the composition of the products were investigated. In Figure 2.1, the test variables and on-line and post-test analyses performed are identified.

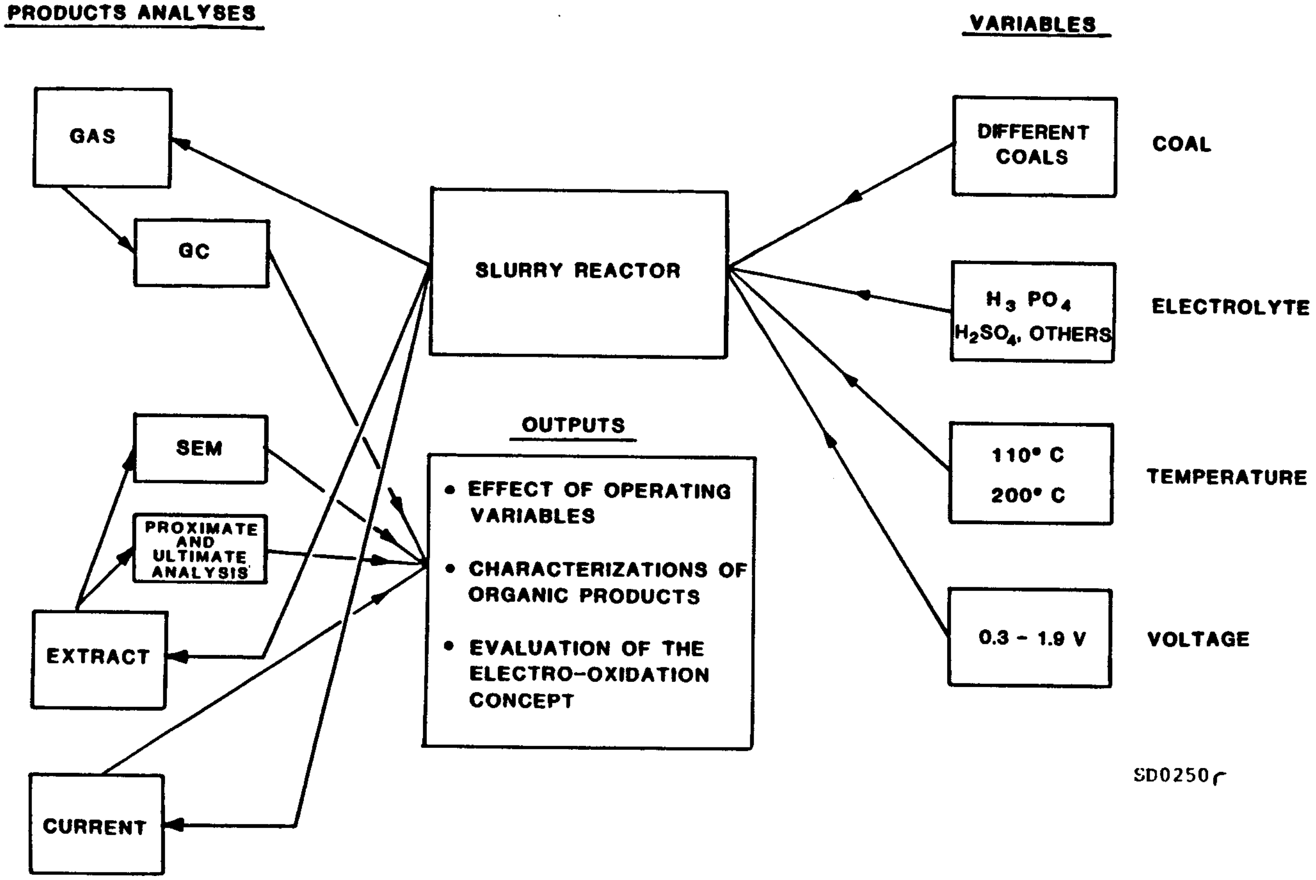


FIGURE 2.1 TEST SUMMARY OF ELECTRO-OXIDATION PROCESS:

Well Planned Investigation Led to Characterization of the Electro-Oxidation Process.

Test Setup

The experimental setup is shown in Figure 2.2. Each cell compartment was provided with a condenser through which the gases were cooled. The flow rates of gases from both the anode and cathode compartments were measured, and the gases were analyzed using a Gow Mac (Series 580) gas chromatograph. Vaporized liquid products were collected. Power for the electro-oxidation reactions was supplied with a Brinkman Potential Control Amplifier (Wenking Model 72M).

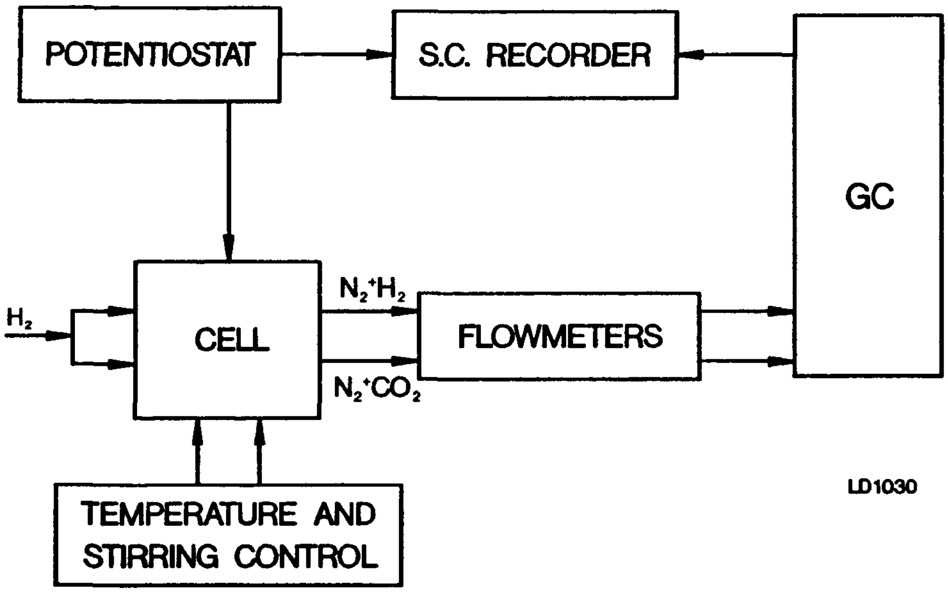


FIGURE 2.2 ELECTRO-OXIDATION TEST SETUP SCHEMATIC:
The Anode and Cathode Gaseous Products Where Metered and Analyzed On-Line.

Electrochemical Cell

The cell design is described in Figure 2.3.A. The anode was made of platinum electrode (platinum gauge 52, 0.1 mm diameter wire of area 45cm^2, obtained from Aesar) and a 2.5 mm diameter platinum rod connected to the potentiostat. This part of the cell was also provided with a Luggin capillary filled with saturated KCl solution and communicating with a saturated calomel reference electrode (SCE). A thermometer was also inserted in the slurry. All potentials in this study refer to the calomel electrode, which is 0.244V on the hydrogen reference electrode scale.

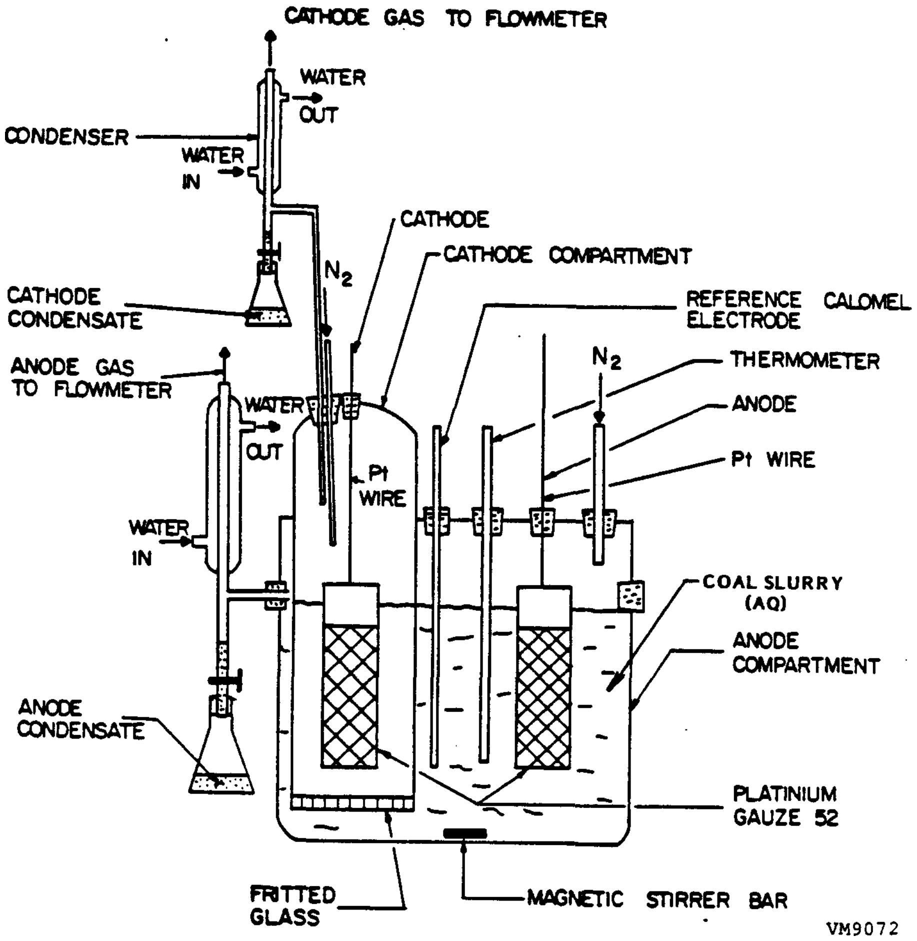


FIGURE 2.3.A ELECTROCHEMICAL CELL FOR ELECTRO-OXIDATION REACTION:

The Cathode Compartment is Isolated from the Coal Particles.

In order to enhance the contact between the coal particle and anode, an auxiliary device, referred to as a 'rotating disk' (shown in Figure 2.3.B), was put into the anode compartment. It consisted of an inducing tube connected to a disk. The anode was inserted into that inducing tube and the magnetic stirrer was in the disk chamber. When the stirrer rotated, coal slurry in the disk was driven away through the holes on the rim of the disk by centrifugal force and fresh slurry was drawn down through the inducing tube and came into contact with the anode. The speed of the coal slurry passing through the electrode was approximately 4.8 m/sec.

The counter electrode (cathode) compartment was separated from the working electrode compartment by a fritted glass that confines the coal particles to the anode compartment. The cathode was also a platinum electrode, the same as the one used for the anode.

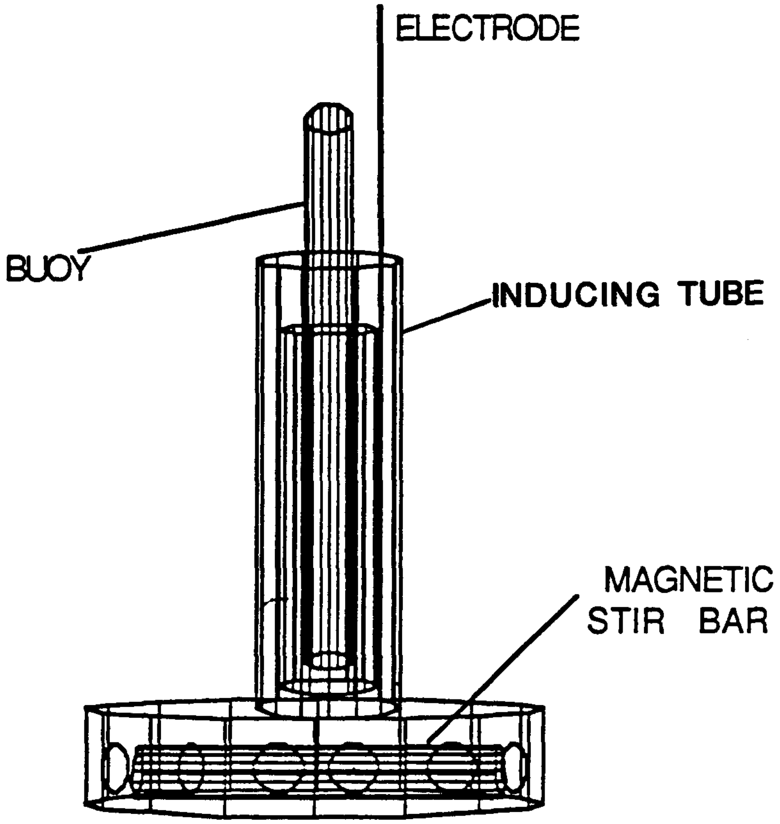


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FIGURE 2.3.B ROTATING DISK ELECTRODE WITH INDUCING TUBE:

This Arrangement Permits Better Contact Between the Coal Particle and the Anode Compartment.

Each compartment was also provided with a condenser through which the gases from the cell were cooled. Also the vaporized liquid products of reaction were collected in the graduated flasks as shown in the figure. Bubble meters were used to measure the flow rates of gases from anode and cathode compartments. The system was purged continuously with high purity nitrogen. A hot plate was used to control the temperature and stirring speed.

Materials

Sigma's Analytical grade sulfuric acid, phosphoric acid, acetic acid, HCl and sodium carbonate were tested as electrolytes. Illinois #2, #6 coals, and desulfurized coal were obtained from Illinois State Geological Survey, Urbana. Pittsburgh coal was obtained from Pittsburgh Energy Technology Center, Pittsburgh. Peat-96 was obtained from ESS-1, Geology & Geochemistry. Charcoal was obtained from Sargent-Welch. 2-propanethiol and Thiophene were obtained from Fisher.

The compositions of all tested materials are listed in Table 2.1

Table 2.1 COMPOSITION OF MATERIALS USED IN THE ELECTRO-OXIDATION TESTS:

Samples with Varying Volatile Matter, Sulfur, and Ash Contents Were Investigated.*

Samples	Pittsburgh	IL#2	IL#6	Charcoal	Peat**	Pyrite	Desulfurized coal	Oil Shale
Moisture	1.08	14.14	10.21	5.0	-	-	38	-
Volatile Matter	23.42	29.3	20.09	15	-	-	-	-
Fixed Carbon	49.8	49.9	31.6	75	19	0	55	20
Ash	25.7	6.66	38.1	5	26	45	3.8	50
Carbon	64.93	73.3	45.97					12.4
Hydrogen	3.6	5.21	3.46					1.52
Nitrogen	1.01	1.47	0.8					
Oxigen	2.57	10.09	7.43					
Sulfatic Sulfur	0.01	0.1	0.1			-	-	
Pyrite Sulfur	1.74	2.34	2.33	0	0	29	0.81	4
Organic Sulfur	0.5	0.92	4.19					
Total Sulfur	2.24	3.23	4.19					

* Values reported are on a moisture-free basis except for the moisture.

** Sample PT-96 supplied by Los Alamos National Laboratory.

2.2 TEST RESULTS

Parametric Study

Initially a parametric evaluation of the variables was conducted to define the preferred choice of variables. The variables include:

- Experimental Variables
  - Particle Size
  - Coal Loading
  - Cell Voltage
  - Electrolyte
  - Temperature
  - Stirring Speed

- Coal Types
  - Illinois #2
  - Illinois #6
  - Pittsburgh
  - Charcoal
  - Oil Shale
  - Desulfurized Illinois #6

A discussion of the important findings is presented below.

Particle Size

Particle size impacts both the coal surface area and population in contact with the current collector and appears to be an important rate-contributing variable. The results presented in Figure 2.4 indicate that the smaller particles provide a better coal conversion rate; however, no improvement in rate is observed with particles smaller than 53µm.

Coal Loading

The coal loading effect was investigated using Illinois #2 coal concentrations of 0.04 gm/ml to 0.25 gm/ml. The results shown in Figure 2.5 indicate that an increase of coal concentration beyond a certain level, 0.1 gm/ml in this case, does not impact the rate of conversion.

Cell Voltage

Test results presented in Figure 2.6 indicate that the coal electro-oxidation initiates at about 0.3 to 0.4 V (WRT calomel) and a limiting current is reached at about 0.8V.

Electrolytes

Experiments were conducted to identify the best choice of electrolyte for enhancing the electro-oxidation rate of coal and facilitating the removal of sulfur from coal (coal beneficiation). A total of five electrolytes including one basic and four acidic systems were examined:

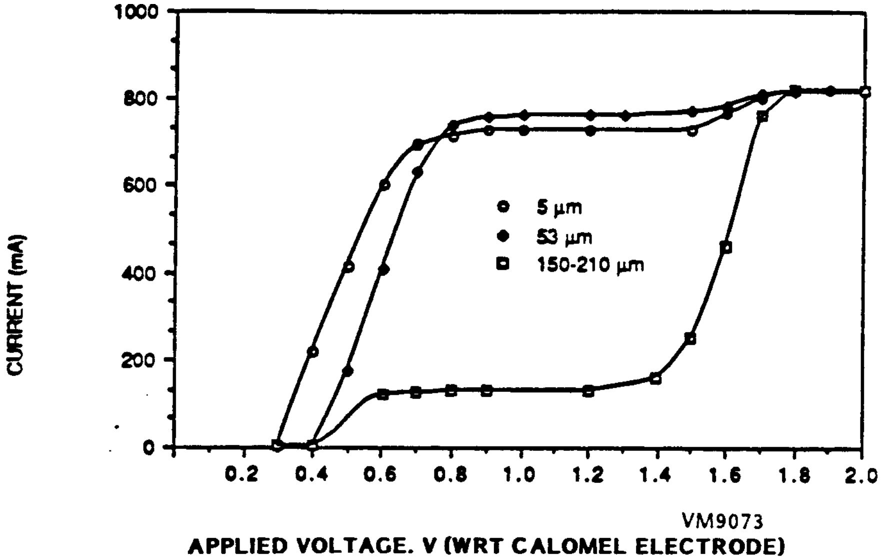
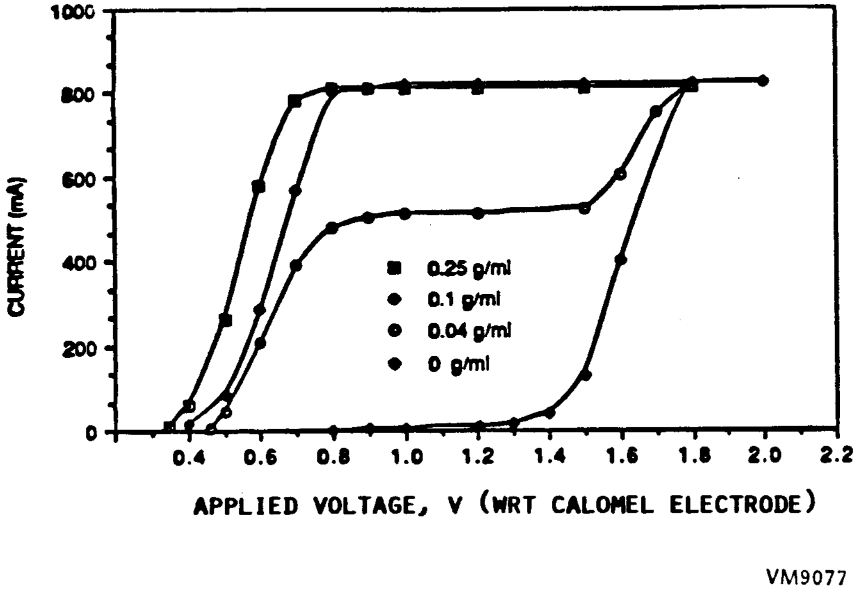


FIGURE 2.4 EFFECT OF COAL PARTICLE SIZE:

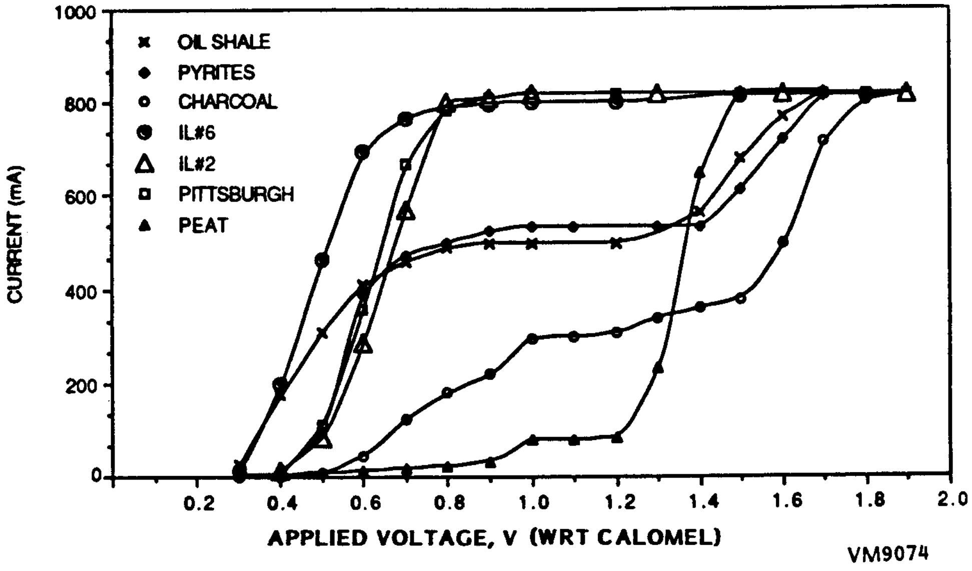
Smaller Particles Provide Better Rate, but the Rates for 53µm Particles are in the Same Range with 5µm Particles.



(Operating Conditions: Temperature: 110°C; Velocity of Coal Slurry Passing Anode: About 4.8 m/sec; Slurry Composition: Illinois #2 Coal in 5 M Sulfuric Acid; Electrode Area: 44 cm^2 each; Particle Size: 53µm.)

FIGURE 2.5 EFFECT OF COAL LOADING

Coal Conversion Rate does not Increase with Loading Beyond 0.1 g/ml.



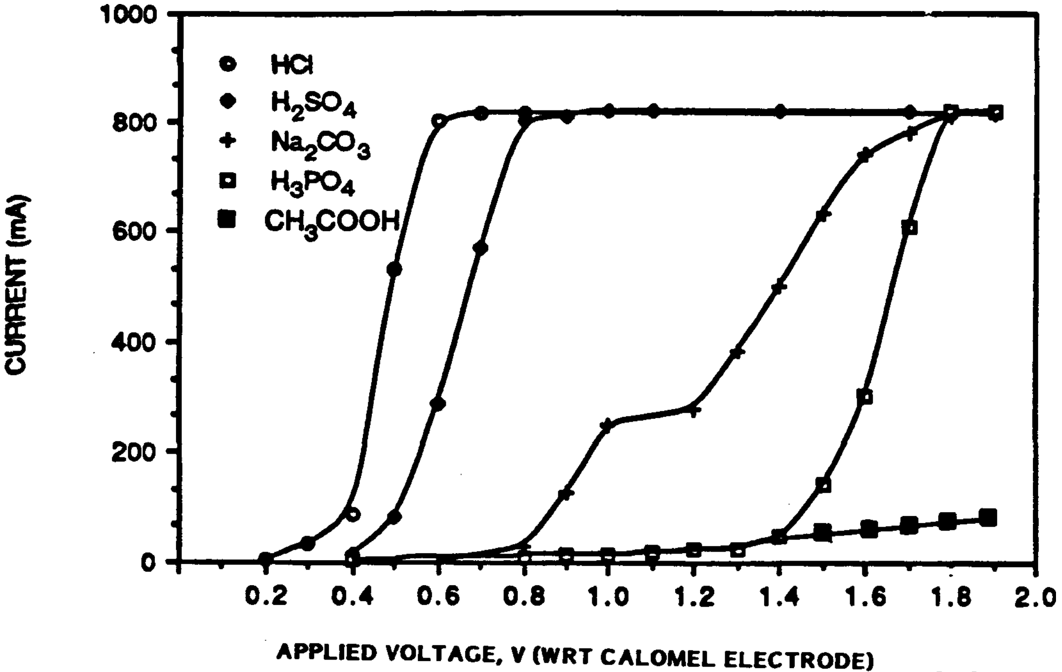
(Operating Conditions: Temperature: 110°C; Velocity of Coal Slurry Passing Anode: About 4.8 m/sec; Slurry Composition: 0.1 g/ml Coal in 5 M Sulfuric Acid; Electrode Area: 44 cm^2 each; Particle Size : 53µm)

FIGURE 2.6 EFFECT OF CELL VOLTAGE:
Limiting Current is Reached at About 0.8V with Coals

1. 5M sulfuric acid (110°C)
2. 50 wt % phosphoric acid (110°C)
3. 3M acetic acid (25°C)
4. 3M hydrochloric acid (25°C)
5. 10 wt % sodium carbonate solution (25°C)

Initial rates of coal electro-oxidation as a function of cell voltage are compared in Figure 2.7.A. The choice of operating temperature for each system was based on electrolyte stability considerations. Negligible reaction current is observed with acetic acid, phosphoric acid and sodium carbonate at potentials below 1.0V. The conductivity of acetic acid is low. H_3PO_4 and Na_2CO_3 leads to water electrolysis at the high potential (>1.4V) where appreciable current is observed.

The current verses time behavior of coal electro-oxidation with different electrolytes, shown in Figure 2.7.B, indicates that the sulfuric acid maintained reaction rate for the whole duration of the study, whereas HCl showed a high current only for a short period, reaching limiting current quickly and slowing down in 6 hours. It is speculated that, in HCl, the reaction activity is limited to electrochemical decomposition of liberated sulfur (H_2S) to S and H_2 and not oxidation of the carbon itself. Based on these results, sulfuric acid was identified as the best choice.



(Operating Conditions: Temperature: 25°C for HCl, Acetic Acid and Sodium Carbonate, 100°C for Sulfuric Acid and Phosphoric Acid Electrolytes; Velocity of Coal Slurry Passing Anode: About 4.8 m/sec; Electrode Area: 44 cm² each; Illinois #2 Coal Particle Size: About 53μm.)

FIGURE 2.7.A ELECTROLYTE EFFECT:
H_2SO_4 Appears to be the Best Choice.

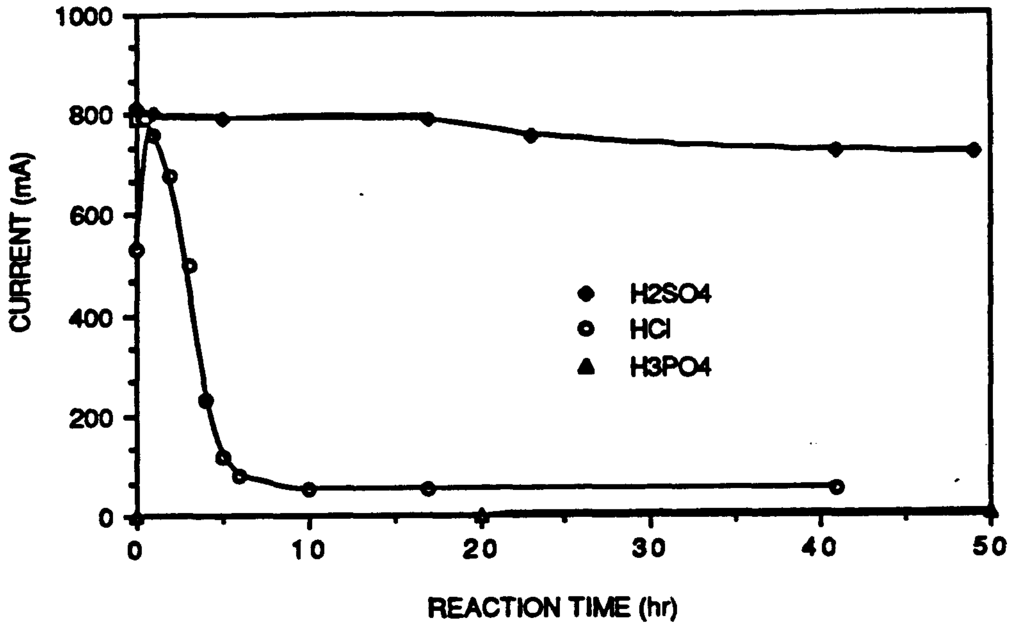
The Effect of Stirring Speed

Stirring in an electrolytic cell system enhances the contact between the coal particles and anode, accelerating the reaction rate. A 'rotating disk' arrangement, described before, was used to induce the coal slurry to pass the anode with a certain speed. This also served to maintain inner circulation of the coal slurry during the course of the reaction.

The effect of stirring speed on the contact-limited current is shown in Figure 2.8. At low speeds, as the speed of stirring increased, the coal oxidation current increased greatly. Further increase in slurry speed beyond 3 m/sec did not affect the oxidation current.

The Effect of Temperature

The effect of temperature is shown in Figure 2. 9. The observed limiting oxidation current increased when temperature was increased from 30°C to 110°C. The temperature effect follows the Arrhenius equation and an apparent activation energy of $\simeq$ 11 kcal/g-mole was estimated at 0.8V. Although higher temperature favors the reaction rate, the test temperature was restricted to 110°C because the 5M H_2SO_4 boils at about 115°C.



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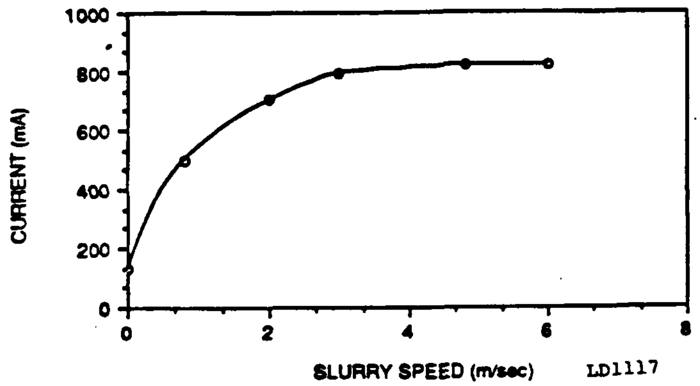
(Operating Conditions: Applied Voltage: 0.8V for Sulfuric Acid and Phosphoric Acid, 0.6V for HCl, Temperature: 25°C for HCl, 110°C for Sulfuric and Phosphoric Acid Electrolytes; Velocity of Coal Slurry Passing Anode: About 4.8 m/s.; Slurry Composition: 0.1g/ml IL#2 Coal Particle Size: About 5 μm; Electrode Area: 44cm^2 each.)

FIGURE 2.7.B CURRENT VERSUS TIME FOR COAL ELECTRO-OXIDATION IN VARIOUS ELECTROLYTES:

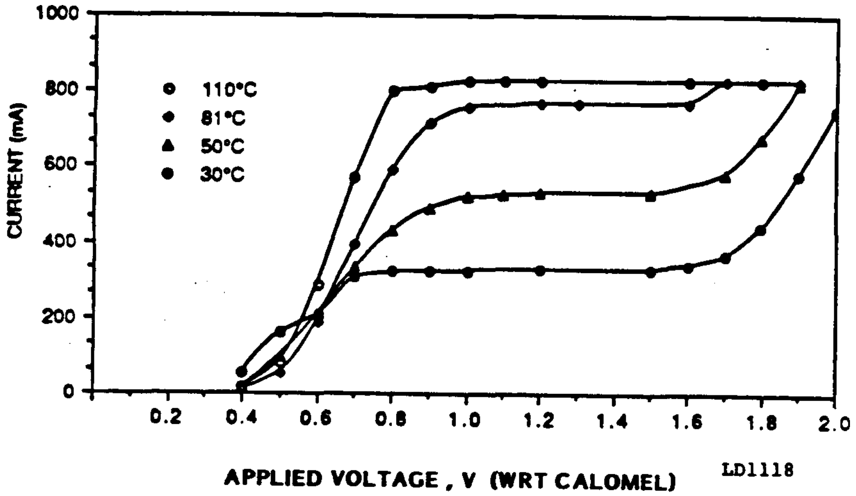
Sulfuric Acid Maintained Reaction Rate for the Duration of the Study.



(Operating Conditions: Applied Voltage: 0.8 V (WRT Calomel; Temperature: 110°C; Slurry Composition: 0.1 g/ml Illinois #2 Coal in 5 M Sulfuric Acid Solution; Electrode Area: 44 cm² each; Particle Size: 53μm)

FIGURE 2.8 THE EFFECT OF STIRRING SPEED ON THE CONTACT-LIMITED CURRENT:

Increase in Slurry Speed Beyond 3 m/s Did Not Affect the Oxidation Current.



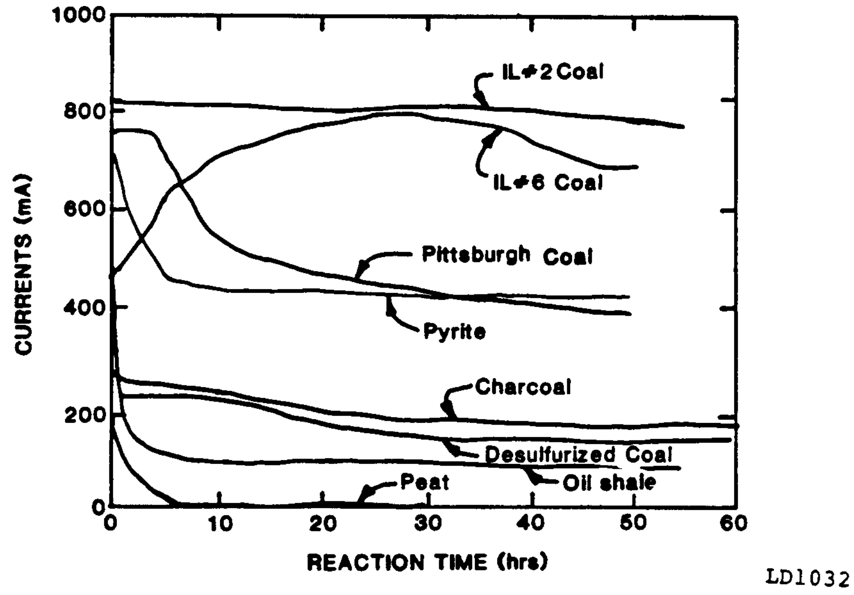
(Operating Conditions: Velocity of Coal Slurry Passing Anode: About 4.8 m/sec; Slurry Composition: 0.1 g/ml Illinois #2 Coal in 5 M Sulfuric Acid Solution; Electrode Area: 44 cm² each; Particle Size: 53μm)

FIGURE 2.9 CURRENT AS FUNCTION OF APPLIED VOLTAGE AT VARIOUS TEMPERATURES:

Coal Electro-Oxidation Rates Increase with Temperature.

Coal Types

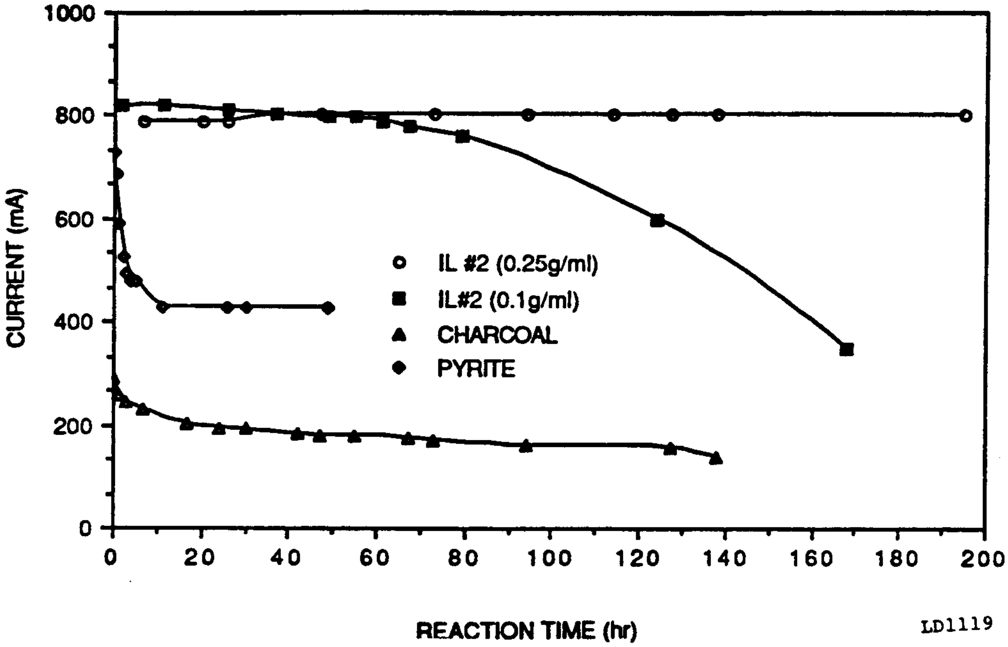
Oxidation rates obtained with four different coals, an oil shale, a pyrite, a charcoal and a desulfurized coal (desulfurized Illinois #6) are compared in Figure 2.10. The results indicate that higher rates are obtained with coals containing high volatile matter and sulfur contents. The desulfurized coal gave a significant reduction in oxidation rate as compared to the parent as-received Illinois #6 coal. This result suggests that the oxidation current is contributed by both hydrocarbon molecules and coal borne pyrites. An oxidation rate of ~19 mA/cm^2 obtained with Illinois #2 coal in this study is at least 100% greater than coal oxidation rates previously reported in the literature. This is mainly attributed to high contact between the coal particles and the anode achieved in the test apparatus used in this study.



(Operating Conditions: Temperature: 110°C; Velocity of Coal Slurry Passing Anode: 4.8m/s; Slurry Composition: 0.1 g/ml Coals in 5 M H_2SO_4; Electrode Area: 44 cm^2 each; Particle Size: 53μm)

FIGURE 2.10 EFFECT OF COAL TYPES ON ELECTRO-OXIDATION RATE:

Higher Rates are Obtained with Coals Containing High Volatile Matter and Sulfur Contents.



(Operating Conditions: Applied Voltage: 0.8 V (WRT Calomel); Temperature: 110°C; Velocity of Coal Slurry Passing Anode: 4.8 m/sec; Slurry Composition: Illinois #2 Coal in 5 M Sulfuric Acid; Electrode Area: 44 cm^2 each; Particle Size 53μm)

FIGURE 2.11 CURRENT PRODUCED VS. REACTION TIME: Reaction Rate Drops as the Active Components are Consumed.

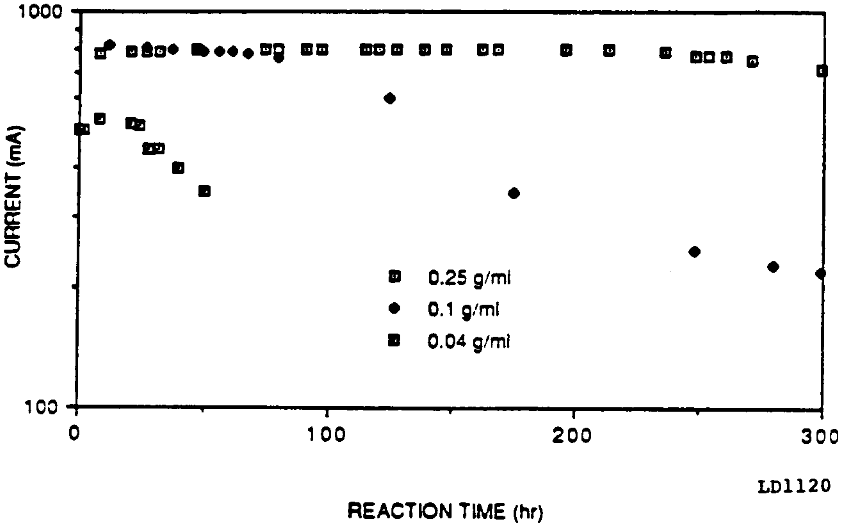
Mechanistic Insight

After parametric evaluations, tests were conducted for elucidation of the electro-oxidation reaction mechanism and characterization of reaction products. Time dependence of coal oxidation rates, shown in Figure 2.11, indicate that the reaction rate decreases as the active coal components are consumed. The Illinois $\gamma 2$ coal samples, having loadings of 0.1 gm/ml and 0.25 gm/ml, were oxidized for 300 hours; the lifegraph is shown in Figure 2.13. These data indicate an initial oxidation rate of $\sim$ 800 mA dropping to $\sim$ 300 mA after 200 hours for the 0.1 gm/ml loading case. The time-current plot in Figure 2.10 indicates an oxidation rate of 500 mA for the pyrite alone as opposed to 200-300 mA for 'pure' carbonaceous materials. These results suggest that the initial oxidation current of 800 mA is contributed jointly by the following pyrite oxidation and carbon oxidation reactions:

$$FeS_2 + 8\,H_2O \longrightarrow Fe^{3+} + 2SO_4^{=} + 16H^+ + 15e; \quad E_0 = -0.39V \text{ (RHE)}$$

$$\text{(Complete reaction:} \longrightarrow Fe_2(SO_4)_3 + H_2SO_4 + 14H_2)$$

$$2\,H_2O + C \longrightarrow 4H^+ + CO_2 + 4e; \quad E_0 = -\,0.21V \text{ (RHE)}$$



(Operating Conditions: Applied Voltage: 0.8 V (WRT Calomel) Temperature: 110°C Velocity of Coal Slurry Passing Anode: About 4.8 M/Sec. Slurry Composition: Illinois #2 Coal in 5 M Sulfuric Acid; Electrode Area: 44 cm² each; Particle Size: 53μm)

FIGURE 2.12 LONG TERM OXIDATION OF ILLINOIS #2 COAL:

The Reaction Rate Drops as the Pyrites Are Fully Consumed.

The pyrites are consumed within ~ 200 hours for the 0.1 gm/ml loading case, and the electro-oxidation rate thereafter represents mostly carbonaceous material oxidation.

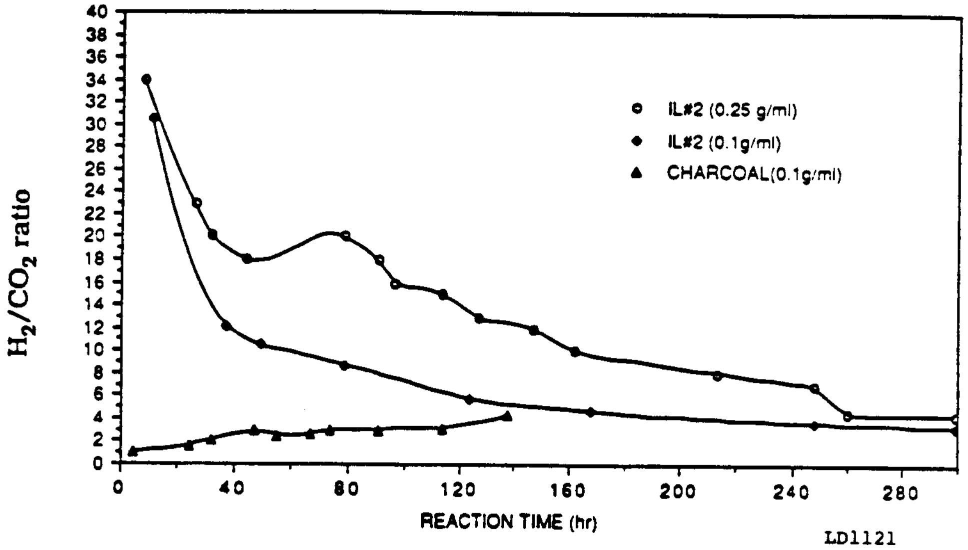
The H_2/CO_2 ratios presented in Figure 2.13 indicate that relative CO_2 production is quite low at the beginning, supporting the pyrite oxidation hypothesis and unsteady state formation of surface oxides at that time. As the pyrites are consumed, CO_2 production increases, approaching the ratio obtained with pyrite-free carbonaceous materials.

Current efficiencies of hydrogen production calculated as:

$$\text{Current Efficiency} = \frac{H_2 \text{ Production Rate}}{\text{Current Measured/nF}}$$

are presented in Figure 2.14. The current efficiency depends on coal type and reaction time; most importantly, values higher than 100% have been observed for several coal samples.

Since the hydrogen is collected in a separate cathode compartment where coal particles are absent, the source of hydrogen appears to be an electrochemical reaction. It is difficult to explain higher than 100% current efficiency for an electrochemical reaction. However, comparing the results, one can find that only carbonaceous materials containing sulfur provide higher current efficiency, and sulfur-free carbon samples (i.e.; peat and charcoal) provide current efficiencies below 100%. Also,



(Operating Condition: Temperature: 110°C; Applied Voltage: 1.0 V (WRT Calomel)for Charcoal, 0.8 V for Il #2 Coal; Slurry Composition: 0.1 g/ml Samples in 5 M Sulfuric Acid; Velocity of Slurry Pass Anode Electrode: About 4.8 m/sec; Electrode Area: 45 cm² each; Particle Size: 53μm.)

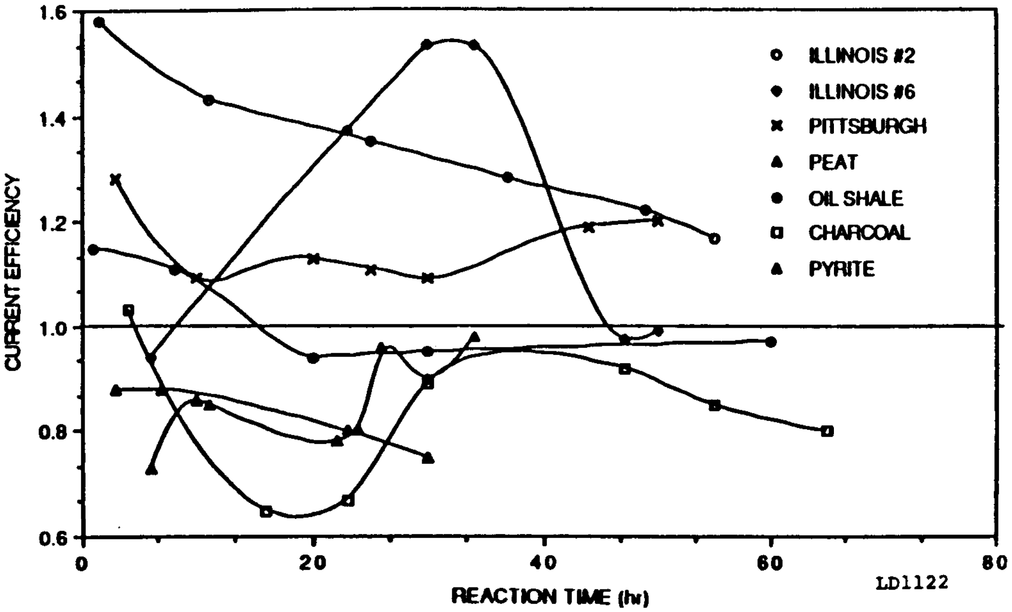
FIGURE 2.13 RATIO OF HYDROGEN TO CARBON DIOXIDE AS A FUNCTION OF REACTION TIME:

The H_2/CO_2 Ratio Approaches the Value Obtained with Carbonaceous Materials as Pyrites are Consumed.

the H_2/CO_2 ratio tends to be higher for sulfur-containing coals (>4) compared to sulfur-free carbons (<3). For complete carbon-water reaction, a H_2/CO_2 ratio of only 2 is expected. These observations suggest that reactions involving sulfur in the coal may play a role in the higher than 100% current efficiency.

Experiments were conducted to explain the unusual observation of more than 100% current efficiency of hydrogen production. Electro-oxidation experiments were conducted with 1% model organic compound, 2-propanethiol, mixed in with charcoal (0.1 g/ml) slurried in 5M sulfuric acid solution. The current efficiencies of hydrogen production for charcoal, charcoal plus 1% thiophene, and charcoal plus 1% 2-propanethiol are presented in Figure 2.15. The results indicate that only in the case of 2-propanethiol was a current efficiency of more than 100% observed. Note that the current efficiency started at 90%, at about the same value as others, increased to 130% and then gradually dropped off. At the end of the experiment, free sulfur was detected at the cathode surface. The current efficiency with thiophene was less than 100%. The difference between these two organic compounds lies in their thermal stability behaviors. The thermodynamic properties of the most common organic compounds found in coal are shown in Figure 2.16: 2-propanethiol represents the most easily decomposable organic compound. Thiophene is the hardest compound to decompose. It is expected that, under the conditions of coal oxidation, the 2-propanethiol decomposes to H_2S.

$$(CH_3)_2\,CHSH \longrightarrow CH_3CH = CH_2 + H_2S$$



(Operating Conditions: Temperature: 110°C; Electrode Area: 45 cm² each; Slurry Composition: Samples in 5 M Sulfuric Acids; Applied Voltage: 0.8 V. (WRT Calomel); Velocity of Slurry Passing Anode Electrode: About 4.8 m/sec.)

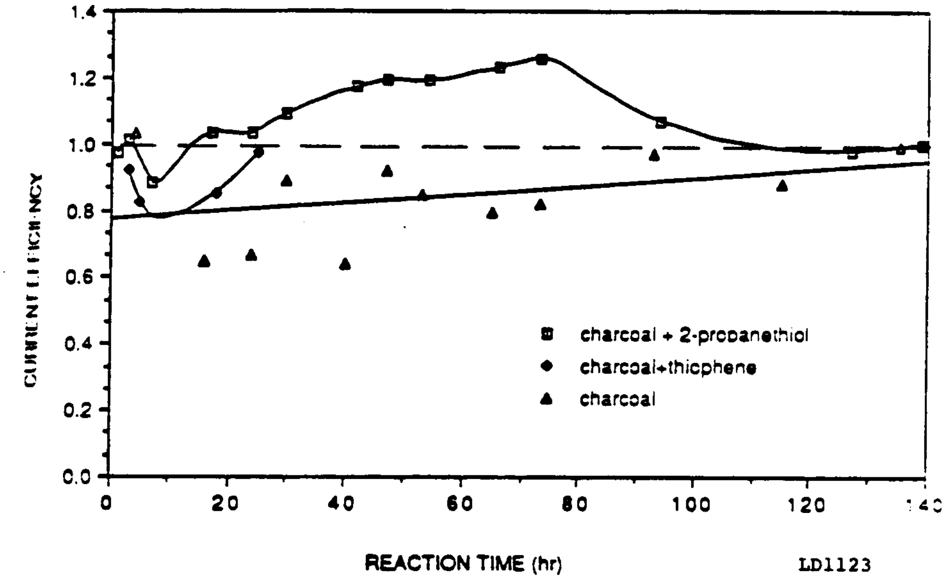
FIGURE 2.14 CURRENT EFFICIENCY vs. REACTION TIME FOR DIFFERENT COALS, PYRITE, OIL SHALE AND CHARCOAL:

Observed Current Efficiency of More than 100% has Been Explained in Terms of Decomposition of H_2S in the Cathode Compartment.

The liberated H_2S is dissolved in the electrolyte and subsequently further decomposes on the cathode to S and H_2. At 110°C, the decomposition free energy (ΔG°) of H_2S is -5.3 kcal/mol. The reaction steps are:

$$\left.\begin{array}{l} H_2S \longrightarrow 2H^+ + S^= \\ S^= \longrightarrow S^\circ + 2e \\ 2\,H^+ + 2e \longrightarrow H_2 \end{array}\right\} \quad \text{Both charge transfer reactions occur on the cathode.}$$

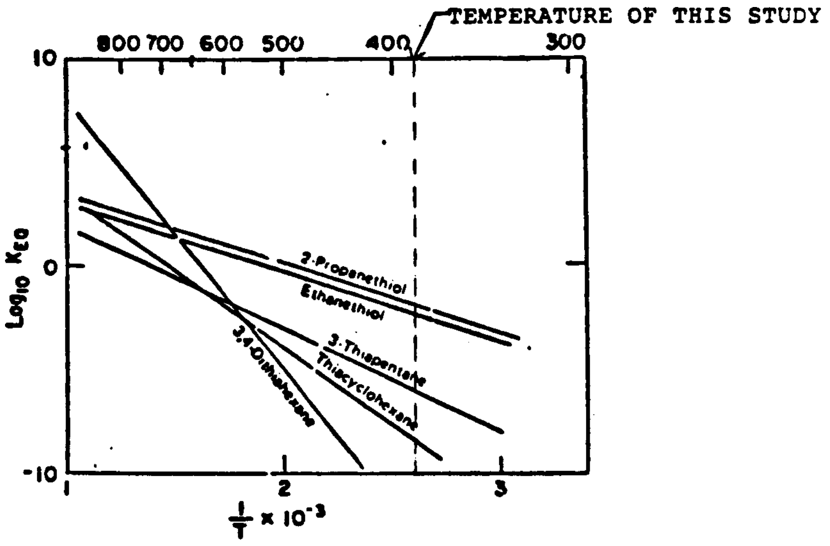
It may be noted that the observed current efficiency with pyrites was less than 100%. The pyrites do not react with sulfuric acid and form H_2S. The pyrites do not produce extra hydrogen like the organic sulfur compound. The more than 100% current efficiency observed with different coals relates to electrochemical decomposition of H_2S derived from organic sulfur in the coal. This is indirect evidence of at least partial removal of organic sulfur from coal during electro-oxidation.



(Operating Conditions: Temperature: 110°C; Applied Voltage: 1.0 V (WRT Calomel); Slurry Composition: 1% Model Organic Sulfur Compounds Added to Charcoal 0.1 g/ml Charcoal in 5 M Sulfuric Acid; Velocly of Slurry Passing Anode Electrode: About 4.8 m/sec.; Electrode Area: 45 cm^2 each)

FIGURE 2.15 CURRENT EFFICIENCIES FOR HYDROGEN PRODUCTION AS FUNCTIONS OF REACTION TIME

2-Propanethiol Additive Resulted in More than 100% Current Efficiency.



Source: LBL-5216 [Ref. 33]

FIGURE 2.16 EQUILIBRIUM CONSTANTS FOR THE DECOMPOSITION OF SULFUR COMPOUNDS TO FORM H_2S:

2-Propanethiol is an Easily Decomposable Compound.

2.3 DISCUSSION

The test results presented thus far show that coal electro-oxidation leads to production of pure hydrogen at the cathode and pure CO_2 at the anode. Also, humic acids and traces of formaldehyde, phenol, benzene and toluene were detected in the electrolyte. The overall product balance for a 300 hour test run with Illinois #2 coal is presented in Table 2.2. The results show that partial electro-oxidation leads to production of 0.3 moles of electrolytic grade hydrogen per gm-atom of carbon in the coal (as opposed to ~ 1.4 moles of hydrogen per gm-atom of carbon from complete gasification by the Texaco process). Also, 0.03 moles of pure CO_2 per gm-atom of carbon in the original coal was produced.

A total sulfur balance was conducted on both the as-received and test-product coals. As speculated from the previously discussed mechanism, these results, reported in Table 2.3, indicate that the pyritic sulfur is essentially completely removed from the 53 µm size coal by the electro-oxidation reaction. Whereas, the percent sulfur which is liberated by grinding, with subsequent removal by the electrostatic separation process (presented in Figure 2.17) is only 60% from 53 µm size coal. One hundred percent removal of pyrite by the latter process would require coal grinding to ~ 5 µm size particles, requiring large amounts of grinding energy (115 kWh per ton of coal), and is, therefore, not practicable. Thus the electro-oxidation process provides an alternate route for pyrite removal from practical size coal particles, possibly using particles as large as 74µm, the size which is currently used in pulverized coal boilers.

The results in Table 2.3 also indicate that coal electro-oxidation leads to significant reduction of coal ash content (~ 60%) and simultaneous lowering of the heating value, by roughly 18%. This residual coal from electro-oxidation will still be useful for most conventional applications. A preliminary economic analysis of the electro-oxidation process was evaluated and is presented in Table 2.4. Additional details of this economic evaluation are presented in Appendix A. This analysis indicates that, without considering the credit for pure CO_2 product, the net value added by the electro-oxidation treatment of the coal is about $8 per ton for the Illinois #2 coal. Thus the electro-oxidation appears to provide a potential route for the production of pure H_2, pure CO_2, simultaneous pyrite removal, and reduction of ash, with a small penalty in heating value and consumption of electricity. A flow schematic of this potential process is given in Figure 2.18.

Table 2.2 PRODUCT MASS BALANCE: Roughly 22% of the Total Hydrogen Obtainable by the Conventional Coal Gasification is Produced in 300 Hours of Electro-oxidation. (Illinois #2 Coal, 300 Hour Test, 53 μm Particle)

Input	Output
340 gm Coal	H_2 = 6.43 Moles
(20.8 g-atoms carbon)	CO_2 = 0.64 Moles
	H_2/Carbon* in Coal = 0.31

* This ratio is $\simeq$1.4 for Texaco Gasification

Table 2.3 SULFUR BALANCE: Pyritic Sulfur is Completely Removed from 53 μm Coal Particles (Illinois #2; 53 μm Particles; 300 Hour Test)

		SULFUR	
SULFUR		FEED %	PRODUCT
PYRITIC SULFUR		2.34%	0.01%
SULFATE SULFUR		0.1%	0.03%
BALANCE		0.92%	1.16%
	TOTAL	3.36%	1.2%
ASH		6.66%	2.31%
HEATING VALUE, Btu/lb		13,526	11,108

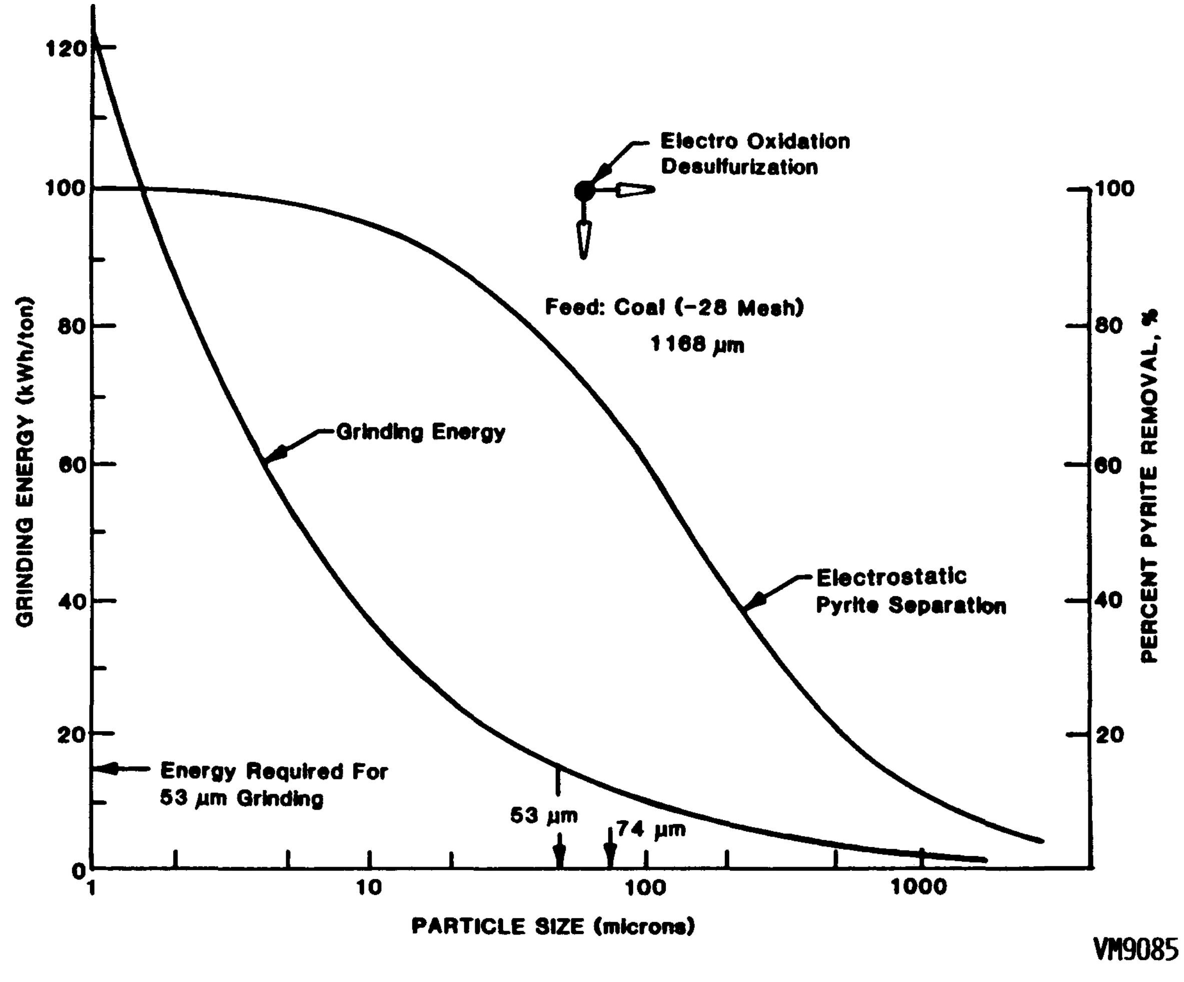


FIGURE 2.17 ENERGY REQUIREMENTS IN GRINDING; OBSERVED PYRITE REMOVAL:

Electrochemical Coal Desulfurization Does not Require Grinding to Low Particle Size.

Table 2.4 PRELIMINARY ECONOMICS OF THE ELECTRO-OXIDATION PROCESS:*

The Electro-Oxidation Coal Pretreatment Projects an Economic Benefit of ∿ $8 Per Ton of Coal.

STEP	COST/Ton of Coal $	BENEFIT/Ton of Coal $
1. Electrolysis (Energy Cost)	20.16	
2. Hydrogen Production (Pure Hydrogen Credit)		29.61
3. Increase in Coal Price (Beneficiation)		11.34
4. Penality for Loss in Btu	7.27	
5. Capital Charge	5.8	
TOTAL	33.23	41.01

* The assumptions are presented in Appendix A.

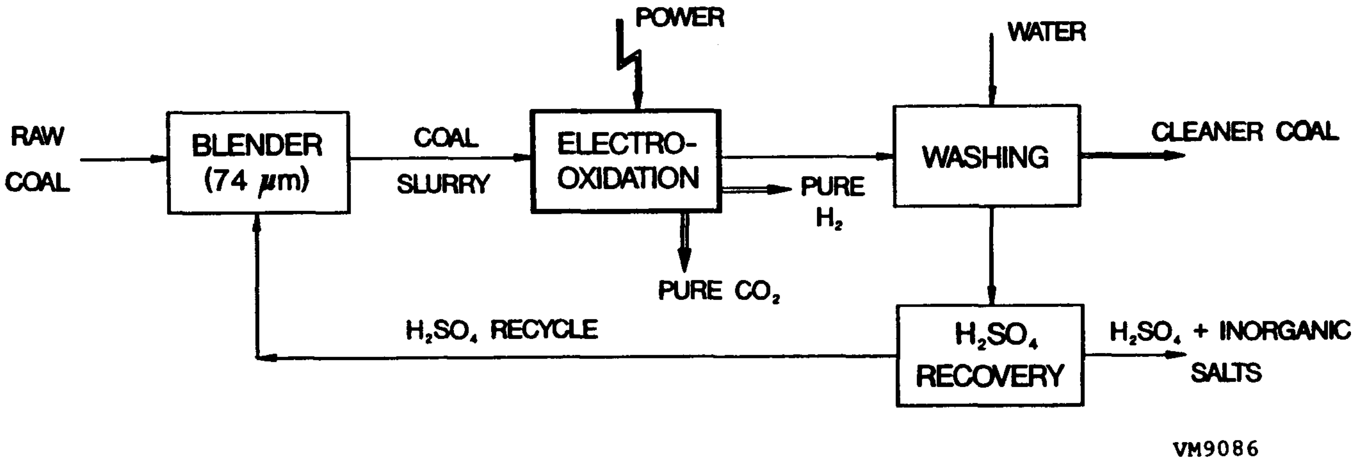


FIGURE 2.18 ELECTROCHEMICAL COAL TREATMENT PROCESS SCHEMATIC: Useful Products and Simultaneous Upgrading of Coal.

3.0 COAL ELECTRO-REDUCTION

It is expected, similar to the chemical coal hydrogenation process, that an electrochemical reaction in aqueous electrolyte involving coal and H^+ may lead to additions of hydrogen to coal through reduction of unsaturated aliphatic bonds, aromatic rings, and other functional groups:

Anode $H_2 \longrightarrow 2H^+ + 2e$

Cathode $\text{Coal} + 2H^+ + 2e \longrightarrow \text{Coal} - H_2$

Reduction of molecular weight through cleavage of etheral, oxygen, sulfur and other bonds is also possible. It is likely that most of these reduction reactions will require the supply of a small amount of external power.

The electro-reduction cell potential is expected to be very small and dependent only on the cathode potential, because anode overpotential is negligible (less than 5 mV per 100 mA/cm^2). The selectivity and extent of the hydrogenation of coal will depend on the cathode potential. Hydrogen evolution over-voltage on carbon is < -350 mV vs RHE at 5 mA/cm^2, which may prevent hydrogen evolution from competing with the desired hydrogenation reaction at cathodic potentials.

In the electro-reduction of coal, the following electrochemical reaction of H_2 with carbon and unsaturated carbon-hydrogen bonds may occur, and others are possible:

Cathode

$-C{\equiv}C- + 2H^+ + 2e \longrightarrow -CH=CH-$

$-CH=CH- + 2H^+ + 2e \longrightarrow -CH_2-CH_2-$

$-CH_2-CH_2- + 2H^+ + 2e \longrightarrow -CH_3$ and $-CH_3$

Anode

$H_2 \longrightarrow 2H^+ + 2e$
(same for all cases)

Table 3.1 gives the overall cell reactions and corresponding standard EMFs. These values suggest that the reduction of unsaturated aliphatic bonds in a cell using a hydrogen anode should be spontaneous and may produce power in a fuel cell mode. However, because of the high polarization potential, the supply of a small quantity of external power may be required to run some of these hydrogenation reactions at a reasonable rate. Previous attempts to electrochemically hydrogenate olefinic compounds were limited to the use of water electrolysis [28] as the source for H^+:

$$H_2O \longrightarrow 2H^+ + 2e + 1/2\ O_2$$

TABLE 3.1 THERMODYNAMICS OF ELECTRO-HYDROGENATION OF CARBON AND SOME HYDROGEN COMPOUNDS:

Saturation of Unsaturated Aliphatic Bonds in Coal by Electro-Reduction Should be Possible.

	CATHODIC REACTION	OVERALL REACTION	298 K	
			STANDARD FREE ENERGY CHANGE, kcal/g mole	STANDARD POTENTIAL, VOLTS
1.	$C + 4H^+ + 4e \longrightarrow CH_4$	$C + 2H_2 \longrightarrow CH_4$	-12.14	+ 0.132
2.	$C_2H_2 + 4H^+ + 4e \longrightarrow C_2H_6$	$C_2H_2 + 2H_2 \longrightarrow C_2H_6$	-57.86	+ 0.628
3.	$C_2H_4 + 2H^+ + 2e \longrightarrow C_2H_6$	$C_2H_4 + H_2 \longrightarrow C_2H_6$	-24.142	+ 0.524
4.	$C_3H_6 + 2H^+ + 2e \longrightarrow C_3H_6$	$C_3H_6 + H_2 \longrightarrow C_3H_8$	-20.971	+ 0.455

Use of this type of anode reaction leads to a significant consumption of power (adds ~ 2V to the cell potential) and also causes product loss through oxidation at the high anodic potential.

Limited studies on electro-reduction of coal are available in the literature [23]. Early coal and coal-extract related reduction experiments were performed in nonaqueous solvents, using mostly polarographic methods [24-27]. Electrochemical reduction of a vitrain from low volatile bituminous coal in ethylene diamine saturated with lithium chloride resulted in hydrogen addition to the vitrain sample [32], providing extracts having molecular weights of 800 to 900. Recent work by Park [29] focused on the electro-reduction of coal in a rigorously dried nonaqueous medium. This process has not been successful in the production of coal derived products. Limitations on the choice of electrolyte media, cell temperature, and the apparatus restricted the observations of these early studies. Electro-reduction of coal in aqueous media had not been investigated prior to the present work. Furthermore, production of coal-derived liquid products by the electro reduction route has not been demonstrated previously either.

The present study was intended for proof-of-concept demonstrations of coal hydrogenation by electro-reduction leading to formation of useful liquid products.

3.1 EXPERIMENTAL

The coal electro-reduction experiments were conducted at 1 atm, 150 to 250°C, and at cathodic overpotentials of 0 to 900 mV (RHE) using H_3PO_4 electrolyte. Hydrogen from a pure hydrogen stream was oxidized to H^+ using a fuel cell type gas diffusion anode, transported through H_3PO_4 acid electrolyte immobilized in a porous matrix structure, and reduced on a porous coal electrode. The products of the reaction were identified and the effects of process variables on electro-reduction kinetics and product spectra were investigated. A list of the test variables and on-line and post-analyses conducted is provided in Figure 3.1. A total of 8 single cells were tested.

Test Setup

The experimental setup is described in Figure 3.2. A cold trap was used to collect condensible products of the electro-reduction reaction for appropriate analyses. The chemical compounds which were produced and came off at the cell operating conditions were trapped in the cold 'box'. The gas production was measured and a gas chromatograph was used for gas analysis. A Princeton Applied Research (PAR Model 173) potentiostat/galvanostat was used to supply power for the potentiostatic electro-reduction experiments.

Electrochemical Cell

The cell design is described in Figure 3.3. The two end-plates, made from heat-treated graphite-glassy carbon composite material, provide current collection and flow field for hydrogen (reactant) gas on the anode side and a product flow field on the cathode side.

The anode is a state-of-the-art gas diffusion electrode, with a porous thin layer of Pt catalyst laminated on a porous, conductive graphite support layer. The matrix consists of a thin porous layer of silicon carbide (SiC) soaked with H_3PO_4 electrolyte. The coal electrode is a porous thin layer made from pulverized coal using a rolling press and then laminated on a porous wetproofed graphite support layer. The coal loading in the test electrodes is $\sim$ 0.03 mg per cm^2 of electrode geometric area. The Teflon binder content was 20%. Attempts to prepare coal electrodes with no or smaller amounts of Teflon resulted in non-uniform coal layers which did not adhere to the porous carbon paper, and were considered inadequate for use in the electro-reduction experiments.

Only potentiostatic electro-reduction reactions were conducted in this study. In all experiments, the anode of the cell was used to control the electro-reduction cathode potential. The H_2 anode overpotential is known to be $\simeq$ 5 mV per 100 mA/cm^2 for the supported Pt catalyst. Cell resistance was measured using a miliohmeter. From these values, the true potential of the cathode was easily ascertained.

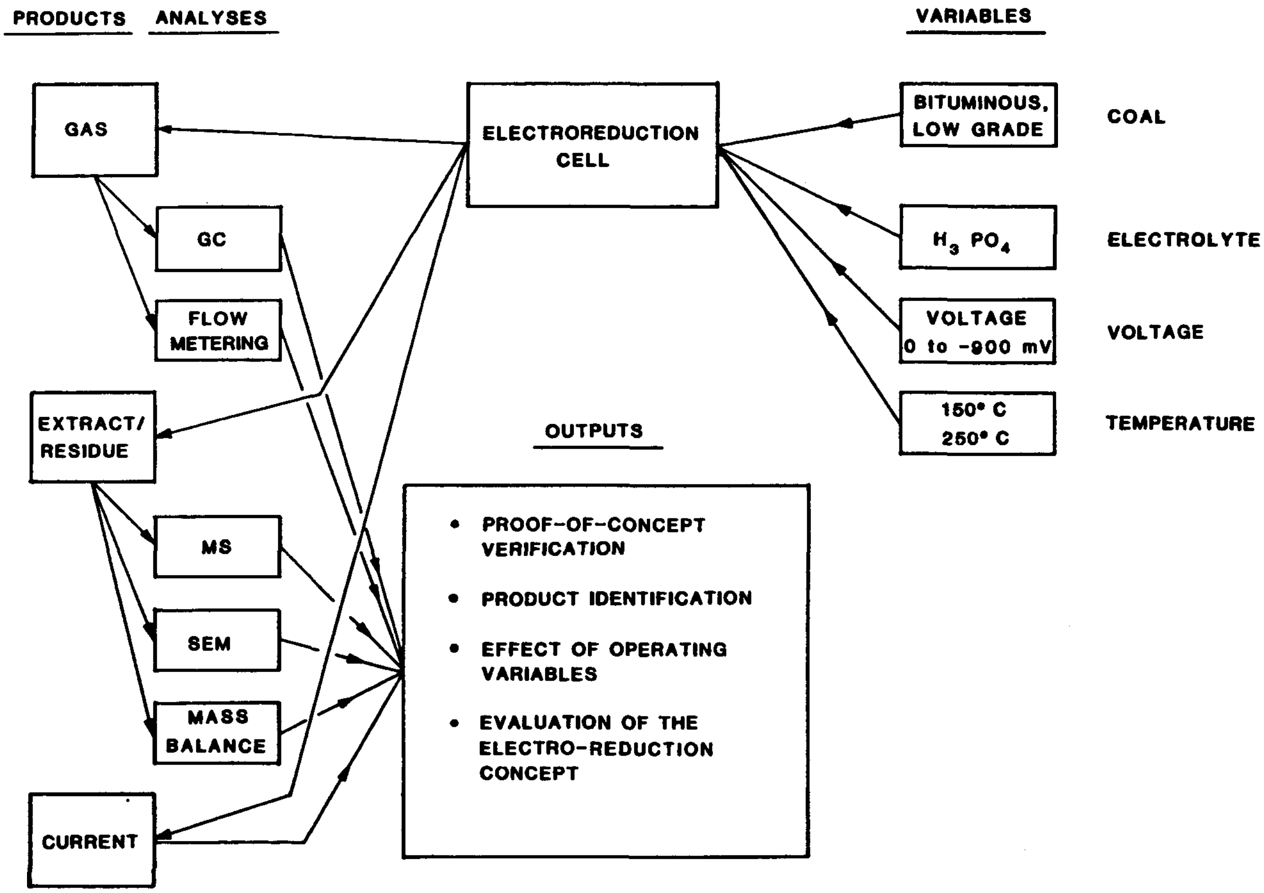


FIGURE 3.1 TEST SUMMARY OF ELECTRO-REDUCTION PROCESS:
The Effect of Process Variables on Product Spectrum was Investigated.

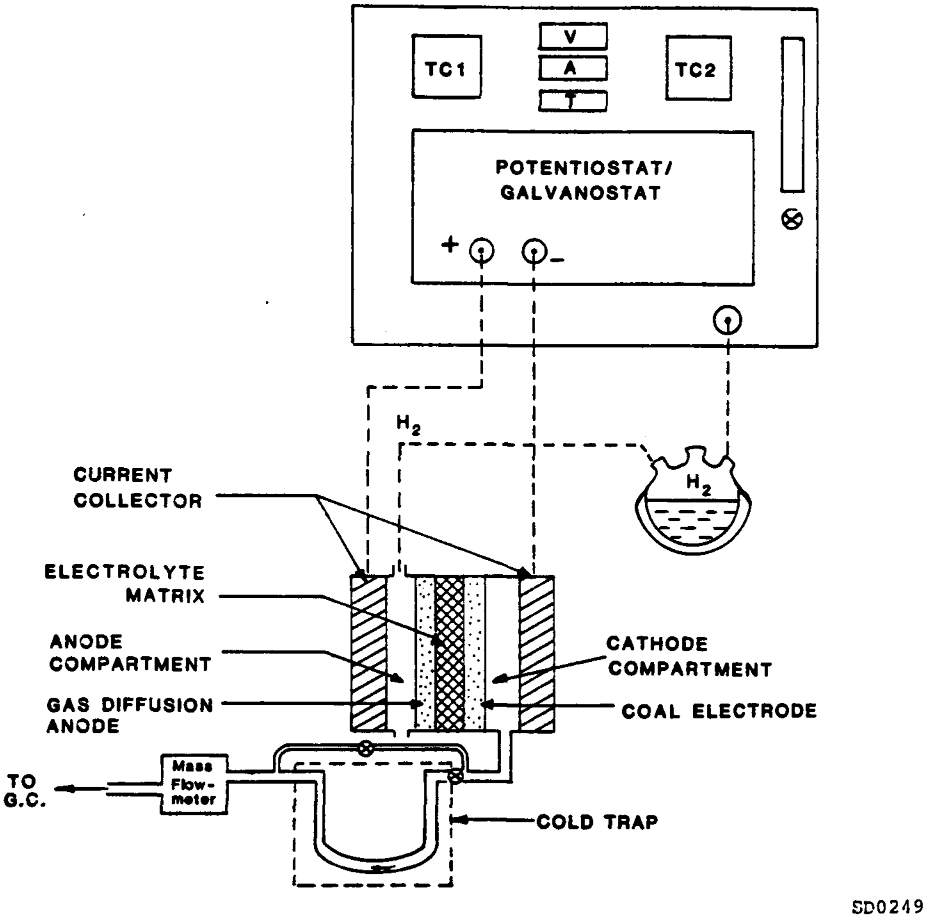
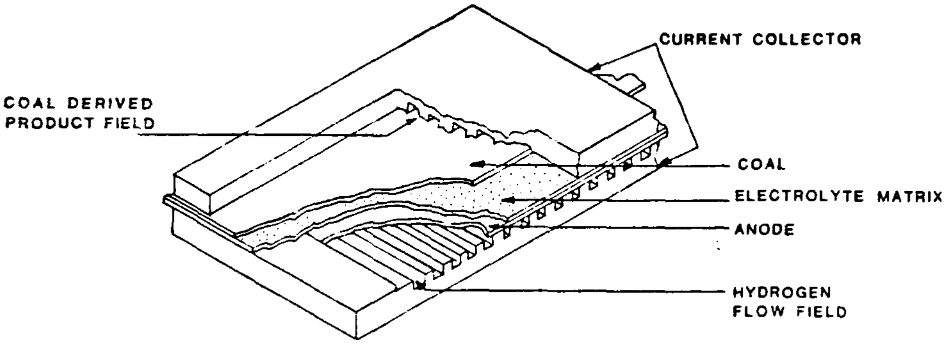
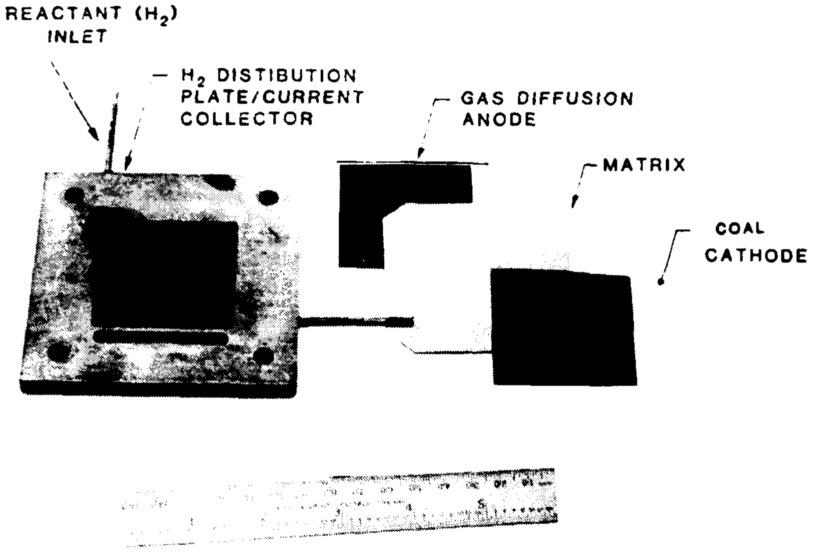


FIGURE 3.2 APPARATUS FOR ELECTRO-REDUCTION OF COAL:

This Simple Setup was Used for Proof-Of-Concept Verification of the Electro-Reduction Coal-Conversion Concept.



a) Cutaway View



b) Photograph of Components

FIGURE 3.3 COAL ELECTRO-REDUCTION CELL DESIGN:

This Electrochemical Cell is Well Characterized and Provides Low Anode Polarization and Internal Resistive Loss.

Test Variables

The effects of process variables such as temperature, reduction potential, and coal type on product selectivity were investigated. In all, 8 cells were tested. A description of test conditions of these cells is available in Table 3.2. The analysis of the coals used in this study is provided in Table 3.3. Two hydrogen-donors, 9,10-dihydroanthracene and 1,2,3,4 tetrahydroquinoline, were chosen for the investigation of the effect of hydrogen donor on the electro-reduction of coal. In out-of-cell tests, it was determined that these compounds were incompatible with the electro-reduction test temperature. Therefore, the hydrogen-donor studies were eliminated from the test plan.

TABLE 3.2 TEST CELL DESCRIPTION:
Six Coal Types Were Investigated.

TEST CELL	INDEPENDENT VARIABLE	PURPOSE
CER-1	Illinois #6 coal H_3PO_4 electrolyte Temperature: 200-250°C Voltages: 0 to -500 mV (RHE)	To study high-volatile bituminous coal
CER-2	Illinois #6 coal H_3PO_4 electrolyte Temperatures: 250°C Voltages: no applied voltage	Blank test to determine whether liquid products are result of chemical or electrochemical reaction
CER-3	Illinois #2 coal H_3PO_4 electrolyte Temperatures: 250°C Voltages: 0 to 600 mV	To study another high-volatile bituminous coal
CER-4	Pittsburgh coal H_3PO_4 electrolyte Temperatures: 250°C Voltages: 0 to -400 mV (RHE)	To study medium-volatile bituminous coal
CER-5	Charcoal H_3PO_4 electrolyte Temperature: 200-250°C Voltages: 0 to -900 mV (RHE)	To study charcoal
CER-6	Devolatized Illinois #6 H_3PO_4 electrolyte Temperature: 250°C Voltages: 0 to -400 mV (RHE)	To study the role of volatiles
CER-7	Montana Rosebud H_3PO_4 electrolyte Temperature: 200-250°C Voltages: 0 to -900 mV (RHE)	To study sub-bituminous coal and also maceral content
CER-8	North Dakota Velva Lignite H_3PO_4 electrolyte Temperature: 200-250°C Voltages: 0 to -500 mV (RHE)	To study lignite coal

Table 3.3 AVERAGE ANALYSIS OF COALS * TESTED IN ELECTRO-REDUCTION

Different Coal Types were Investigated for Characterization.

Property	Illinois #6	Illinois #2	Pittsburgh	Charcoal	Montana Rosebud	North Dakota Velva Lignite
PSOC #	1493	N/A	320	N/A	1485	N/A
Moisture	9.43	13.62	2.03	5	25.37	28.7
Volatile Matter	37.91	43.34	21.72	18-23	36.75	40.80
Fixed Carbon	46.92	49.92	62.50	---	51.81	46.4
Ash	15.17	6.66	15.78	5	11.44	12.8
Carbon	66.23	73.31	74.31	75	67.11	60.21
Hydrogen	4.17	5.21	4.26	---	4.69	3.98
Nitrogen	1.27	1.47	1.86	---	1.05	0.91
Oxygen	8.18	10.09	2.63	—	14.83	21.90
Sulfatic Sulfur	0.04	0.10	0.07	0	0.00	N/A
Pyritic Sulfur	2.61	2.34	0.45	0	0.02	N/A
Organic Sulfur	2.33	0.92	0.64	0	0.86	N/A
Total Sulfur	4.98	3.23	1.16	0	0.88	0.20

* Values are reported on a moisture-free basis except for the moisture.

3.2 RESULTS

The electro-reduction behavior of the following coals was investigated: two high volatile bituminous (Illinois # 6 and Illinois #2), one medium volatile bituminous (Pittsburgh), one sub-bituminous (Montana Rosebud), and one lignite (North Dakota Velva), as well as one charcoal and one devolatilized coal. The average analyses of these materials are given in Table 3.3.

Liquid products were obtained from the electro-reduction of each of the samples studied. A solid waxy material was also produced with each. No gaseous products were formed. Pyritic sulfur was found to be removed during the electro-reduction treatment.

The compositions of the liquid products were dependent upon the parent coal and varied greatly. Short-and long-chain aliphatic, cyclic, aromatic, and fused ring aromatic hydrocarbons were detected.

In order to ascertain whether the liquid products are a consequence of chemical rather than electrochemical reaction, a blank test was conducted with Illinois #6 coal in which no voltage was imposed on the coal electrode. Conditions were otherwise similar to those under which liquid product had been obtained with Illinois #6 coal. In the blank test, no liquid product and negligible solid waxy material were formed. It was concluded that the liquid produced is indeed the result of electrochemical rather than chemical reaction.

The liquid products were always collected along with water and were separated with chloroform from the water associated with them. The chloroform extracts were analyzed by gas chromatography/mass spectroscopy (GC/MS). The mass spectrometer was not activated until the chloroform had been eluted. A blank chloroform sample was also analyzed by this technique to establish the background. Descriptions of the products derived from the various coals tested are given in the following.

Illinois #6 provided the greatest quantity of product, as well as the most varied. Eighty-one compounds were separated; of those present in quantity sufficient for identification (listed in Table 3.4), aliphatics and aromatics occurred in a 1:1 volume ratio. A typical chromatographic analysis of the liquid products from Illinois #6 is given in Appendix B. There were high concentrations of phenol derivatives and long chain hydrocarbons and mono-alcohols. One cyclic aliphatic compound was also detected. The estimated/calculated molecular weights (108 - 354) of coal liquifaction products correspond to the oils ($\leq$ 400) and asphaltenes (300 - 1000). Liquid products appeared at a relatively low electrode potential (-335 mV RHE)). A 25% current efficiency for product reaction was estimated.

With Illinois #2, a moderate quantity of liquid products was obtained, at an electrode potential of -500 mV (RHE) with <20% current efficiency. The products were comprised almost entirely of aromatics (Table 3.5), and were predominantly phenols with small quantities of acid and ketones.

In the case of the medium volatile Pittsburgh coal, only a small quantity of product was collected; 10 compounds were separated. The aromatics, which accounted for 80% of the product volume, included phenol derivatives, acids and esters. These are listed in Table 3.6. A current efficiency of <10% was measured at the electrode potential of -600 mV (RHE) required for the electro-reduction reaction.

Montana Rosebud, a sub-bituminous coal, likewise yielded a small quantity of liquid product. A high potential (-800 mV (RHE)) was required, at which a 22% current efficiency was measured. Sixty-seven compounds were separated; all of the identified compounds were phenol derivatives, within a fairly narrow molecular weight range (94 - 136). These are listed in Table 3.7.

North Dakota Velva lignite was the only coal from which liquid products were obtained at 200°C. The electrode potential required was also relatively low (-300 to 500 mV), with a 5% current efficiency. A moderate quantity of liquid was collected, in which 26 compounds were separated. The identified products (Table 3.8) were also predominantly aromatic (90%), with a wider molecular weight range (94-230). This was the only coal product in which a fused aromatic compound, naphthalene, was detected. The remainder of the aromatic compounds were phenol derivatives. A cyclic aliphatic compound was present, as well as straight-chain diols, which were approximately half the length of the long chain aliphatic mono alcohols found in the Illinois #6 product.

Table 3.4 ILLINOIS #6 COAL DERIVED LIQUID PRODUCT ANALYSIS: Over Eighty Compounds Detected

Major Components	Concentration %	Molecular Weight (Estimated/Calculated)
Aromatic		
4-hydroxybenzenesulfonic acid	6.8	174
2-methylphenol	3.0	108
methylphenol derivative	7.2	-
3-ethylphenol	3.0	112
2,4-dimethylphenol	2.3	112
isobenzofuranone	2.0	-
Aliphatic		
4,5-dimethylundecane	1.3	184
C_{18} hydrocarbon or alcohol	1.9	254 or 270
C_{20} hydrocarbon or alcohol*	3.8	282 or 298
C_{22} hydrocarbon or alcohol*	5.4	310 or 326
C_{22} hydrocarbon or alcohol	3.4	310 or 326
C_{22} hydrocarbon or alcohol	3.1	310 or 326
C_{22} hydrocarbon diol	2.3	342
C_{24} hydrocarbon alcohol	2.1	354
Total identified	47.6	
Impurities	8.8	
Other Unidentified Compounds in Small Quantities	43.6	

*Cyclic; The Remaining Aliphatic Compounds are Straight Chain

Molecular weights correspond to oils ($\leq$ 400) and asphaltenes (300 - 1000).

Table 3.5 ILLINOIS #2 COAL DERIVED LIQUID PRODUCT ANALYSIS: Mostly Aromatic Compounds Were Detected

Major Components

Aromatic	Concentration %	Molecular Weight
1-butyl-2-methylpropyl-1,2 benzenedicarboxylate	2.7	280
2,4-bis [(trimethylsilyl) oxy]-tribenzoic acid	1.2	-
p-2(2-methylallyl)-phenol	0.6	-
1-(2,4-dimethylphenyl)-ethanone	0.8	-
isobenzofuranone	4.5	-
2,5-dimethylbenzaldehyde	2.8	134
2,3-dihydro-1H-inden-5-ol	3.7	-
3-propylphenol	2.6	136
7 chloro-1,3 dihydro-2H-1,4-benzodiazepin-2-one	3.0	-
1-methylene-1H-indene	3.4	-
2,3-dimethylphenol	2.2	122
2-ethylphenol	9.3	122
3-methylphenol	20.5	108
3,3 dimethylypentyl-cyclohexane	0.7	183
2 methylphenol	8.1	108
phenol	17.7	94
Aliphatic		
1,1'-oxybis [2-methoxy]ethane	1.1	
Total identified	84.9	
Impurities	8.7	
Other Unidentified Compounds in Small Quantities	6.4	

Table 3.6 PITTSBURGH COAL DERIVED LIQUID PRODUCT ANALYSIS: Mostly Aromatic Compounds Were Detected

Component	Concentration %	Molecular Weight
Aromatic		
di-2-ethylhexylbenzenedicarboxylate	20.3	280
1-butyl,2-methylpropylbenzenedicarboxylate	3.6	280
3-methylphenol	12.7	108
2-methylphenol	10.0	108
4-hydroxybenzenesulfonic acid	24.0	174
Aliphatic		
9-octadecen-1-o1	19.0	270
Total identified	89.6	
Other unidentified compounds in small quantities	10.4	

Least reactive coal resulted in the least varied products

Table 3.7 MONTANA ROSEBUD COAL DERIVED LIQUID PRODUCT ANALYSIS: Only Phenol and Phenol Derivative Compounds Were Detected

Major components	Concentration, %	Molecular Weight
phenol	21.1	94
2-methylphenol	11.4	108
3-methylphenol	20.5	108
2,3-dimethylphenol	6.9	122
2-ethylphenol	1.5	122
3-ethylphenol	5.7	122
4-propylphenol	1.1	136
3-propylphenol	2.0	136
Total identified	70.2	
Other unidentified compounds in small quantities	29.8	

Table 3.8 VELVA LIGNITE COAL DERIVED LIQUID PRODUCT ANALYSIS: The Products Were Predominantly Aromatic.

Major Components Aromatic	Concentration %	Molecular Weight
phenol	26.1	94
2-methylphenol	7.8	108
3-methylphenol	21.5	108
2-ethylphenol	1.0	122
2,3-dimethylphenol	2.5	122
3-ethylphenol	6.7	122
naphthalene	3.7	128
3-propylphenol	1.1	136
Aliphatic		
1-methyl,-3-propylcyclohexane	4.1	140
4-methylheptane	4.1	114
1,14-tetradecanediol	1.8	230
1,12-dodecanediol	2.0	202
Total identified	82.4	
Other unidentified compounds in small quantities	17.6	

The electro-reduction behavior of a charcoal sample was also investigated. The charcoal analysis is included in Table 3.3. The liquid products were formed only at 250°C and at high electrode potentials, -700 to -900 mV, with a measured current efficiency of ~ 19%. Only a small quantity of product was collected; it was quite varied, however, with 79 compounds separated. Fused aromatics (substituted naphthalenes) were present in a fairly high concentration (~ 8%). The other aromatic constituents contained phenol, aldehyde, acid and ester groups. The products are listed in Table 3.9.

The role of the maceral contents of coal in the electro-reduction of coal was examined. The maceral contents of the coals of interest are given in Table 3.10. No correlation was observed between the maceral compositions and the reactivities of the coals tested.

Table 3.9 CHARCOAL DERIVED LIQUID PRODUCT ANALYSIS:

A Variety of Liquid Products Were Obtained But High Overpotentials Were Required.

Major Components	Concentration, %	Molecular Weight
Aromatic		
2-methylphenol	7.8	108
2,3-dimethylphenol	2.3	122
2-ethylphenol	2.1	122
2-methylnaphthalene	1.6	142
ethylbenzaldehyde	5.5	134
2,3-dihydro1-H-inden-5-ol	3.9	134
1,3-dimethylnaphthalene	3.7	156
1,4,6-trimethylnaphthalene	2.6	170
2,3-dimethyl-1,1'-biphenyl	1.3	182
3-methyl,-1,1'-biphenyl	3.4	168
1-butyl,2-methylpropyl-1,2-benzene dicarboxylate	1.0	278
1,2-ethylhexyl-1,2-benzene dicarboxylate	6.0	278
Aliphatic		
2-butoxyethanol	6.3	118
1,13-tetradecadiene	3.4	194
2,3,5-trimethyldecane	0.8	184
Total identified	51.7	
Other unidentified compounds in small quantities	48.3	

Table 3.10 MACERAL ANALYSIS OF COALS TESTED IN ELECTRO-REDUCTION INVESTIGATION:

No Correlations of the Maceral Compositions with the Products were Observed.

Coal	Active, volume %				Inert, volume %		
	vitrinite	exinite	resinite	Total	fusinite	semi fusinite	Total
Illinois #6 (HVB)	86.4	—	0.2	86.6	3.6	5.4	9
Illinois #2 (HVB)	85.3	3.1	0.0	88.4	5.9	1.2	7.1
Pittsburgh	92.5	0.1	0.0	92.6	1.1	5.0	6.1

	"Active", volume %					"Inert", volume %			
Montana Rosebud*	ulminite	humodetrinite	gelinite	corpohuminite	Total	semifusinite	macrinite	sclerotinite	Total
	66.5	4.6	4.9	1.1	77.1	9.2	3.6	0.8	13.6

* sub-bituminous

To provide clarification of the role of the volatile materials in the formation of the liquid products obtained in the electro-reduction of coal, a portion of Illinois #6 coal was devolatized by heat-treatment. Proximate and ultimate analyses (Table 3.11) performed on the devolatilized Illinois #6 coal indicated that the volatile content was almost completely removed by the heat-treatment.

A TGA analysis performed on Illinois #6 coal determined that the temperature range in which the volatiles are expelled is 400 - 900°C. The thermogravimetric scan is provided in Figure 3.4. The volatiles were analyzed by GC/MS to identify the constituents, which are listed in Table 3.12. The majority have much lower molecular weights than those produced in the electro-reduction of Illinois #6 coal; therefore, the liquid product collected from Illinois #6 coal is not the result of simple devolatilization during the test.

During electro-reduction of the devolatilized Illinois #6 coal, a much smaller quantity of liquid product was obtained than with the parent coal. There were also much fewer compounds isolated: 20 compared to 81 with the parent Illinois #6 coal. A description of the products identified in the product from the devolatilized Illinois #6 coal is given in Table 3.13. There were significant differences in the compositions

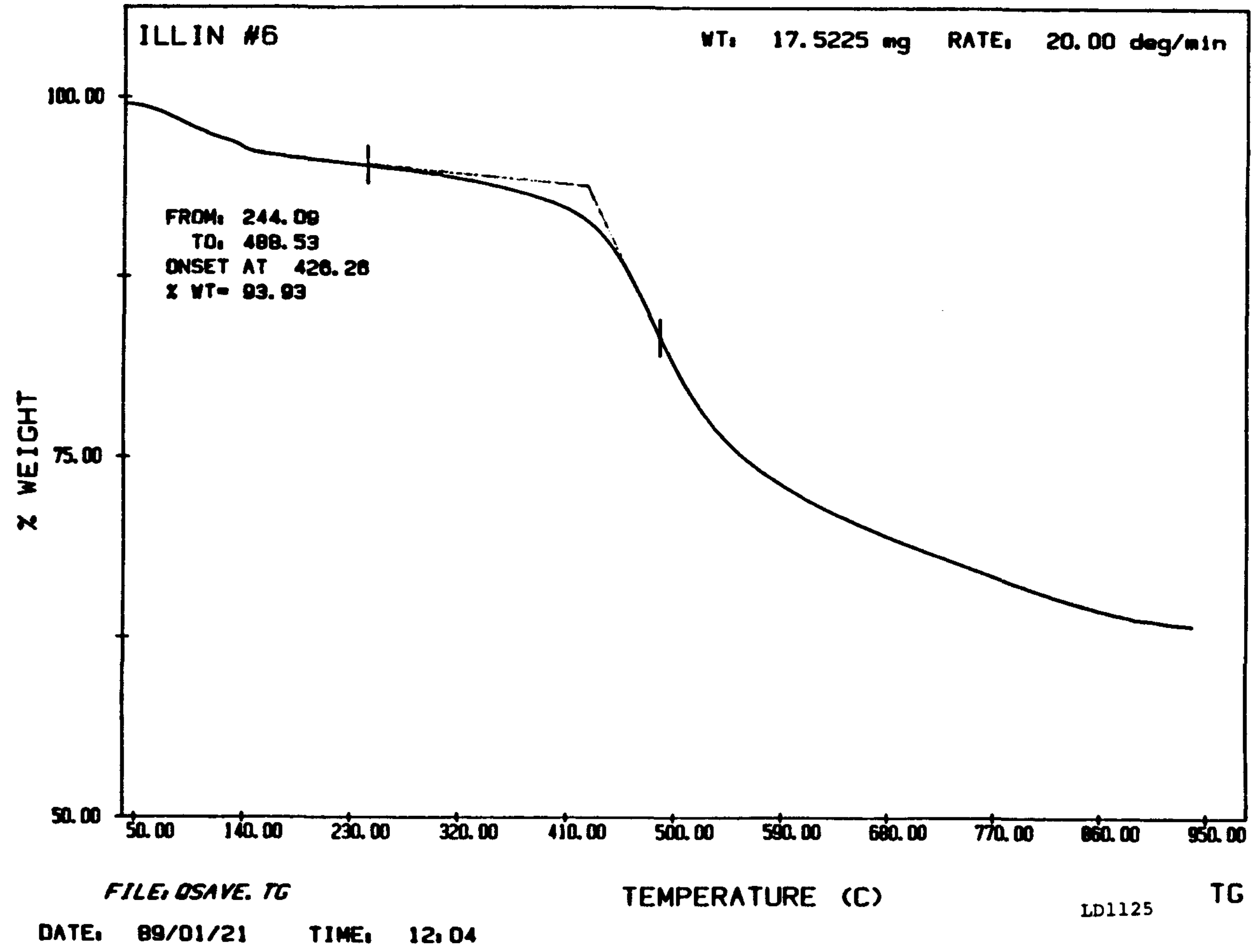


FIGURE 3.4 THERMOGRAVIMETRIC SCAN OF ILLINOIS #6

The Volatiles are Expelled in the 400 to 900°C Temperature Range.

of the products with respect to both aromatic and aliphatic compounds. In the devolatilized product the longest chain aliphatic hydrocarbon is hexane, whereas C_{22} and C_{24} chains were found in the parent Illinois #6 coal product. The percentage of aromatic compounds increased from 50% with Illinois #6 coal to 65% with the devolatilized coal. In addition, compounds with much lower molecular weights were reported for the devolatilized product, in which the molecular weights of all components were less than 150. In the Illinois #6 product, the molecular weights of the aliphatics ranged from 184 to 354. Considering that there is only one compound in common (2-methylphenol) together with the great differences between the devolatilized and Illinois #6 coal products, the volatiles appear to play a large role in the electro-reduction of Illinois #6 coal.

The white solid waxy deposits were observed in the water in which the coal electrode exit gases were collected and were found to be partially soluble in acetone and chloroform and insoluble in sulfuric, nitric, or hydrofluoric acids and sodium hydroxide.

Table 3.11 PROXIMATE AND ULTIMATE ANALYSIS OF DEVOLATILIZED ILLINOIS #6 COAL

Proximate Analysis	% *
Volatile Matter	1.96
Fixed Carbon	75.29
Ash	22.75
Ultimate Analysis	**%**
Carbon	72.91
Hydrogen	0.27
Nitrogen	0.74
Oxygen	0.0**
Sulfur	4.0
Ash	22.08

* dry basis
** by difference

Table 3.12 IDENTIFIED VOLATILE COMPOUNDS FROM HEAT-TREATMENT OF ILLINOIS #6 COAL (900°C):

Lower Molecular Weight Compounds Were The Major Products.

Hydrogen sulfide
Long chain unsaturated hydrocarbon
Long chain organic alcohols or acids
Hexadecanoic acid
Xylene
Toluene
Acetic acid
Sulfur dioxide
Propionic acid
Formic acid
Pentyl alcohols
Low mol. wt sulfur compound (possibly S_2)

Table 3.13 DEVOLATILIZED ILLINOIS #6 COAL DERIVED LIQUID PRODUCT ANALYSIS:

The Products Are Significantly Different Compared to the Products From The As-Received Illinois #6 Coal.

Major component	Concentration, %	Molecular Weight
Aromatic		
2-methylphenol*	11.5	108
2,6-dimethylphenol	20.2	122
chlorocresol	6.9	140
Aliphatic		
3,3,4,4-tetramethylhexane	17.8	142
3-ethyl-5-methylheptane	3.6	142
2,3,4-trimethylpentane	0.6	114
Total identified	60.6	
Other unidentified compounds in small quantities	39.4	

* Only this compound was present in the liquid products from both as-received and devolatilized coals.

A deuterated chloroform extraction of a sample of the deposits was utilized in analyses by Nuclear Magnetic Resnance (NMR) and infrared spectrophotometry (IR). The NMR analysis indicated that the aliphatic to aromatic C-H bond ratio was approximately 5:1. The extract and the residue were both analyzed by IR. The spectrum of the organic portion of the deposit, which was extracted in the deuterated solvent, was typical of long-chain esters or ester alcohols. The characteristic aromatic bands were absent, which is consistent with the NMR data.

The residue from the extraction was typical of a silicate or related compound. The waxy colloidal deposits consisted predominantly of the silicates, although the relative concentrations were not determined. These results help to explain the solubility behavior of the waxy deposits. The nuclei of the colloidal particles appear to be silicate, which became coated with the organic material, which formed a protective layer with respect to the acids and bases.

A small amount of fluorine (~ 1%) was detected in the waxy deposit. This suggests that the Teflon used in the coal electrode fabrication is a contributor, but not a major one, to the formation of the deposits.

In order to determine how the sulfur contained in the coal is affected by the electro-reduction reaction, sulfur analyses were performed on Illinois #6 coal electrodes in untested, blank-tested, and electro-reduction tested conditions. Sulfur analyses performed with a Parr bomb indicated that the pyritic sulfur was essentially completely removed during the electro-reduction test and partially removed during the blank test. The applied voltage resulted in somewhat greater sulfur removal. The sulfur balance is given in Table 3.14. If the sulfur content in the untested electrode is assumed to represent total sulfur, the sulfur lost in the electro-reduction tested electrode corresponds closely to the pyritic portion of the total sulfur, and the sulfur content of the electro-reduction tested electrode corresponds closely to the organic portion of the total sulfur. These results were supported by Energy Dispersive X-Ray Spectroscopy. Sulfur contents were significantly reduced in both blank and electro-reduction tested electrodes compared to the untested electrode.

Table 3.14 SULFUR BALANCE:

Somewhat Greater Sulfur Removal with Applied Potential was Observed.

	Total Sulfur %
Untested*	4.04
Blank Test (with H_2)	2.24
Electrochemically Reduced	1.79

* Illinois #6 coal

3.3 DISCUSSION

Production of liquid hydrocarbon products by electrochemical reduction of coal at low severity conditions has been successfully demonstrated. Liquid hydrocarbon products in the 100 to 300 molecular weight range were obtained from each of the coals tested in this program. An overall summary of observations is presented in Table 3.15. Phenolic aromatic compounds appear to be the predominant product. The products varied greatly and depended on the coal type. Methylated phenol was the only compound which occurred in the product from each coal. The current efficiency of the electro-reduction reaction, estimated by hydrogen balance, was less than 25% for all cases.

Table 3.15 COAL ELECTRO-REDUCTION OBSERVATIONS:

Products Depended On Coal Type; No Other Correlations Were Deduced.

Coal Type	Current Efficiency	'Reactivity'	Product Description
Illinois #6 (HVB)	<25%	Highest; product collected at -335 mV(RHE)	81 compounds; High concentration of phenols and long chain hydrocarbons and alcohols
Illinois #2 (HVB)	<20%	Product collected at -500 mV(RHE)	32 compounds; Predominantly phenols with small quantities of acid and ketones
Pittsburgh (MVB)	<10%	Product collected at -600 mV(RHE)	10 compounds; 20% aliphatic/80% aromatic
Montana Rosebud (Sub-bituminous)	<22%	Product collected at -800 mV(RHE)	67 compounds; All phenols
North Dakota Velva Lignite*	<5%	Product collected at -300 to-500 mV(RHE)	26 compounds; Predominantly aromatic (90%) Fused aromatics present
Charcoal	<19	Product collected at -700 to-900 mV(RHE)	79 compounds; Predominantly aromatic (80%) Fused aromatics ≃8%
Devolatilized Illinois #6	N/A	Product collected at at -355 to -400 mV (RHE)	20 compounds; Phenols and short chain hydrocarbons

* North Dakota Velva lignite was the only coal from which liquid product was produced at 200°C; others at 250°C.

One high-volatile bituminous coal, Illinois #6, provided the greatest quantity of product, also with the greatest variation, with the largest percentage of aliphatics (mostly long chain). The products (predominantly phenols) obtained with the other high-volatile bituminous coal, Illinois #2, were quite different from the Illinois #6 products. With the other coals tested, there was no obvious qualitative correlation between the volatile content and the products. This is in accordance with the liquefaction experience, where there is also no clear relationship between conversion and volatile matter content of the coal [31].

In the electro-reduction of devolatilized Illinois #6 coal only a very small quantity of product (compared with the other coals) was obtained, and a higher potential was required for liquid production than with the as-received Illinois #6 coal. There were significant differences, as well, between the compounds removed from Illinois #6 coal by devolatilization and those produced in the electro-reduction of as-received Illinois #6 coal. The products resulting from the devolatized coal were of much lower molecular weights. This demonstrates that the liquid products obtained in the electro-reduction reaction at <250°C are not the result of simple devolatization of the coal. Further important differences between the liquid products obtained with the electro-reduction of the devolatized and as-received Illinois #6 coals indicate that the volatiles do, however, play an important role in the electro-reduction process.

There was some influence of coal rank on the product composition. No direct influence of structural origin (maceral composition) was deduced in the coal electro-reduction experiments conducted in this program. Likewise, no direct correlation was observed between the applied potential required for the electro-reduction reaction and the composition of the products.

The present program was focused on proof-of-concept demonstration of coal conversion by electrochemical reduction. This coal conversion process has been successfully demonstrated. Some variations in product spectrum, reactivity and conversion was observed with different coals. No attempt has been made in this study to define these variations quantitatively. The cell design used in this study was not suitable for detailed mass balance permitting estimation of coal conversions and product-quantification. An economic analysis has not been pursued in this study because of the absence of sufficient rate and conversion information. Mass balance and economic evaluation should be addressed in a future study to evaluate the attractiveness of this novel process of coal conversion.

4.0 CONCLUSIONS AND RECOMMENDATIONS

This study has investigated the feasibility of two distinctly different routes to coal conversion at low severity conditions. An electrochemical approach utilizing both the electro-oxidation and electro-reduction routes was employed. The main advantage of an electrochemical approach is that the energy of activation for the conversion reaction is supplied in the form of electricity, possibly allowing low temperature operation and product control.

The electro-oxidation route consists of an electrochemical reaction involving H_2O and coal, leading to the breakup of coal molecules. This part of the study, conducted at Illinois Institute of Technology under the supervision of Prof. Gidaspow, has resulted in improved understanding of the mechanistic aspects of coal electro-oxidation. The observed reaction rate has been explained as a combination of the coal and pyrite electro-oxidation currents. Organic sulfur has been identified as the contributing factor for the observation of more than 100% H_2 production current efficiency with several coal samples. Also, an attractive coal pre-treatment process has been identified. This process, as described in Figure 4.1, results in production of useful products and simultaneous upgrading of the coal. Electrochemical oxidation of coal with H_2O leads to the production of hydrogen, CO_2, simultaneous removal of pyritic sulfur, and significant reduction of ash content. There is also indirect evidence that the organic sulfur may be removed in the process. A preliminary economic evaluation of this process has projected a cost advantage of > $8 per ton of Illinois #2 coal.

A lab-scale cell has been successfully employed in this study for generating process data useful for future design calculations. However, this cell design is not quite suitable for cost-effective scaleup. Commercial implementation of this unique coal treatment process will require the development of a cost effective, scaleable cell design. Such a reactor concept, utilizing a reactant flow through an electrode arrangement, is identified in Figure 4.2. Fabrication of such a reactor and demonstration of performance can be considered as the next important milestone towards successful development of this coal pre-treatment process and should be the subject of a future study.

This study also explored the electro-reduction route of coal conversion and has successfully demonstrated production of liquid products from different coal types at low severity conditions, 1 atmospheric pressure and less than 250°C. The coal electro-reduction products indicated a low (100-400) molecular weight range which corresponds to oils (<400). A variety of aliphatic and aromatic compounds have been identified in the products. Coal type has been observed to be the most important parameter affecting the product spectrum.

The present study has mainly focused on proof-of-concept demonstration of coal conversion by electro-reduction. No attempt has been made to pursue quantitative characterization of the process and evaluate its commercial feasibility. The cell design used in this study was not conducive to a detailed mass balance analysis permitting estimation of coal conversion. Therefore, a future study should focus on a detailed mass balance and the commercializable cell design development aspects. The data from this study could then be utilized to evaluate the economic feasibility of the process.

The present study has identified two distinctly different processes for coal conversion. The economic attractiveness of the electro-oxidation approach, which is further developed than the electro-reduction approach, has been identified. Additional development of this process, leading to development of a practicable cell design, is recommended. The technical feasibility of the electro-reduction route has successfully been demonstrated. However, further characterization of this process is necessary for a reliable evaluation of its economic potential.

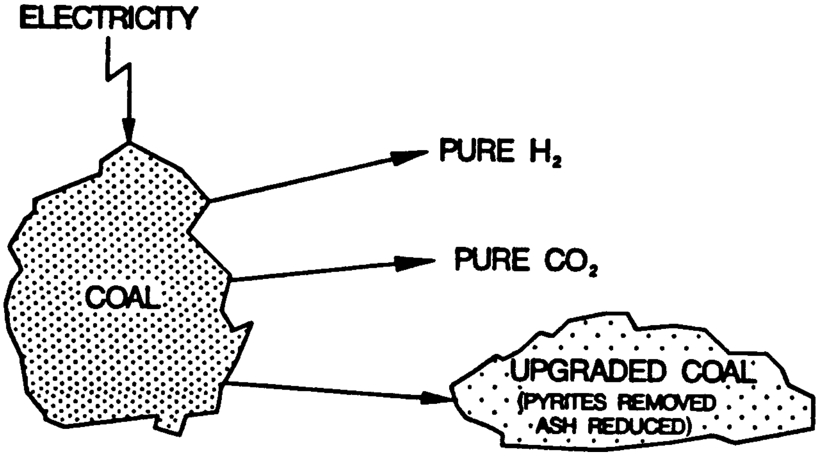


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FIGURE 4.1 POTENTIALLY ATTRACTIVE COAL PRE-TREATMENT APPROACH:

Electro-Oxidation Processing Allows Production of Pure Hydrogen and Simultaneous Coal Upgrading.

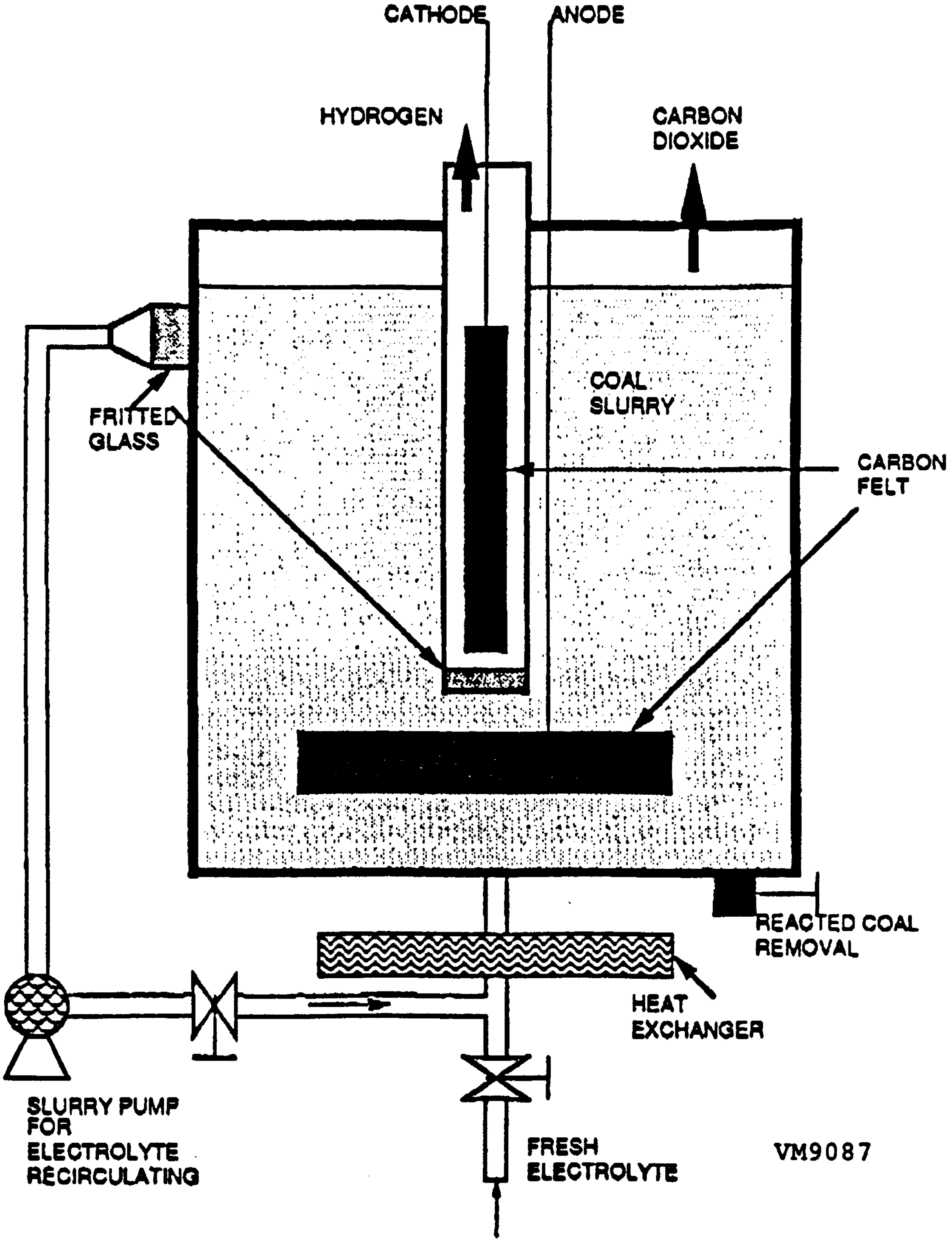


FIGURE 4.2 SCALEABLE ELECTRO-OXIDATION CELL:

Development of a Scalable Electro-oxidation Cell will be the next Logical Step for Process Development

5.0 REFERENCES

1. C.S. Lynch and A.R. Collet, Fuel, 11, 408 (1932).
2. Robert W. Coughlin and M. Farooque, Nature, 279, 301 (1979).
3. M. Farooque and Robert W. Coughlin, Nature, 280, 666 (1979).
4. M. Farooque and Robert W. Coughlin, Fuel, 58, 705 (1979).
5. Robert W. Coughlin and M. Farooque, Ind. & Engrg. Chem, 19, 211 (1980).
6. Robert W. Coughlin and M. Farooque, J. Appl. Electrochem., 10, 729 (1980).
7. Robert W. Coughlin and M. Farooque, Proc. American Chem. Soc., 24 (3), 41 (1979).
8. Robert W. Coughlin and M. Farooque, Electrochemical Gasification of Peat, Symposium Papers, IGT Paper No. 29, p. 439 (1980).
9. S.M. Park, J. Electrochem. Soc., 131 (9), 363C (1984).
10. R.L. Clarke, P.C. Foller and A.R. Wasson, J. Applied Electrochem., 18, 546 (1988).
11. K.E. Anthony and H.G. Linge, J. Electrochem. Soc., 130, 2217 (1983).
12. G. Okada, V. Guruswamy and J. O'M Bockris, J. Electrochem. Soc., 128, 2097 (1981).
13. P.M. Dhooge, D.E. Stilwell and S.M. Park, J. Electrochem. Soc., 129 (8), 1719 (1982).
14. P.M. Dhooge and S.M. Park, J. Electrochem. Soc., 130,1029 (1983).
15. P.M. Dhooge and S.M. Park, J. Electrochem. Soc., 130, 1539 (1983).
16. N. Taylor, C. Gibson, K.D. Bartle, D.G. Mills and D.G. Richards, Fuel, 64, 415 (1985).
17. P.M. Dhooge, S.M. Park and K.M. Jeong, J. Electrochem. Soc., 132, 1158 (1985).
18. F.E. Senftle, K.M. Patton and I. Heard, Fuel, 60, 1311 (1981).
19. H.G. Linge, Abstract #0310, Extended Abstracts; presented at the 34th Meeting of the International Society of Electrochemistry, Sept. 18-23, 1983, Erlangen, Germany.
20. S. Lalvani, M. Pata and R.W. Coughlin, Fuel, 62, 427 (1983).

21. S. Lalvani and R.W. Coughlin, Proceedings of the Workshop on the Electrochemistry of Carbon, Proc. Vol. 84-5, ed. S. Sarangapani, J.R. Akridge and B. Schumm, The Electrochem. Soc., Inc., Pennington, NJ, 492 (1984).

22. O.J. Murphy and J. O'M Bockris, Int. J. Hydrogen Energy, 10, (7/8), 453 (1985).

23. G. Kreysa and W. Kochanek, J. Electrochem. Soc., 132, 2084 (1985).

24. J.K. Brown and W.F. Wiss, Chem. Ind., 1118 (1955).

25. P.H. Given and J.M. Schoen, J. Chem. Soc., 2680 (1958).

26. P.H. Given, V. Lupton and M.E. Peoven, Nature, 181, 1059 (1958).

27. P.H. Given and M.E. Peoven, Fuel, 39, 463 (1960).

28. Z. Ogumi, K. Nishi and S. Yoshizawa, Electrochim. Acta, 26, (12), 1779 (1981).

29. S.M. Park, Electrochemical Characterization and Derivation of Coal: Technical Progress Report, Sept. 15, 1988 - Dec. 15, 1988. DOE Contract FG22-86 PC 90519 (1988).

30. H.W. Sternberg, R.E. Markby, C.L. Delle Donne and I. Wender, Electrochemical Reduction of Coal, Bureau of Mines Report of Investigations 7017 (1967).

31. D. Duayne Whitehurst, ed., Coal Liquefaction Fundamentals, ACS Symposium Series 139 (1980).

32. Heinz, Wi, et al., Electrochemical Reduction of Coal, Bureau of Mines Report of Investigations 7017 (Sept. 1967).

APPENDIX A. ECONOMIC ANALYSIS

An economic analysis was conducted based on the results of a 300 hour test run. The test conditions are identified in Table A.1 and the feed and product coal analyses are presented in Table A.2. These data indicate that all of the pyritic and sulfate sulfur were removed. Approximately two-thirds of the ash was also removed. There is some decrease in heating value due to the reaction of some of the fixed carbon in the coal to form either CO_2 or organic liquids. The increase in the sulfur in other forms can be attributed to the H_2S (reaction mechanism explained previously in Section 2) adsorbed on the coal surface which is believed to be highly porous. The organic sulfur could not be characterized properly. A summary of the economics of the process is given in Table A.3.

The following costs and benefits incurred in the process were considered in arriving at some preliminary estimates.

(1) Energy required or supplied for electrolysis.
(2) Saving in grinding energy from elimination of grinding to a size (5μm) small enough to liberate the same amount of sulfur.
(3) Credit for hydrogen production
(4) Increase in value of coal due to sulfur and ash removal
(5) Penality due to loss in heating value
(6) Capital charge

No credit for pure CO_2 was considered. Also, it was assumed that no net addition of H_2SO_4 will be required because the H_2SO_4 produced by electro-oxidation will compensate for process loss through ash neutralization. The overall process mass balance is given below:

(1) Total hydrogen production during the entire run = 144 liters
(2) Total carbon dioxide production = 1.44 liters

Economic Calculations

(a) Energy Required for Electrolysis:

Energy Required for 340 gm Coal = 1.05 (V) x 0.8 (A) x 300 (h) = 252 Wh

Energy Required for 1 Ton of Coal = 252 Wh x 1/340 gm x 453 gm/lb x 2000 lb/T x 10^{-3} kW/W = 672 kWh

Assume the cost of electricity = 3¢ per kWh*

Therefore, the cost of electrolysis = 672 kWh/T x $0.03/kWh = $20.16 per ton of coal

* Cheap electricity from hydro-power

(b) Energy Saving for Elimination of Step Required for grinding to 5 μm:

Bond's law can be used to estimate this energy saving. (Reference: Unit Operations in Chemical Engineering by McCabe and Smith, 1976, pp843-).

This saving amounts to approximately 215 KWh per ton of coal.

Therefore the energy saving = 215 x 0.04 = $8.6 per ton of coal.

(This figure-of-merit is included within the credit calculated under Section D. Therefore it was not included in Table A.3).

(c) Credit for Hydrogen Production:

144 liters of hydrogen were produced from 340 gms of coal. Therefore, 144 l x 1/340 gm x 453 gm/lb x 2000 lb/T x 10^{-3} m^3/l = 384 m^3 of hydrogen will be produced from 1 ton of coal.

The cost of hydrogen energy = $6.44/MM Btu (An average value)

The combustion energy of hydrogen = 0.012 x 10^6 Btu/m^3

The price of hydrogen produced = 384 m^3 H_2/T coal x 0.012 x 10^6 Btu/m^3 H_2 x $6.44/MM Btu = $29.67 per ton of coal.

(d) Increase in coal price due to sulfur and ash removal

An approximate formula, used by the New York State Energy Research and Development Authority, gives an estimate of this value. (Ref: Advanced Coal Cleaning Technology Assessments, volume 1 and 2, # 87-5, May 1987). According to this formula:

Price of Clean Coal = $25 + (fraction of total sulfur removal) x $18 = $25 + 0.63 x $18 = $36.34 per ton of coal

Therefore, the increase in coal price due to sulfur removal = $11.34 per ton of coal.

(e) Penalty due to loss in heating value:

Approximately 20% of the heating value was lost during the electrolysis. Therefore, the economic penalty for this loss in heating value = 0.2 x $36.34 price of clean coal) = $7.27 per ton of coal.

(f) Capital charge

Electrolysis Capital Investment = $29/ton of coal
(Assumes $14 x 10^6 for 1500 tons/day plant which is 4 times the coal handling cost in a Texaco gasification plant)

Assuming a 20% capital charge per year including depreciation, the capital cost will be $29 x 0.2 = 5.8

Table A.1 System Operating Conditions

Coal Sample Used: Illinois #2 Coal
Particle Size: 53µm
Electrolyte: 5 M H_2SO_4
Applied Potential: 0.8 volts vs SCE
Temperature: 110°C
Slurry Concentration: 0.25 gm/ml. of electrolyte
Electrode Area: 44 cm^2 each, cathode and anode
Run Time: 300 Hours

Table A.2 Analysis of Feed and Product Coal Samples

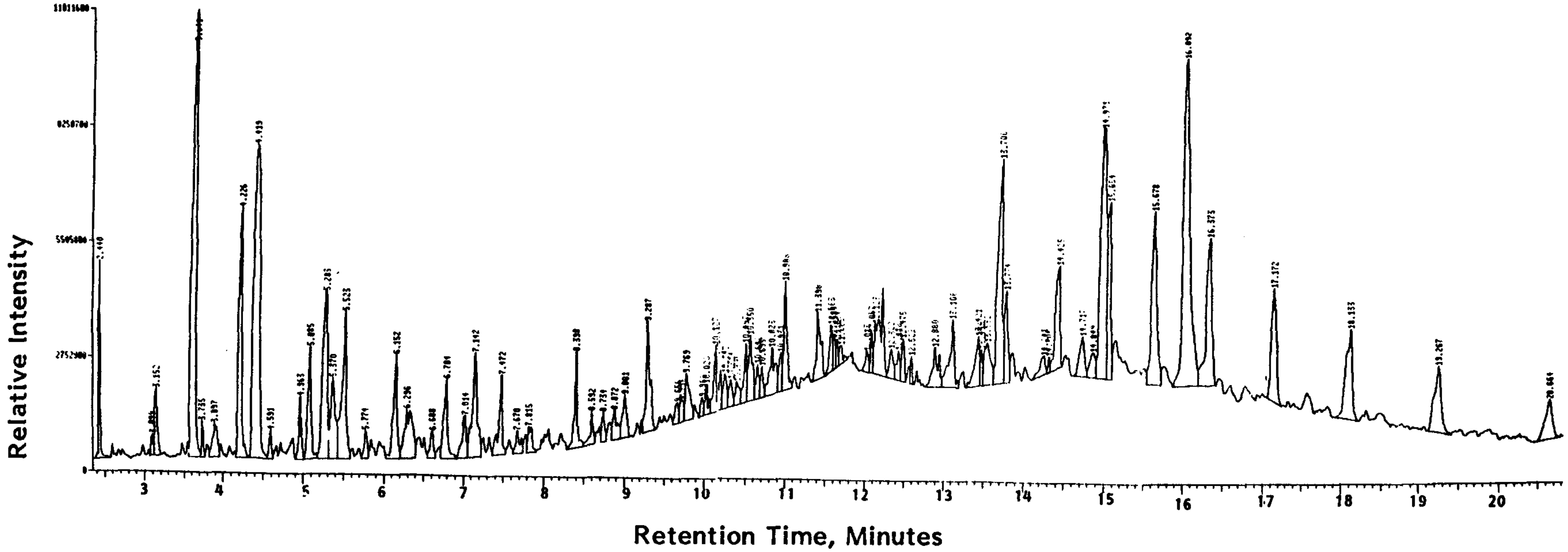
COMPONENT	FEED[1]	RESIDUAL COAL[1]	% REMOVAL
Pyritic Sulfur	2.34	0.01	99.6
Sulfate Sulfur	0.10	0.03	70.0
Other S Forms[2]	0.92	1.16	-
Total Sulfur	3.23	1.20	62.8
Ash Minerals	6.66	2.31	65.3
BTU/lb[3]	13526	11108	-

1. Determined by ASTM analysis; results are reported on dry basis.
2. Other sulfur forms are organic, sulfide, elemental. The increase in this sulfur value is most probably due to the sulfides and elemental sulfur adsorbed on coal surface.
3. The decrease in BTU content is due to the reaction of some fixed carbon to form either CO_2 or liquids.

Table A.3 SUMMARY OF ECONOMICS OF THE PROCESS:

The Electro-oxidation Coal Pretreatment Appears to Project an Economic Benefit of $\simeq$ \$8 per Ton of Coal.

STEP	COST/Ton of Coal	BENEFIT/Ton of Coal
1. Electrolysis	20.16	
2. Hydrogen Production		29.67
3. Increase in Coal Price		11.34
4. Penality for Loss in BTU	7.27	
5. Capital Charge	5.8	
	------	-------
TOTAL	33.23	41.01



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APPENDIX B. GAS CHROMATOGRAM OF LIQUID PRODUCTS FROM ILLINOIS #6 COAL