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FINAL REPORT

ON PROJECT NUMBER OCDO/R-90-3

THE USE OF ETHANOL TO REMOVE SULFUR FROM COAL

FOR THE PERIOD SEPTEMBER,1991 TO DECEMBER,1992

BY

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EXECUTIVE SUMMARY

Chemical removal of sulfur from coal is being studied using ethanol in the process. This report covers that portion of an on-going project which was funded in part by the Ohio Coal Development Office (OCDO) from September, 1991 through February, 1993. Prior to the support by OCDO, the objective of the project was to verify and scale-up a process disclosed in U.S. Patent 4,888,029. This patent was assigned to Southern Illinois University and the Illinois Geological Survey. A memorandum of understanding between these organizations and Ohio University included exchange of information and an agreement to negotiate a license to Ohio University to license the patent on a commercial scale.

The long range goal of this project was to demonstrate that ethanol can be used to remove sulfur from coal. The short range, immediate objectives were to confirm that the process described in U.S. Patent 4,888,029 would work on a laboratory scale of 5 to 20 grams of coal using etanol to remove sulfur from coal. If the laboratory experiments using methods described in U.S. Patent 4,888,029 were successful we were to attempt to scale up the experiments to one to ten pounds per batch or per hour. Because the laboratory experiments using the methods in U.S. Patent 4,888,029 were not successful, the objective was changed to develop a new laboratory procedure to use etanol to remove sulfur from coal. This has been achieved.

The laboratory work in Illinois, on which U.S. Patent 4,888,029 was based, had been done using 50 to 100 milligrams (0.050 to 0.100 grams) of powdered Illinois coal. The Illinois experiments were done in a thermogravimetric analyzer consisting of a miniature screen on which the powdered coal sample was placed in a heated vertical tube. The tube was heated to the desired temperature while ethanol vapors were carried up through the coal on the screen by helium plus nitric oxide gas. The loss in weight of the coal was measured and the off-gases were analyzed to detect the removal of sulfur from the coal. According to the patent, the pyrite in the coal served as a catalyst for the dehydrogenation of ethanol to form nascent hydrogen, a very reactive form of hydrogen. This active hydrogen could react with the sulfur in the coal to form hydrogen sulfide gas (H_2S) which could be recovered and marketed.

The attempts at Ohio University to scale up U.S. Patent 4,888,029 in the laboratory used 5 to 60 grams of coal in a stainless steel reactor. Results in the 105 laboratory experiments prior to OCDO support gave up to 90% removal of sulfur (down to 0.5% S) from both Ohio and Illinois coals with good reproducibility. However, as the work progressed we reached a point where we could not get more than 50% removal of sulfur and we concluded that the pyrite in the coal was not the critical catalyst for the process. In addition, we found that the conditions according to U,S, Patent 4,888,029 do not assure an overcoming of the thermodynamic limitations of the pyrite reduction reactions, especially of the troilite (FeS) reduction.

While trying to determine why the results of the laboratory experiments had changed, we developed a new laboratory procedure to use ethanol to remove sulfur from coal and other carbonaceous materials. It was found that copper was not only an effective catalyst for the reaction but also copper serves as a scavenger to remove the hydrogen sulfide as soon as it is formed and thereby prevent its contact with the desulfurized coal.

In the work at Ohio University, 5 to 60 grams of pulverized coal were placed on a screen in the bottom of a copper cup suspended inside a stainless steel autoclave. The autoclave was heated to the desired reaction temperature (400 to 600°C) and a flow of ethanol vapors in helium plus 0.5% nitric oxide was introduced below the coal where the gases passed up through the coal and were vented from the autoclave. The sulfur content of the beginning coal and of the product coal was measured to determine the amount of sulfur removed from the coal during each experiment.

Achievements.

In developing the new Ohio University procedure, the thermodynamic limitations of the reactions for removal of both pyritic and organic sulfur from coal at 400-600°C were studied using copper as a very strong H_2S-acceptor. Copper serves as a catalyst for ethanol dehydrogenation to form nascent hydrogen. Copper also serves as a scavenger to form copper sulfide from the hydrogen sulfide evolved during the reaction. Copper sulfide in turn serves as a catalyst for organic sulfur hydrodesulfurization reactions. If the coal to be desulfurized contains pyrite (FeS_2) or FeS, the copper scavenger effect reduces any back reaction of hydrogen sulfide with the iron and increases the removal of sulfur from the carbonaceous material. The desired effect of using copper can be achieved by using copper or copper containing alloys as materials of construction or as liners for a regenerable reactor.

During the time period that OCDO supported this work, small scale (5-60 grams) laboratory experiments with coals containing about 3.5% sulfur have achieved up to 90% desulfurization at temperatures of 500°C when using a copper reactor. Results from the autoclave experiments have identified the nature of the chemical reactions taking place. Because the process removes both pyritic and organic sulfur in coal, the successful scale up of the process would have important economic significance to the coal industry. Even though this and other chemical processes may be relatively expensive and far from being commercial, the reason for further development is that this process may hold the promise of achieving much greater sulfur reduction and of producing a cleaner coal than other methods. This would be especially important for small or older power plants and industrial boilers.

The clean coal produced in the laboratory is a dry, finely pulverized powder suitable for direct firing in a pulverized coal boiler. However, until successful larger scale experiments have been completed, it is too early to make a meaningful projected timetable for the commercialization of the process, an estimate of operating costs, or the potential impact on the use of Ohio coal.

Anticipated next steps.

The project is being continued with funding from other sources and a patent application has been filed for a new process. The technical work will develop the process on a laboratory scale and will scale up the operation to work with one to ten pound batches to get design and operating data for a pilot plant.

FULL REPORT

INTRODUCTION.

The initial technical goal in the project was to develop a chemical method for the cost effective removal of both inorganic and organic sulfur from Ohio coals. Verifying and using a process of reacting ethanol vapors with coal under conditions disclossed in U.S.Patent 4,888,029, the immediate technical objectives were to convert a small scale laboratory batch process to a larger scale continuous process which can serve as the basis for commercial development of the technology. This involved getting as much information as possible from small scale batch autoclave or fluid bed laboratory reactors for use in pilot plant studies. The laboratory data included material balances on the coal and sulfur, temperature and pressure ranges for the reaction, minimum reaction times at different conditions, the effectiveness of different activators such as oxygen and nitric oxide, the amount and nature of by-products such as sulfur dioxide, hydrogen sulfide and acetaldehyde, the effect of coal particle size on the speed and completeness of the reaction, and the effectiveness of the reaction on different Ohio coals.

Because the laboratory experiments using the method disclosed in U.S. 4,888,029 were not successful, the objective for the project was changed to develop a new laboratory process to use ethanol to remove sulfur from coal. This has been achieved.

This project has been funded by the Ohio Corn Marketing Board in previous years for a total of $199,910. from November,1989 through December,1992; by the Ohio Coal Development Office for $75,000. from September,1991 through December,1992; and by the National Corn Growers Association for $68,300. from March,1992 to February,1993. Additional funds of $37,500.for this project have been granted from the Kentucky Corn Growers Association and additional matching funds from the Ohio Corn Marketing Board for $37,500. A proposal to the National Corn Growers Association for $75,000. is under consideration for April, 1993 through December, 1993. A pre-proposal was submitted to the Alternative Agriculture Research and Commercialization Center (AARC) but we were not invited to submit a full proposal because the project was still in the research stage rather than being ready for commercialization.

TECHNICAL DISCUSSION

Previous Work

Results during work on the project for two years prior to OCDO funding included over 105 laboratory autoclave experiments. Reproducible results for the removal of up to 90% of the sulfur from Ohio and Illinois coals were obtained using 5 to 20 grams of coal in each experiment. During this time period neither the investigators at the Illinois Geological Survey (where the process was originally developed on a 50 milligram (0.050 gram) scale) nor at the Energy and Environmental Center at Grand Forks, N.D. (using an autoclave similar to ours) could repeat our results. Investigators from these two laboratories had visited our facility to observe our operations and had taken samples of the cleaned coal to their laboratory for analysis. The analyses of the cleaned coal in their laboratory agreed with our analysis within 0.1% in the less than 0.5% sulfur range.

Work under OCDO co-sponsorship

However, as work continued with OCDO co-sponsorship, the results in our laboratory changed dramatically. The percentage removal of sulfur from coal in the autoclave experiments dropped from the 80 to 90% range to the 30 to 40% range. An intense effort has been made to determine what change has caused the loss of effectiveness of the procedure as it was being used at that time, but no adequate explanation has been found.

During the period of previous work and the start of the work under OCDO co-sponsorship the results of sulfur removed from coal were measured only on the analysis of total sulfur in the coal before and after being processed in the autoclave. With 90% removal of total sulfur, we knew that both inorganic and organic sulfur were being removed, but we did not know how much of each. With the addition of a new staff member on the project, new information about the chemistry of the process was developed. The untreated coal and the product coal after treatment were analyzed for the different forms of sulfur. After a very thorough literature search (p 25) on reactions involving these forms of sulfur, Dr. Lazarov has developed an interpretation of the chemistry of the process which had not been in the patent disclosure and which explains the low desulfurization yields when attempting to use the methods of U.S. Patent 4,888,029. By gradually modifying the patented process we developed a new process with an interpretation of the chemistry as set forth below (p.4) The reactions are significantly different from those proposed in the original patent by Shiley (U.S. Patent 4,888,029) and will be the basis for filing a patent application on the new laboratory process.

A tabulation of the experiments which have been run during the period of funding by OCDO are attached as Appendix II (p 27). The experiments using the new copper cup start with No.193. Independent verification of our results were obtained at the Center for Applied Energy Research in Lexington, KY in November, 1993, after the OCDO support had stopped. Their result of 0.88% sulfur in the char compared favorably with an Ohio University result of 1.08% sulfur for the same coal and operating conditions.

A Description of the Technology

As a result of experiments using copper as a catalyst and as an H_2S scavenger, a new laboratory procedure to use ethanol to remove sulfur from coal has been developed at Ohio University and a patent application covering this process was filed in March, 1993. The process is based on the use of copper as a catalyst for the dehydrogenation of ethanol to produce nascent hydrogen to remove sulfur from the coal and the use of copper as a scavenger to capture the hydrogen sulfide formed from the sulfur removed from coal.

The thermodynamic limitations of the reactions for removal of both pyritic and organic sulfur from coal at 400-600°C both in an autogenous reductive atmosphere and in the presence of ethanol were studied using copper as a very strong hydrogen sulfide acceptor. Two substantial changes with respect to U.S. Patent 4,888,029 were introduced. A copper cup replaced a stainless steel cup as a reaction vessel mounted in a one liter autoclave and water was included also as a reactant fed in series with the ethanol.

Treatment of coal at 400-600°C in the presence of copper and water vapors leads to an almost complete removal of inorganic sulfur. The removal of sulfur from pyrite proceeds in two steps. The first step, the reaction of pyrite (FeS_2) with gaseous hydrogen to form iron sulfide (FeS) has a favorable equilibrium constant above 380°C and can go nearly to completion [Eq.1]. The equilibrium constant for the second step to reduce FeS to Fe is not favorable ($K<1$) at temperatures up to 1000°C [Eq.2]. Therefore only half of the inorganic sulfur in the form of pyrite is removed by treating coal with gaseous hydrogen if H_2S is not removed very quickly from the reaction bed of coal. A reveresible reaction can run in an unfavorable direction if the concentration of the product is maintained very low, and if the reaction rate is sufficiently high. This is the case for $FeS + H_2O$ to form $FeO + H_2S$ at 500°C. in the presence of copper (Eq.3). By maintaining a very low concentration of hydrogen sulfide, the reaction can go substantially to completion within a reasonable time and can lead to an almost complete removal of inorganic sulfur.

PYRITE REDUCTION

$$FeS_2 + H_2 \rightleftharpoons FeS + H_2S \qquad (1)$$

$$FeS + H_2 \leftarrow Fe + H_2S \qquad (2)$$

REACRION OF FeS WITH H_2O

$$FeS + H_2O \rightleftharpoons FeO + H_2S \qquad (3)$$

While the inorganic sulfur removal is determined by the equilibrium of the ferrous sulfide reduction reaction, the organic desulfurization depends only on the kinetics of the reactions and their catalysis. If coal is pyrolysed at 400-600°C in the presence of copper and the vapor of a low molecular alcohol, eg. ethanol, up to 70% of the organic sulfur is removable. The alcohol dehydrogenates extensively under the catalytic influence of copper in these conditions to produce nascent hydrogen [Eq.4.] which reacts with the organic sulfur in the coal to form hydrogen sulfide (H_2S) [Eq.5]. The gaseous H_2S reacts with the copper in the reactor to form copper sulfide (Cu_2S) [Eq.6] as a result of the scavenging effect of the copper. The copper sulfide thus formed catalytically influences the hydrogenolysis [Eq.5] of the organic sulfur-containing products of coal. The desired effect of using copper can be achieved by using copper or copper containing alloys as materials of construction or as liners for a regenerable reactor. Copper can be regenerated by roasting the sulfided copper with air at about 500°C [Eq.7] followed by reduction by hydrogen. The sulfur dioxide formed during regeneration could be converted directly to sulfuric acid.

ETHANOL DEHYDROGENATES TO ACETALDEHYDE AND NASCENT HYDROGEN

$$C_2H_5OH \rightleftharpoons CH_3CHO + 2\,\dot{H} \qquad (4)$$

ORGANIC SULFUR GROUP HYDROGENOLYSIS

(5)

REACTION OF H_2S IN A COPPER REACTOR LEADS TO REGENERATION OF THE HYDROGEN CONSUMED

$$2\,Cu + H_2S \rightleftharpoons Cu_2S + H_2 \qquad (6)$$

THE REGENERATION OF THE Cu_2S COVERING IS BY ROASTING WITH AIR AT 500-700 C.

$$Cu_2S + 4O_2 \rightarrow Cu_2O + CuO.CuSO_4 + SO_2 \qquad (7)$$

Using these reactions, in experiments with coals containing about 3.5% sulfur up to 90% desulfurization has been achieved at temperatures of 500°C. Successful scale up of the process to commercial operation would allow the use of Ohio coals to meet the strict acid rain restrictions which now prevent their use unless expensive wet scrubbers are installed and operated.

Because our inability to duplicate the favorable autoclave results obtained during the early months of 1991, the objective for the project was changed. Originally the plan was to run a selected coal in a batch stainless steel pipe reactor using two pounds of coal rather than the 5 to 10 grams used in the autoclave experiments. The objective was changed to a systematic evaluation of the reaction parameters in the autoclave to re-establish the reaction conditions needed to get good removal of sulfur from coal using ethanol. A complete and detailed knowledge of the operation parameters such as temperature, pressure, gas flow rate, amount and type of activator, amount and type of catalysts, materials of construction, reaction time, ratio to coal and number of portions of ethanol, water or hydrogen, and coal particle size, and kind of coal was needed for successful operation on a larger scale than the autoclave experiments.

The successful development of a new laboratory procedure has been the result of a careful review of related literature, the application of thermodynamic and kinetic considerations and careful laboratory experiments to confirm the theoretical concepts and the use of copper as an H_2S acceptor.

The main conclusion is that more than 90% of the inorganic sulfur and about 70% of the organic sulfur can be removed from different coals using both ethanol and water as reactants (in series) at 500°C. in a regenerable copper reactor. The sulfur removed from the coal is released as SO_2 during the regeneration of the reactor.

Experimental Procedure.

The batch one-liter stainless steel autoclave which has been used throughout the project was further modified to provide a copper cup, a copper thermocouple tube and a brass gas inlet tube which also suspends the copper cup inside the autoclave (Fig.1,p.8). Five grams of coal were placed on a copper perforated plate and screen about at the middle of the copper cup. By this arrangement, the incoming gases containing activator and ethanol or water vapors were in contact only with copper before contacting the coal. The coal and byproduct gases and vapors were in contact with the surface of the top part of the copper cup before being vented from the autoclave. During the heating up to a selected temperature, a constant flow of 60 ml/min of inert gas (helium) containing 0.5% NO (nitric oxide) as a reaction accelerator was driven through the reactor system.

Before the introduction of each portion of reactant (ethanol and/or water) the gas flow rate was reduced to 5-10 ml/min and maintained at this low level during the entire reaction residence time of the respective reactant. The total holding time at a given temperature was kept at 120 min. In practice, in the three portion experiments with 5 g coal and reactant portions of 2.5 ml (0.5 ml/g coal), each reactant was introduced for 5 min (0.5 ml/min) and treated for 25 min at a reduced gas flow rate of 5-10 ml/min. Between the portions (two intervals of 15 min) a higher gas flow rate of 80-150 ml/min was resumed when the pressure reverted to its initial level (50 psig). In the case of the two portion experiments with 5 g coal and reactant portions of 5 ml (1 ml/g coal), each reactant was introduced for 5 min (1 ml/min) and treated for 45 min at a reduced gas flow rate of 5-10 ml/min. During an interval of 20 min between the portions a higher gas flow rate of 80-150 ml/min was maintained until the pressure reverted to its initial level of 50 psig after having increased to >200 psig during the addition of reactants.

For the regeneration of the copper reactor successive treatments (blowing through) with air (80 ml/min) at 500°C. and with hydrogen (30 ml/min) at 200°C. were applied. The bulk of the sulfur, retained in the sulfide layer, was burned off for 30 minutes but the roasting continued until below 20 ppm SO_2 was present in the outlet air stream (about two hours). During the subsequent reduction with hydrogen, an additional amount of SO_2 was produced. A 30 minute reduction was usually applied. After regeneration, the reactor was dismantled and cleaned by means of an air jet in preparation for the next run.

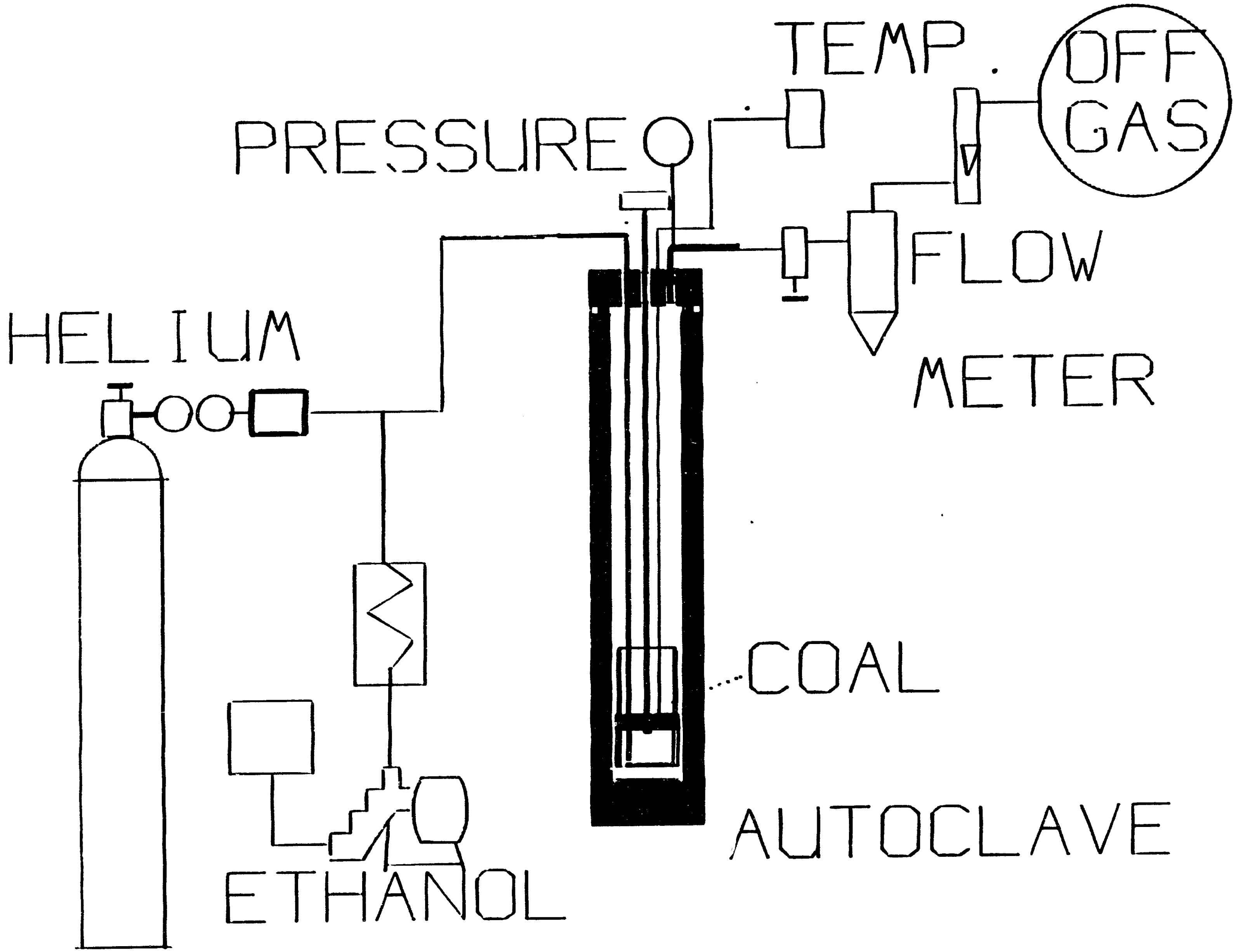

FIGURE 1. LABORATORY APPARATUS

Three Ohio high-volatile bituminous coals were used in these experiments. They were a sample of Ohio #6 (Middle Kittanning) coal obtained from the Penn State Coal Bank (PSOC-1518) and two washed samples (Ohio #4A and #11), collected from Sands Hill and Marietta Coal Companies, respectively. The sulfur analyses of these coal samples are as follows.

Coal	Total Sulfur	Pyritic Sulfur	Sulfate Sulfur	Organic Sulfur (by difference)**
	Percent, Dry Basis			
PSOC-1518	3.7	0.9	1.1*	1.7
Ohio #4A	4.0	2.0	0.0	2.0
Ohio #11	2.5	0.9	0.5	1.1

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* This sulfate sulfur content indicates some oxidation of the sample.

** Total S - Pyritic S - Sulfate S = Organic S
Total sulfur was determined by a Leco SC32 combustion analyzer
Pyritic sulfur was determined by the wet chemical method in ISO 157-1975 (International Organization for Standardization)
Sulfate sulfur was determined by ASTM 2492.

The apparent % sulfur removed as listed in the Table of Experiments in Appendix I was calculated by the following formula which does not take into account the weight loss of the coal during the experiment.

$$\textit{Apparent \% Sulfur Removed} = \frac{\textit{\% Initial S - \% Final S}}{\textit{\% Initial S}} * 100$$

The real (actual) % sulfur removed takes into account the loss in weight of the coal in the autoclave during the heating period. It was calculated by the following formula.

$$\textit{Actual \% S removed} = \frac{\textit{\% Initial S} - \left[\frac{\textit{\% Final S} * 100 - \textit{Wt. Loss}}{100}\right]}{\textit{\% Initial S}} * 100$$

Results

The important results from PSOC-1518 (Ohio #6) and Ohio #4A are presented in Table 1. (p.10). A tabulation of all runs conducted during the period of OCDO support for the project is in Appendix II (p.27)

TABLE 1. TABULATION OF SELECTED AUTOCLAVE EXPERIMENTS

#	COAL	TEMPERATURE °C	REACTOR	GAS FLOW	REACTANT # OF PORTIONS	% S IN THE COAL	% S IN THE PRODUCT	% DESULFURIZATION		
								TOTAL	INORGANIC	ORGANIC
138	PSOC 1518	450	Stainless Steel	nitrogen	no reactant	3.61	2.73	41.3	47.7	31.2
160	"	"	"	He + 0.5% NO	Ethanol 3 portions	3.57	2.39	47.3	44.2	51.4
189	"	460	copper, non-sulfided	"	"	3.65	1.52	69.2	78.8	60.1
185	"	"	copper, sulfided	"	"	3.83	1.27	75.1	80.6	68.1
195	Ohio #4 A -20 mesh	480	"	"	no reactant	3.97	3.08	46.3	65.3	27.9
197	"	"	"	nitrogen	Ethanol, 3 portions	3.76	2.38	57.7		
194	"	"	"	He+0.5%NO	"	3.86	2.06	63.5	66.8	60.2
198	"	"	"	hydrogen	no reactant	3.90	2.43	59.2	54.6	63.9
200	Ohio # 4 A -100 mesh	"	"	He + 0.5% NO	Ethanol, 3 portions	3.72	1.56	69.6	69.9	69.4
204	Ohio # 11 -100 mesh	"	"	"	"	2.41	0.78	76.3		
202	Ohio # 4 A -100 mesh	500	"	"	Ethanol, 2 portions water, 1 portion	3.64	0.98	82.5	90.4	72.9
206	Ohio # 4A -100 mesh	500	copper, sulfided	H+0.5%NO	Ethanol, 2 portions Water, 1 portion	3.80	0.98	82.7	93.2	72.6
209	"	"	"	"	"	3.80	0.55	90.4		
208	"	"	"	"	Water, 1 portion Ethanol, 1 portion	3.73	1.01	81.5	93.6	69.0
212	"	"	"	"	Water, 1 portion** Ethanol, 1 portion**	3.86	0.71	87.95		
214	"	"	"	"	Water, 1 portion** Hydrogen-gas-1 portion (0.1 mol)	3.87	1.36	78.3	88.6	68.0

**Double the amount of reactant portions (1 ml/gm coal) were added.
Total sulfur was determined by a Leco SC32 combustion analyzer
Pyritic sulfur was determined by the wet chemical method in ISO 157-1975
(International Organization for Standardization)
Sulfate sulfur was determined by ASTM 2492.
Total S - Pyritic S - Sulfate S = Organic S

Discussion of Results.

The autoclave experiments included in Table 1 were selected to demonstrate the conditions, reactants and materials of construction needed to achieve successful removal of sulfur from coal using ethanol as a source of active hydrogen to react with the sulfur in the coal.

Experiments 138 and 160 demonstrate the low removal of sulfur from coal when using a stainless steel autoclave with no copper present and with or without ethanol present as a reactant, 41.3% and 47.3% desulfurization. Experiment 160 can be considered as corresponding to the conditions disclosesd in U.S. Patent 4,888,029.

In experiments 189 and 185 the improved removal of sulfur from the coal is demonstrated due to the presence of copper in different forms, 69.2% and 75.1% desulfurization.

Experiment 195 shows the low level of desulfurization of the coal in the absence of a source of hydrogen (either ethanol or water). This is the amount of desulfurization resulting from just heating the coal to 480 C, 46.3% desulfurization.

Experiment 197 shows the limited effect of ethanol in the absence of an activator such as 0.5% NO, 57.7% desulfurization.

Experiments 194 and 198 compare the amount of desulfurization with ethanol, 63.5%, and gaseous hydrogen under the same operating conditions, 59.2%.

Experiments 200 to 212 show the effects of variations of the amounts of ethanol or water or combinations of the two on the amounts of desulfurization of Ohio coals. The results range from 69.6% to 90.4% total sulfur removal. These results do not reflect a scatter of results from duplicate experiments but rather the effects of intentional variations in reactants or operating conditions and consequently an average of the results would have no significance. They do demonstrate that, at 500°C with copper as the material of construction and ethanol and water as the reactants, up to 90.4% total desulfurization of Ohio coals can be achieved.

Experiments 214 and 212 show again that the use of gaseous hydrogen with water is not so effective as ethanol and water, 87.9% versus 78.3% total desulfurization.

Reproducible laboratory autoclave experiments now can be made to produce low sulfur coal. However, attempts to operate the process in larger scale equipment have not been successful.

Scale-up Experiments.

A batch fluidized bed reactor (Fig.3, p.16) was operated to test the effectiveness of a fluidized bed for contacting the ethanol vapors with the coal. In the batch mode, the unit was heated to reaction temperature with a flow of nitrogen at a rate required to fluidize the coal. A cold-flow model, a clear plastic pipe, had been used to determine the minimum gas flow required to fluidize the coal particles. As soon as the fluidized bed unit reached reaction temperature, a charge of coal was introduced through the feed pipe and allowed to heat to reaction temperature. The gas flow was then be switched to nitrogen plus activator (0.5% nitric oxide or 1.5% oxygen) and the ethanol vapors were pumped into the reactor below the distribution screen for a predetermined period of time, then the coal was discharged through the outlet pipe for analysis for sulfur. Gas samples were collected and analyzed for H_2S. In this unit a series of experiments, using one, two and four pounds of coal to get different contact times and three different amounts of ethanol to observe the minimum alcohol requirement could be run. If the results were favorable, then the fluid bed unit could be operated to simulate a continuous flow fluid bed reactor over a period of time by sequentially adding coal through the top hopper and removing coal through the bottom hopper. At a later date, units could be added to provide continuous feed and continuous discharge of the coal.

A batch cross-flow reactor (Fig.2,p.15) was operated to determine if this type of reactor will result in uniform sulfur removal from the coal being tested. Similar in operation to the autoclave experiments, two pounds of coal were charged into the screen basket, the unit assembled, and the unit heated to temperature with a flow of nitrogen. As soon as the coal in the basket reached the desired reaction temperature, the gas flow was switched to nitrogen plus activator (0.5% nitric oxide or 1.5% oxygen) and ethanol vapors were pumped through the cross-flow bed. Gas samples were collected for analysis of H_2S. After the unit was cooled, the reactor was opened, and the coal removed for weighing and for analyzing for sulfur.

For a batch mode of operation of the fluid bed unit to simulate a larger scale autoclave experiment, a 3-inch o.d. copper cup with a perforated bottom plate was inserted into the bottom of the reactor to a position where the bottom layer of coal was at the mid-point of the bottom heater. The reactor was heated to the operating temperature and the charge of -20+100 mesh coal was dropped into the copper cup. The activator gas, nitrogen plus 1.5% oxygen, and ethanol vapors were preheated to 290-300°C in the lower gas pre-heater section of the unit and introduced into the reactor below the perforated bottom of the copper cup. At the end of the run, the reactor was unbolted from the gas preheated section and the copper cup containing the treated coal was withdrawn from the bottom of the reactor. Treated coal from the top third, middle third and bottom third of the cup was collected and analyzed separately. All runs were at atmospheric pressure and the average starting value of the raw coal was 3.31% sulfur. The results follow.

TABLE 2. BATCH FLUID BED REACTOR

DATE	COAL WEIGHT GMS.	COAL TEMP. °C	TIME AT TEMP.	ACTIVATOR	ETHANOL TOTAL ML	TREATED RATE ML/MIN	RAW COAL % S	PRODUCT % S
6/16/92	575 No.6	390	3hr	Nitrogen+ 1.5% O_2	180	9.6	3.31	Top=2.83 Mid=2.88 Btm=3.28
6/17/92	"	400	5hr	None	None	0		Top=2.78 Mid=2.88 Btm=3.0
6/23/92	"	400	"	Nitrogen+ 1.5% O_2	None	0	3.31	Top=2.63 Mid=2.68 Btm=2.86
6/25/92	"	390	6hr	"	180	1.0	3.31	Top=2.62 Mid=2.81 Btm=2.83
7/ 1/92	150	400	2.5hr	"	50	1.0	3.31	3.19
7/ 8/92	None	"	6hr	"	None	0	Preconditioning Run	
7/14/92	575	430	4.5hr	"	180	1.0	3.31	Top=2.36 Mid=2.49 Btm=2.83
7/22/92	"	420	"	"	"	"	3.31	Top=2.25 Mid=2.46 Btm=2.9
8/25/92	575	350	3hr	Nitrogen+ 1.5% O_2	180	1.0	3.31	Top=2.61 Mid=2.94 Btm=2.94
9/1/92	575** No. 8	340	3hr	N_2 + 0.5% NO	180	3.0	**	
9/18/92	140gm No. 6	360	5.5	N_2 + 1.5% O_2	45	0.5	3.31	1.9
9/25/92	140gm No. 8	420	3hr	Ditto	15	0.5 ?	3.45 **	
10/ 7/92	140gm NO. 6	450	3hr	Ditto 50ml/m	15	0.5	3.31 ***	1.9
10/16/92	Ditto	420	2.5	Ditto 115ml/m	30	3.0	3.31	1.4
10/21/92	Ditto	415	3hr	Ditto 1000ml/m	15	3.0	3.31	1.5
10/26/92	Ditto	450	2.2hr	Ditto 75ml/m	30 +15H_2O	3.0	3.31 ****	1.5
10/28/92	Ditto	450	3.0	Ditto 100ml/m	30 +15H_2O	3.0	3.31 ****	1.75

** Pittsburgh No.8 coal has a high free swelling index (FSI) of 6 to 8 and was coked into a solid mass in the cup.

*** The following runs were attempts to duplicate the conditions the successful autoclave experiments.

**** Alternate injections of 15 ml EtOH and H_2O

The necessary sections of flanged stainless steel pipe and tubing were on hand to assemble each of the reactors. Additional controllers, on line gas analyzers and data acquisition units were purchased or adapted to this use. All of these were selected so that they can be used on the continuous reactor when it is assembled.

Various configurations of the batch fluid bed reactor and the batch cross-flow reactor were examined to get the best control of the temperature of the coal in the reaction zone and the best preheat of the gas and alcohol vapors. Because of non-uniform heating along the reactor wall, new heaters were installed on the reactor section of the batch fluid bed unit. Three six-inch cylindrical heaters, each with a separate temperature controller, were used. Tests using separate thermocouples inserted at the mid-point of each heater showed uniform wall temperatures for each heater section.

As in the batch autoclave experiments, the test procedures consisted of weighing the raw coal, analyzing the raw coal for sulfur, measuring gas flow, temperature and pressure during the reaction, sampling and analyzing the off-gas stream for hydrogen sulfide, weighing the product coal, and analyzing the product coal for sulfur.

None of the product coals were within a sulfur range that would make them a compliance coal. The difference in sulfur level between the top of the product sample and the bottom of the sample is yet to be explained. Until the conditions used for successful results in the autoclave experiments can be duplicated in the fluid bed or the cross flow batch reactor to get 80 to 90 per cent removal of sulfur from the coal, we cannot make a decision on which type of reactor will be the better choice. Work with these two reactors will continue during 1993 under different sponsors.

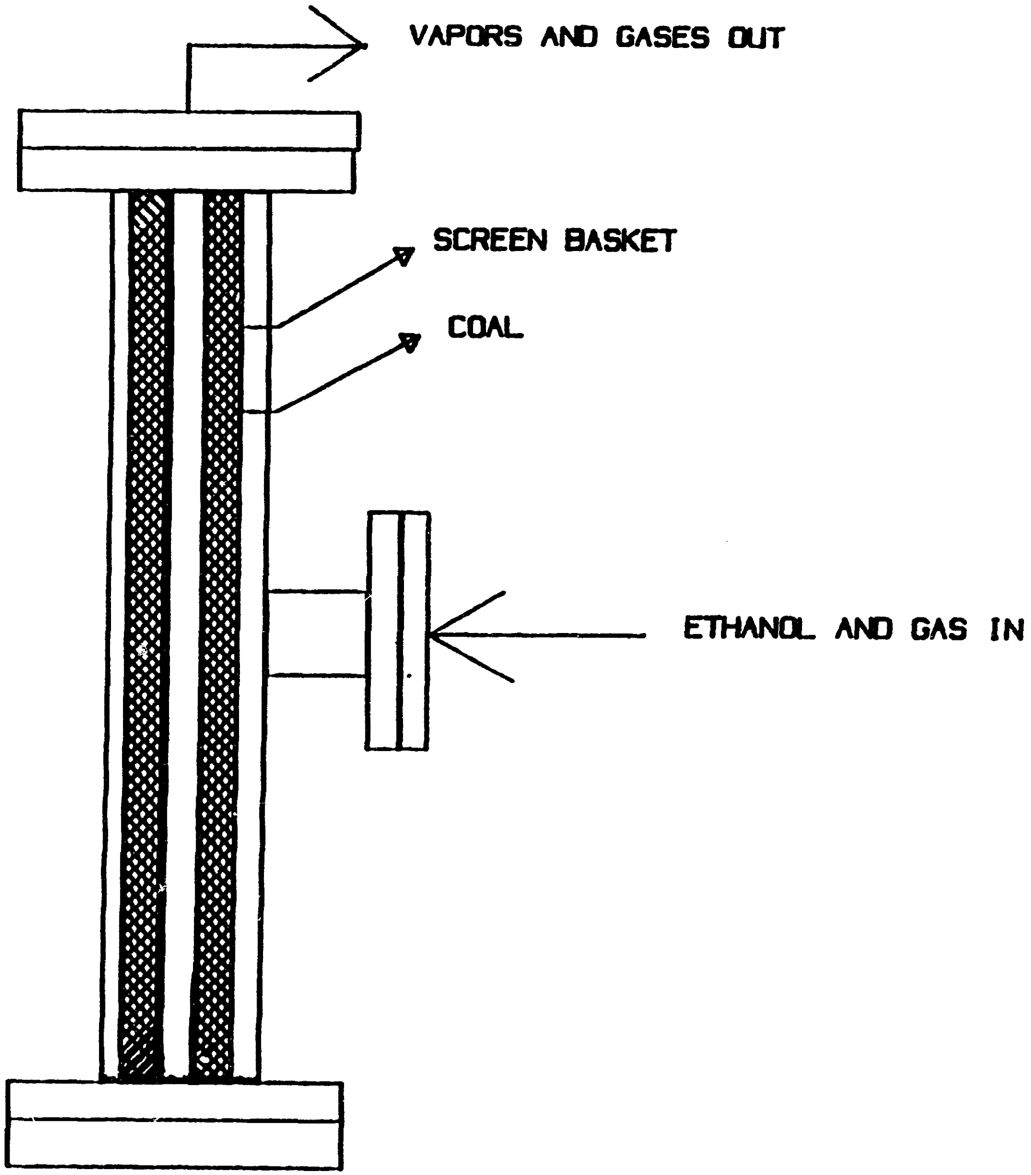

FIG. 2

BATCH CROSS FLOW REACTOR

OHIO UNIV. 9/90 RLS

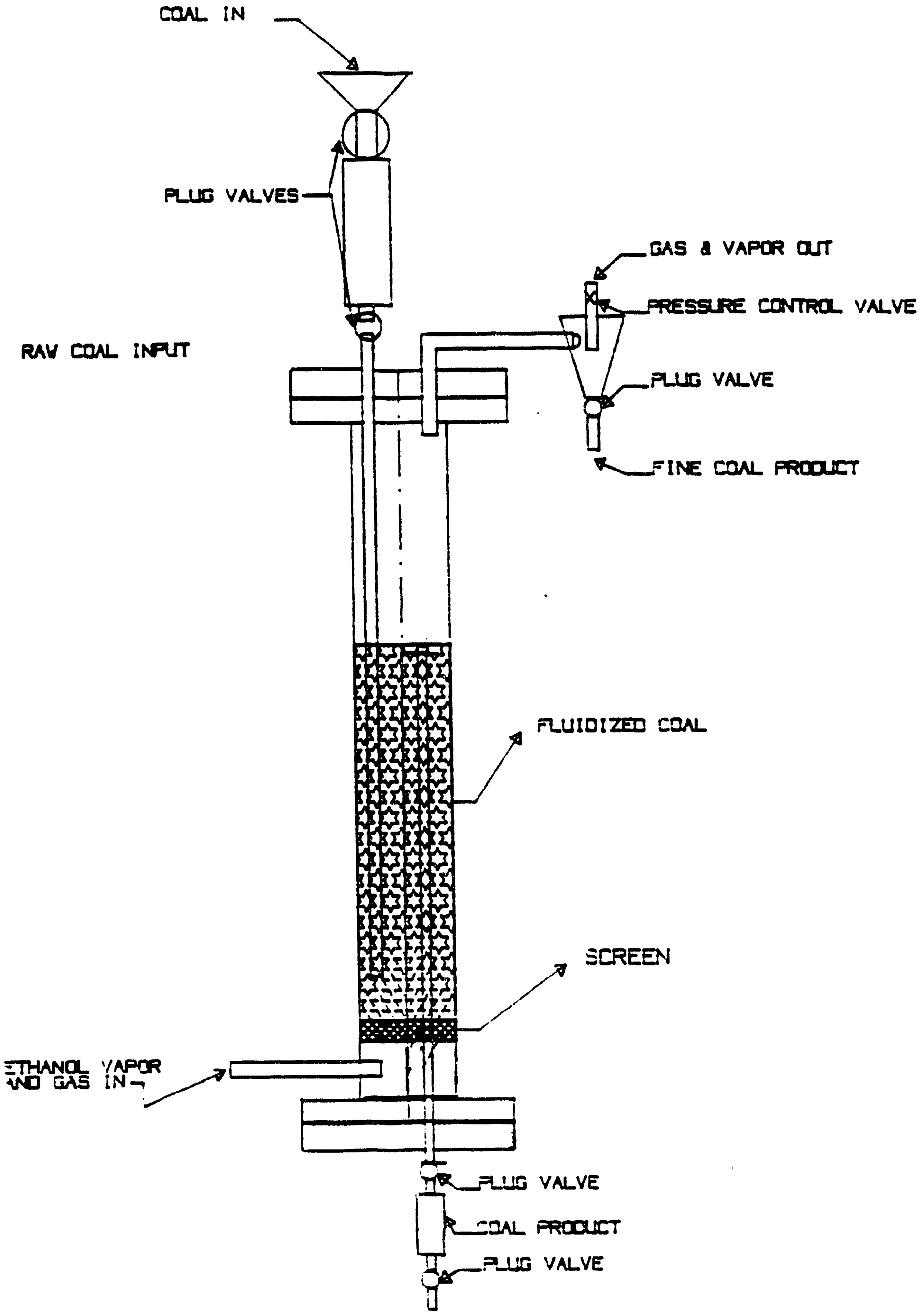

FIG.3

4"DIA.X 5FT FLUIDIZED BED REACTOR

OHIO UNIV. 9/90 RLS

Selection of Ohio Coals

During the initial work on this process, an Ohio No. 6 coal from the Middle Kittanning seam was used to investigate the effectiveness of the process. In order to permit other investigators to use the same coal, a sample of the Ohio No. 6 seam was obtained from the Penn State Coal Sample Bank and is identified as PSOC-1518. This was a whole seam channel sample taken in Carroll county. Reported sulfur content of the coal in the sample is 3.86%.

It was considered important to determine what other Ohio coals can be used as feed stock for the process to use ethanol to remove sulfur from coal. Because of the possible in situ catalytic effect of pyrite in the coal, the amount and distribution of pyrite in different coals may be an important factor in the suitability of a particular coal for use in the desulfurization process, but this has not been found to be the case.

Based on the 1988 production figures, coal samples from the five highest tonnage seams in Ohio were collected and tested for sulfur removal using ethanol as the reactant. Sample selection was based on the following table:

TABLE 3. OHIO COAL PRODUCTION BY COAL SEAMS

Priority	Coal seam	Counties	1988 tonnage
1	No.8 Pittsburgh	Belmont, Harrison, Jefferson, Monroe	7,598,745
2	No.9 Meigs Creek	Belmont, Noble	5,614,248
3	No.4A Clarion	Jackson, Meigs, Vinton	5,526,633
4	No.6 Middle Kittanning	Columbiana, Coshocton, Perry, Tuscarawas	3,979,549
5	No.5 Lower Kittanning	Coshocton Jackson, Stark, Tuscarawas, Vinton	2,581,480
6	No.11 Waynesburg	Belmont	1,430,089
7	No.7 Upper Freeport	Coshocton Harrison Tuscarawas	1,027,384
8	No.4 Brooksville	Columbiana Mahoning, Stark, Vinton	976,247

Two five-gallon samples of each of the top five coals have been collected. The samples needed for this project are production samples of washed coal in current production.

During a meeting to discuss the ethanol process, Robert Lenko of the Cravat Coal Company volunteered to locate sources of samples of the desired coals. Based on the information and help by Mr. Lenko, we have collected two 5-gallon plastic cans of each of the following coals:

TABLE 4 - SOURCE OF OHIO COAL SAMPLES

No.8 coal seam	-Ohio Valley Coal Co. Belmont County, cleaned in Jeffry Baum Jig washed to 1.6 sp.gr. Ohio Mine # Bt-68
No.9 coal seam	-Marietta Coal Co. Belmont County, Pit #702,Ohio Mine #Bt- Washed, 3/4 x 0, heavy media @ 1.6 sp.gr.
No.4A coal seam	-Sands Hill Coal Co. Vinton County, Sugar Run Mine Washed, 3/4 x ?
No.6 coal seam	-Crooksville Coal Co. Perry County,Bearfield Twp.,Sec3, State Min No.Py-317. Washed, heavy media @ sp.gr. 1.45, 1 1/2 x 1/2.
No.11 coal seam	-Marietta Coal Co. Belmont Co.,Pits 758-798,Ohio Mine #Bt-1104 Washed, 3/4 x 0,heavy media @ 1.6 sp gr.

Using the samples of the five Ohio coals collected, each sample was processed and tested as follows:

1. Air dry one 5-gallon sample overnight at 105 C.
2. Split and retain 1/4 of sample.
3. Crush retained sample to minus 1/4 inch in Chipmunk jaw crusher.
4. Reduce minus 1/4 inch sample to minus 20 mesh in disc mill.
5. Split and retain one pound of minus 20 mesh coal.
6. Pulverize to minus 200 mesh coal in Wiley impact mill.
7. Screen pulverized coal through 200 mesh Tyler screen in a RoTap shaker.
8. Retain minus 200 mesh coal as raw coal for autoclave experiments.

Using conditions as established in previous experiments on Ohio No. 6 coal (PSOC-1518), each minus 200 mesh coal sample was run in the autoclave configured as in Fig.1,(p.8).

Raw coal was analyzed for sulfur, ash, volatile, fixed carbon, moisture and Btu. Ten of coal grams were charged into the autoclave. At the end of the experiment, the treated coal was collected, weighed and analyzed.

The complete analyses of the five coals are shown in Appendix 1 (p.26). The significant results shown in TABLE 5 are that the relative amount of sulfur removed from each of the five Ohio coals was equal to or more than the amount of sulfur removed from the reference coal (Ohio No.6, PSOC 1518). The amount of sulfur remaining in the five Ohio coals was from 0.96 to 1.17 per cent as compared to the values in the reference coal of 0.96 to 1.12. From these results we can conclude that the use of ethanol to remove sulfur from coal can be used in treating coals from the major coal seams in Ohio.

TABLE 5. SULFUR CONTENT OF FIVE OHIO COALS BEFORE AND AFTER TREATMENT

SAMPLE ID.	% SULFUR IN RAW COAL	% SULFUR IN TREATED COAL	AUTOCLAVE TEMP.° C.
Reference Coal-Ohio No.6	3.6	1.12	320
PSOC-1518		.75	450
TASK II SAMPLES			
No.4A	3.37	1.17	320
No.6	2.66	1.12	320
No.8	3.84	1.19	320
		.96	420
No.9	3.16	1.16	320
No.11	3.77	1.13	320

In most samples there was some reduction in the Btu value of the treated coal as compared to the raw coal. This was probably due to the loss in volatiles in the coals as a result of the long heating periods in the autoclave. The results of the Btu measurements are not considered significant because of the small samples of treated coal available and because in larger scale continuous reactors the coal would not be subjected to high temperatures for long periods of time. All of the Btu analyses were run at the Modern Chemical Laboratory in Pomeroy, Ohio because our calorimeter was not in operation.

Ash, sulfur and moisture were also determined at the Modern Chemical Laboratory as a check against the analyses run in the laboratory at Ohio University. Excellent checks were obtained in most of the sulfur values. Variations can be attributed to the small sample sizes and/or coarse particles in a sample.

Waste Disposal.

Waste disposal or other environmental issues are not a major concern in the potential commercial operation of the ethanol process to remove sulfur from coal. There are little or no liquid or solid waste materials that would require a sludge pond, incineration or other waste disposal methods. Waste water treatment would be needed only to treat condenser or scrubber water which had been contaminated from a leak in the piping or equipment.

Sulfur dioxide (SO_2) formed during the regeneration of the copper reactor could be converted directly to sulfuric acid in a contact acid plant. Any gaseous hydrogen sulfide which is formed as a by-product could be recovered and used with essentially zero emission problems. It can be collected and sold as a gas although there is only a limited market for H_2S gas. The H_2S can be burned in a contact acid plant to make concentrated sulfuric acid which has broad industrial use, especially in making some types of fertilizers. By using the Claus process, the H_2S can be converted to elemental sulfur with zero emission problems. The Claus process (a catalytic oxidation process) is used on a large scale in petroleum refineries. The product sulfur is a solid which can be stored or shipped in conventional facilities. Sulfur is used as such for agriculture purposes or as the conventional raw material for the production of sulfuric acid.

Any by-product acetaldehyde from the process is a low-boiling (20°C) liquid which could be condensed and sold. It is used as an intermediate feed stock for the production of acetic acid, acetic anhydride, 2-ethyl hexanol, pentaerythritol, peracetic acid, paraldehyde and other chemicals. One potential market which might develop if cheap acetic acid were available is the production of calcium magnesium acetate (CMA) to be using as a non-corrosive highway and bridge de-icing agent.

Changes in Program

The initial work on the project was based on attempting to scale up a one-step process described in U.S. Patent 4,888,029 to use ethanol to remove sulfur from coal. Although some early results were very good, they could not be duplicated in later work and it was concluded that the process as described in the Shiley patent (U.S. Patent 4,888,029) could not be operated at larger scales even in the laboratory. No adequate explanation has been found for the inability to duplicate the early results in our laboratory autoclave.

An important breakthrough resulted from our development of a new laboratory process using copper as a combined catalyst and scavenger for the use of ethanol to remove sulfur from coal.

Documentation for the executive report is included in the full report.

MARKETING/COMMERCIALIZATION DISCUSSION

Market Potential

The economic merit of 90% removal of sulfur from coal is that the product from most coals would meet the EPA requirement of not more than 1.2 pounds of SO_2 per million Btu of fuel burned. This would permit the continued operation of smaller or older boilers without the installation of expensive wet scrubbers. Installation space, capital and operating costs, and waste sludge disposal costs all would be eliminated. There are several potential markets for the product coal:

- direct delivery of the dry, pulverized low-sulfur coal to a power plant, possibly by an over-the-fence operation.
- shipment of dry pulverized coal, a coal slurry or coal briquettes from a central processing plant located at a mine.
- conversion to a lower ash coal slurry by oil agglomeration.

Until we know the results from larger scale experiments, it is not possible to estimate potential tonnages.

Comparison with competing technologies

There are many review articles in the literature on the chemical cleaning of coal. CHEMICAL ENGINEERING [1] presented a table which listed 13 different methods at various stages of development. Tsai [2] described the reactions of organic sulfur compounds, such as those found in coal, with acids and bases and described several proprietary methods such as the KVB process and the GE microwave process. Even the more recent review articles have not included the ethanol process.

Although several chemical processes for the removal of sulfur from coal have been proposed and some have developed through the pilot plant scale, none has been put into commercial production. These processes have ranged from solvent refined coal to microbial desulfurization, including the TRW gravimelt process, the Battelle Hydrothermal process, the Kennecott Copper Ledgemont process, the IGT Hydrodesulfurization process, the Hazen iron pentacarbonyl process, the Atlantic Research microbial removal of organic sulfur from coal, the General Electric microwave process and others. Among the problems associated with these different processes have been loss of heating value of the coal, corrosive reaction conditions, long reaction times, high temperatures and pressures, waste disposal problems and the inability to market the treated coal. [3].[1]

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[1]**Berry, R.I.,**"Guide to Coal-cleaning Methods",Chemical Engineering,Jan.,pp.47-49 (1981).
[2]**Tsai, S.C.,**"Fundamentals of Coal Beneficiation and Utilization",Coal Science and Technology 2, Elsevier, New York, pp 259 and 362-4 (1982).
[3]**Merritt, P.C.,**"Advanced Coal Cleaning Processes Sought for Superclean Coal",Coal Age,June,pp.94-101 (1986).

The potential importance of the proposed research in providing practical solutions to the problems affecting the use of Ohio coal is very great. Most other proposed processes for the removal of sulfur from coal, regardless of the cost, have been limited in their technical success in removing organic sulfur from coal. Several are able to remove the pyritic sulfur, others can remove pyritic sulfur and part of the organic sulfur but very few can remove both the pyritic and organic sulfur. Those that can remove both have been based on the use of acids, bases or salts at high temperature and corrosive conditions, long reaction times, serious waste disposal problems for the by-products from the reaction and/or loss of heating value of the coal. Successful development of the process to use ethanol for the removal of sulfur from coal would overcome the disadvantages of previous processes.

The economic and commercial feasibility of any process which may eventually result from this research will depend in part on the enforcement of the recent acid rain legislation, the ability of utilities and industry to switch to alternate supplies of low sulfur coal, the price and uninterrupted supply of natural gas or fuel oil, and the speed with which the process can be developed. Even if the process cannot be put into commercial production in time to avoid a significant further reduction in the use of high-sulfur Ohio coal, there will be continuing efforts to use our plentiful coal reserves in an environmentally acceptable manner. This can best be done by removing the sulfur from the coal before combustion but it must be realized and accepted that there will be a significant increase in the cost of producing clean coal.

Cost of clean coal per million Btu should be compared to the cost of fuel oil, to the cost of high sulfur coal plus the capital and operating cost of a scrubber, or to the cost of low-sulfur coal plus shipping costs to deliver it to the Ohio valley users rather than to compare it with the present delivered cost of non-compliance coals.

Next Steps

The project is being continued with funding from other sources. The technical work will consist of developing the process on a laboratory scale and scaling up the operation to one to ten pound batches to get design and operating data for a pilot plant. Steps to commercialization will require the construction and operation of a demonstration plant to operate at 10 tons per hour followed by a commercial plant to operate at 100 or more tons per hour.

Budget removed.
ds

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APPENDIX I

COMPLETE ANALYSES OF FIVE OHIO COALS

SAMPLE Identification	OHIO COAL NUMBER	DATE	STATUS	Btu/lb. Modern Chemical Lab.	% ASH Modern Chemical Lab.	% ASH OHIO U. MAC 400 Analyzer	% SULFUR Modern Chemical Lab.	% SULFUR OHIO U. LECO SC-3 Analyzer	%VOLATILE OHIO U. MAC 400 Analyzer	% FIXED CARBON MAC-400 Analyzer Dry	% MOISTURE OHIO U. MAC 400 Analyzer	%MOISTURE Modern Chemical Lab.	AUTOCLAV TEMP. DEG. C.
Reference PSOC-1518	6	4/23/91	RAW	13,678	10.44	9.47	4.65*	3.51	36.26	53.8	.99	3.97	
Penn.Stat	6	2/14/92	RAW	12,470	9.56		3.87	3.6				4.01	
"	6	6/28/91	TREATED	13,531	4.69		.8	.75				1.81	450
"	6	8/7/91	"	10,469	8.29		1.12	1.07				6.2	320
TASK II	4A	10/24/91	RAW	11,127	20.09	19.6	3.93	3.37	35.06	454.08	2.73	3.13	
SAMPLE	"	10/25/91	TREATED	11,602	17.14		.91	1.17				2.92	320
"	6	10/30/91	RAW	13,340	5.37	5.32	2.38	2.66	38.2	56.48	4.92	4.75	
"	6	10/31/91	TREATED	10,643	15.8		.94	1.12				2.43	320
"	8	10/22/91	RAW	12,281	11.72	11.69	3.74	3.84	35.37	52.94	2.13	1.79	
"	8	10/23/91	TREATED	12,379	16.07		1.01	1.19				3.55	320
"	8	11/06/91	TREATED	10,369	16.8		.8	.96				2.57	420
"	9	10/20/91	RAW	12,748	11.31	11.31	2.69	3.16	36.08	52.65	2.68	2.55	
"	9	10/29/91	TREATED	9,981*	18.54		.85	1.16				3.3	320
"	11	11/01/91	RAW	12,389	13.19	13.02	2.7	3.77	33.5	53.48	2.29	2.15	
"	11	11/04/91	TREATED	9,110*	19.4		.82	1.13				2.32	320

* Low values probably due to small sample size and/or coarse particles.

APPENDIX II

TABULATION OF RESULTS OF ALL EXPERIMENTS DURING OCDO CO-SPONSORSHIP

3/21/92 ALL RUNS TO 2/25/93 TABULATION OF ETHANOL RUNS IN AUTOCLAVE AT OHIO UNIVERSITY

RUN NUMBER	DATE	APPARENT % S REMOVED	% S in PRODUCT	REAL % S REMOVED	% S IN RAW COAL	COAL OHIO #6	MESH SIZE	ACTIVATOR	CARRIER GAS	RATE ml/min	TEMP C	P p
106	10/1/91	17.9	3.06		3.73	PSOC1518	-200	NONE	N2	30	420	
107	10/3/91					PSOC1518	-200		N2	30		
108	10/11/91	69.2	1.15		3.73	PSOC1518	-200	1.5% 02	N2	30	420	
109	10/15/91	59.8	1.5		3.73	PSOC1518	-200	1.5% 02	N2	30	320	
110	10/17/91	33	2.5		3.73	PSOC1518	-200	NONE	N2	30	420	
111	10-21-91	76.4	.88		3.73	PSOC1518	-200	1.5% 02	N2	30	420	
112	10-23-91	67.7	1..19		3.68	NO. 8	-200	1.5% 02	N2	30	320	
113	10-25-91	65.3	1.17		3.37	NO.4A	-200	1.5% 02	N2	30	325	
114	10-29-91	63.3	1.16		3.16	NO. 9	-200	1.5% 02	N2	30	320	
115	10/31/91	57.9	1.12		2.66	OHIO NO.6	-200	1.5% 02	N2	30	320	
116	11/4/91	70	1.13		3.77	No.11	-200	1.5% 02	N2	30	320	
117	11/ 6 91	73.2	.961		3.59	No. 8	-200	1.5% 02	N2	30	420	
118	11/15/91	54	1.69		3.68	No. 8	-200	1.5% 02	N2	30	425	
119	11/20/91	18.8	3.45		4.25	PSOC1518	-200	1.5% 02	N2	30	420	
120	11/26/91	18.8	3.45		4.25	PSOC1518	-200	1.5% 02	N2	30	425	
121	12/3/91	11.6	3.82		4.6	PSOC1518	-200	1.5% 02	N2	30	320	
122	12/ 5/91	18.6	3.45		4.24	PSOC1518	-200	NONE	N2	30	420	
123	12/ 9/91	19.6	3.43		4.27	PSOC1518	-200	0.5% NO	N2	30	420	
124	12/13/91	1.2	3.23		3.27	PSOC1518	-200	0.5% NO	N2	30	420	
125	12/18/91	5.14	3.32		3.5	PSOC1518	-200	0.5% NO	N2	30	410	
126	12/23/91	6.3	3.28		3.5	PSOC1518	-200	1.5% 02	N2	30	430	
127	1/15/92	17	3.53		4.27	PSOC1518	-200	0.5% NO	N2	30	320	
128	1/20/92	13	3.68		4.23	PSOC1518	-200	0.5% NO	N2	30	320	
129	1/22/92	12.7	3.64		4.16	PSOC1518	-200	0.5% NO	N2	30	320	
130	2/11/92	26.4	3.06		4.38	PSOC1518	-100	0.52% NO	HE	30	420	
131	2/ 6/92	27.6	3.27		3.73	PSOC1518	-100	0.52% NO	HE	30	420	
132	2/10/92	29.3	2.74	45.9	3.89	PSOC1518	-100	0.52% NO	HE	30	420	
133	2/12/92	32.4	2.63	45.7	3.89	PSOC1518	-100	0.52% NO	HE	30	420	
134	2/17/92	39.4	2.18	53.3	3.6	PSOC1519	-100	0.52% NO	HE	10	420	
135	2/19/92	32	2.45	46.7	3.6	ILL NO.6	-100	0.52% NO	HE	50	420	
136	2/24/92	30.4	2.98	43.5	4.28	ILL NO.6	-100	0.52% NO	HE	40	420	
137	2/28/92	32.7	2.94	40	4.35	ILL NO.6	-100	0.52% NO	HE	10	420	
138	3/ 3/92	24.6	2.83	39.1	3.64	PSOC1518	-100	NONE	N2	30	420	
139	3/ 4/92	19	2.95	37.1	3.64	PSOC1518	-100	0.5% NO	HE	30	420	
140	3/ 5/92	28	2.67	42.8	3.74	PSOC1518	-100	NONE	N2	30	420	
141	3/ 9/92	31.9	2.45	48.3	3.6	PSOC1518	-100	NONE	N2	30	420	

IVERSITY

E in	TEMP C	PRESS psig	ml ETOH	EXCESS ETOH(X)	ETHANOL RATE	HOURS IN AUTOCLAVE	RAW COAL WEIGHT	GMS.COAL RECOVERY	SAMPLE HOLDER	BEAD BLAST	OPERATOR NUMBER		L Y	SAMPLE HOLDER	BEAD BLAST	OPERATOR NUMBER	NOTES (*)
0	420	50	8.8	13	2.5ml/m	6.5	10	8.8	(*14)	YES	(*5)	BLANK		(*14)	YES	(*5)	BLANK - NO ACTIVATOR
0		50	0	0	0		0				(*5)	ABOR				(*5)	ABORTED - ETHANOL PUMP FAILURE
0	420	50	8.7	13	2.5ml/m	6.5	10	9.24	(*13)	YES	(*5)	STAIN	1	(*13)	YES	(*5)	STAINLESS CUP W/COPPER SCREEN & BLASTING
0	320	50	8.8	13	2.5ml/m	5.5	10.1	9.36	(*13)	YES	(*5)	"	5	(*13)	YES	(*5)	"
0	420	50	8.7	13	2.5ml/m	5.5	10.1	9.23	(*13)	YES	(*5)	" -	3	(*13)	YES	(*5)	" -BLANK - NO ACTIVATOR
0	420	50	8.7	13	2.5ml/m	5.5	10.1	9.14	(*2)	YES	(*5)	OLD	4	(*2)	YES	(*5)	OLD CUP W/STAINLESS SCREEN
0	320	50	8.8	13	2.5ml/m	5.5	10	9.05	(*2) ?	?	(*5)	FIVE	5	(*2) ?	?	(*5)	FIVE OHIO COALS
0	325	50	8.7	14	2.5ml/m	5.5	10	9.64	(*2) ?	?	(*5)	"	4	(*2) ?	?	(*5)	"
0	320	50	8.7	15	2.5ml/m	6.5	9.96	8.96	(*2)	YES	(*5)	"	5	(*2)	YES	(*5)	"
0	320	50	8.8	18	2.5ml/m	6	10	8.56	(*2)	YES	(*5)	FIVE	5	(*2)	YES	(*5)	FIVE OHIO COALS
0	320	50	8.9	13	2.5ml/m	6	10	9.41	(*2)	YES	(*5)	"	1	(*2)	YES	(*5)	"
0	420	50	8.7	13	2.5ml/m	5.5	10	8.32	(*2)	YES	(*5)	No.8	2	(*2)	YES	(*5)	No.8 at hugher temp.
0	425	50	8.6	13	2.5ml/m	5	10	7.51	(*15)	NO	(*5)	GLASS	1	(*15)	NO	(*5)	GLASS CUP,FILTER,TUBING AND BEAKER
0	420	50	10	13	2.5ml/m	6	10	7.51	(*15)	NO	(*6)	REPE	1	(*15)	NO	(*6)	REPEAT W/ NO.6- PSOC 1518
0	425	50	6.5	9	2.5ml/m	6	10	7.75	(*15)	NO	(*6)	REPE	5	(*15)	NO	(*6)	REPEAT RUN
0	320	50	9.2	11	2.5ml/m	6	10	9.09	(*15)	NO	(*16)	REPE	9	(*15)	NO	(*16)	REPEAT RUN AT 320 C.
0	420	50	10	13	2.5ml/m	6	10	7.85	(*15)	NO	(*16)	BLAN	5	(*15)	NO	(*16)	BLANK - NO ACTIVATOR
0	420	50	10	13	2.5ml/m	6	10	7.83	(*15)	NO	(*16)	NEW TA	3	(*15)	NO	(*16)	NEW TANK OF 0.5% NO IN NITROGEN
0	420	50	10	17	2.5ml/m	5.5	10	6.82	(*15)	YES	(*16)	AUOTCL	2	(*15)	YES	(*16)	AUOTCLAVE CHARGED 12/4/91, RUN MADE 12/13/91
0	410	50	10	16	2.5ml/m	5	10	7.73	(*15)	YES	(*16)	REPEA	3	(*15)	YES	(*16)	REPEAT OF 12/13/91
0	430	50	11.	17	2.5ml/m	5.5	10	6.77	(*15)	YES	(*16)	CHECK	7	(*15)	YES	(*16)	CHECK ON EQUIPMENT W/ 1.5% O2 - NO REMOVAL
0	320	50	6	8	2.5ml/m	6	10	8.7	(*1)	YES	(*16)	CHECK		(*1)	YES	(*16)	CHECK ON EQUIPMENT
0	320	50	6	8	2.5ML/M	6.5	10	8.46	(*1)	YES	(*16)	CHECK	6	(*1)	YES	(*16)	CHECK ON EQUIPMENT
0	320	50	6	8	2.5ML/M	6	10	8.7	(*2)	NO	(*16)	CHECK		(*2)	NO	(*16)	CHECK EQUIPMEMT
30	420	50	6	8	2.5ML/M	7	10	7.37	(*2)	YES	(*17)	NEW BA	7	(*2)	YES	(*17)	NEW BAG PSOC1518. NEW TANK HE + 0.52% NO, ANALYZE
30	420	50	6	9	2.5ML/M	7	10	7.3	(*2)	NO	(*17)	(*2) C	3	(*2)	NO	(*17)	(*2) COPPER CUP WITH SS SCREEN
30	420	50	13	19	1.0ML/M	5	10	7.86	(*2)	YES	(*17)	(*2) C	36	(*2)	YES	(*17)	(*2) COPPEWR CUP WITH NEW SS SCREEN
30	420	50	14	20	1.0ML/M	5.5	10	8.07	(*2)	NO	(*17)	(*2) C	07	(*2)	NO	(*17)	(*2) COPPER CUP WITH SS SCREEN + COPPER SCREEN
10	420	50	13	20	0.5ML/M	5.5	10	7.77	(*2)	YES	(*17)	(*2) C	77	(*2)	YES	(*17)	(*2) COPPER CUP WITH SS SCREEN + COPPER SCREEN, CU
50	420	50	56	14	1.6ML/M	8.5	60	47	(*2)	YES	(*17)	(*2) C		(*2)	YES	(*17)	(*2) COPPER CUP WITH SS SCREEN + COPPER SCREEN, CU
40	420	50	20	13	1+ML/M	11	20	17.2	(*2)	NO	(*17)	CHECK	2	(*2)	NO	(*17)	CHECK VALVE REPLACED
10	420	50	20	13	0.5ML/M	8	20	17.5	(*2)	YES	(*17)	NEW CH	5	(*2)	YES	(*17)	NEW CHECK VALVE
30	420	50	NO	0	NONE	3.5	10	7.78	(*2)	NO	(*17)	BLANK	78	(*2)	NO	(*17)	BLANK RUN
30	420	50	NO	0	NONE	4	10	7.76	(*13)	YES	(*17)	STEEL	76	(*13)	YES	(*17)	STEEL CUP WITH SS SCREEN
30	420	50	7	10	1ML/M	4	10	8.07	(*13)	NO	(*17)	NO ACT	07	(*13)	NO	(*17)	NO ACTIVATOR
30	420	50	7	11	1ML/M	4	10	7.6	(*2)	NO	(*17)	COPPER	6	(*2)	NO	(*17)	COPPER CUP + SS SCREEN + COPPER SCREEN

RUN NUMBER	DATE	APPARENT % S REMOVED	% S in PRODUCT	REAL % S REMOVED	% S IN RAW COAL	COAL OHIO #6	MESH SIZE	ACTIVATOR	CARRIER GAS	RATE ml/min	TEMP C	
142	3/10/92	27.3	2.64	43	3.63	PSOC1518	-100	0.52% NO	HE	30	420	
143	3/12/92	35.2	2.36	49.7	3.64	PSOC1518	-100	0.52% NO	HE	30	420	
144	3/16/92	38.5	2.24	54.4	3.64	PSOC1518	-100	0.52% NO	HE	50	420	1
145	3/18/92	39	2.24	53.3	3.62	PSOC1518	-100	1.5% O2	N2	30	420	
146	3/20/92	36.7	2.29	48.9	3.62	PSOC1518	-100	0.52% NO	HE	30	420	
147	3/24/92	32.8	2.44	48.2	3.63	PSOC1518	-100	0.52% NO	HE	20-40	420	
148	3/26/92	32	2.47	47.7	3.63	PSOC1518	-100	NONE	N2	30	420	
149	4/ 2/92	27.4	2.7	41.9	3.72	PSOC1518	-100	0.52% NO	HE	30+/-	420	
150	4/ 6/92	36.2	2.33	53.4	3.65	PSOC1518	-100	0.5% NO	N2	-10	485	
151	4/ 8/92	34.5	2.39	52.2	3.66	PSOC1518	-100	0.52% NO	HE	30	420-490	
152	4/10/92	40.3	2.11	54.7	3.65	PSOC1518	-100	0.52% NO	HE	20 (*21)	420	
153	4/14/92	31.9	2.48	47.5	3.64	PSOC1518	-100	NONE	N2	20	420	
154	4/20/92	29.5	2.94	44.4	4.17	ILL.NO.6	-100	0.52% NO	HE	-450	420	
155	4/22/92	37.5	2.18	54.2	3.49	PSOC1518	-100	NONE	N2	-180	420	
156	4/29/92	33.6	2.29	52.5	3.45	PSOC1518	-100	0.5% NO	He	50*	435	
157	5/14/92	12.1	3.7	25.9	4.28	Ill.No.6	-80	NONE	N2	30	385	
158	5/19/92	20.6	3.4	32.9	4.28	Ill.No.6	-80	NONE	N2	40	430	
159	5/21/92	19.1	3.4	32.4	4.2	Ill.No.6	-80	0.5% NO	He	70	430	
							-80					
160	5/17/92	33.1	1.9	47.3	3.57	PSOC1518	-80	0.5% NO	He	60	440	
161	5/29/92	29.3	2.5	48.6	3.48	PSOC1518	-80	0.5% NO	He	40	420	
162	6/ 3/92	35.4	3.5	50.1	3.47	PSOC1518	-80	0.5% NO	He	100	380	
							-80					
163	6/10/92	46.6	1.72	62.7	3.22	PSOC1518	-80	0.5% NO	He	60-20	480	
164	6/22/92	46.9	1.34	61.4	3.39	PSOC1518	-80	0.5% NO	He	100	480	30
165	6/23/92	44.2	1.94	60.9	3.48	PSOC1518	-80	0.5% NO	He	80	480	
							-80					
166	6/25/92	47.6	1.84	62.4	3.51	PSOC1518	-80	0.5% NO	He	10-20	480	
167	7/ 1/92	47.5	1.87	80.1	3.56	PSOC1518	-80	0.5% NO	He	80	480	
168	7/ 7/92	48.7	1.79	61.9	3.49	PSOC1518	-80	0.5% NO	He	40-80	480	
							-80					
169	7/ 9/92	44.1	2	58.4	3.58	PSOC1518	-80	0.5% NO	He	90	465	
170	7/13/92	44.6	1.96	57.9	3.54	PSOC1518	-80	0.5% NO	He	30-80	475	70
171	7/15/92	37.7	2.1	53.7	3.37	PSOC1518	-80	0.5% NO	He	50-100	475	70
							-80	0.5% NO	He			
172	7/17/92	34.1	2.2	51.9	3.37	PSOC1518	-80	0.5% NO	He	20-90	475	60
173	7/20/92	45.1	1.85	59.6	3.37	PSOC1518	-80	0.5% NO	He	60	480	
174	7/22/92	45.7	1.83	59.9	3.37	PSOC1518	-80	0.5% NO	He	30-60	480	
								0.5% NO	He			
175	7/23/92	43	1.92	57.9	3.37	PSOC1518	-100	0.5% NO	He	30-60	475	
176	7/24/92	43.3	1.91	57.3	3.37	PSOC1518	-100	0.5% NO	He	30-80	480	
177	7/29/92	36.8	2.13	53.7	3.37	PSOC1518	-100	0.5% NO	He	30-80	470	70

ATE /min	TEMP C	PRESS psig	ml ETOH	EXCESS ETOH(X)	ETHANOL RATE	HOURS IN AUTOCLAVE	WEIGHT RAW COAL	GMS.COAL RECOVERY	SAMPLE HOLDER	BEAD BLAST	OPERATOR NUMBER	
30	420	50	7	11	1ML/M	4	10	7.85	(*13)	NO	(*17)	STEE
30	420	50	7	11	1ML/M	4	10	7.96	(*2)	YES	(*17)	COPR
50	420	100+	30	46	50ML/M	7	10	7.42	(*2)	YES	(*17)	COPR
30	420	100	62	95	0.5ML/M	6	10	7.65	(*2)	YES	(*17)	COPR
30	420	35	15	23	0.3ML/M	1.75	10	8	(*2)	YES	(*17)	COPR
-40	420	35	9	14	0.5ML/M	2	10	7.72	(*13)	YES	(*17)	SS C
30	420	50	8	12	1.5ML/M	2.3	10	7.69	(*2)	YES	(*17)	COPR
0+/-	420	35	6	9	.5ML/M	4.2	10	8	(*20)	NO	(*17)	GLAS
-10	485	35	8	12	0.5ML/M	5.3	10	7.3	(*18)	YES	(*17)	COPR
30	420-490	35	12	18	1ML/M	3.5	10	7.3	(*12)	YES	(*17)	ETHA
(*21)	420	60-80	10	15	0.5ML/M	3.4	10	7.6	(*19)	YES	(*17)	FRES
20	420	35	10	15	0.5ML/M	1	10	7.7	(*19)	YES	(*17)	FRES
-450	420	45	6	8	1ML/M	3.5	10	7.89	(*19)	YES	(*17)	FRES
-180	420	48	10	16	.3-1ML/M	2.5	10	7.35	(*18)	YES	(*17)	COPR
50*	435	60		7	1ml/min	1.5	5	3.6	(*14)	NO	(*17)	2 HR
				RATIO								
30	385	75		0.6ML/GM	1ml/min	1.0	10	8.5	(*13)	YES	(*17)	STAI
40	430	85		0.6ml/gm	1ml/min	2.0	10	8.4	(*13)	NO	(*17)	STAI
70	430	80		0.6ml/gm	1ml/min	1.2	10	8.3	(*13)	NO	(*17)	STAI
60	440	75		0.6ml/gm	1-2ml/min	3.0	10	8.2	(*13)	NO	(*17)	FRES
40	420	90		11.0ml/gm	0.5ml/min	2.0	10	7.3	(*13)	NO	(*17)	REC
00	380	65		1.1ml/gm	0.5ml/min	5.0	5	3.86	(*13)	NO	(*17)	PREC
-20	480	100	6.3	1.3ml/gm	0.5ml/min	3.5	5	3.5	(*14)	NO	(*17)	MONE
0	480	30-10	8	1.6ml/gm	0.5ml/min	4	5	3.63	(*12)	NO	(*17)	PRES
	480	100	6	1.2ml/gm	0.5ml/min	3.5	5	3.5	(*12)	NO	(*17)	PRES
-20	480	100	6	1.2ml/gm	0.5ml/min	4	5	3.6	(*12)	NO	(*17)	CU
80	480	100	6	1.2ml/gm	1ml/min	5	5	3.8	(*12)	NO	(*17)	CU
-80	480	85	6	1.2ml/gm	1ml/min	2.5	5	3.43	(*12)	NO	(*17)	CU
90	465	90	6	1.2ml/gm	1ml/min	2.2	5	3.7	(*19)	YES	(*17)	NEW
-80	475	70-90	6	1.2ml/gm	1ml/min	3	5	3.8	(*19)	YES	(*17)	CU
-100	475	70-90	6	1.2ml/gm	1/ml/min	4	5	3.7	(*21)	NO	(*17)	BRA
-90	475	60-90	6	1.2ml/gm	1ml/min	3	5	3.65	(*14)	NO	(*17)	MONI
60	480	60	8	1.6ml/gm	1ml/min	3	5	3.67	(*21)	YES?	(*17)	BRA
-60	480	80	9.5	1.9ml/gm	1ml/min	4.5	5	3.7	(*21)	NO	(*17)	BRA
-60	475	70	9.5	1.9ml/gm	1ml/min	4	5	3.69	(*21)	NO	(*17)	BRA
-80	480	80	9.5	1.9ml/gm	1ml/min	3.5	5	3.77	(*21)	NO	(*17)	BRA
-80	470	70-90	9.5	1.9ml/gm	0.5 ml/min	4.5	5	3.67	(*14)	NO	(*17)	MONI

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AL    SAMPLE     BEAD   OPERATOR                  NOTES (*)
RY    HOLDER     BLAST   NUMBER
35     (*13)       NO     (*17) STEEL CUP WITH SS SCREEN
96      (*2)      YES     (*17) COPPER CUP WITH POROUS SS PLATE + COPPER SCREEN
42      (*2)      YES     (*17) COPPER CUP WITH POROUS SS PLATE

65      (*2)      YES     (*17) COPPER CUP WITH POROUS SS PLATE
        (*2)      YES     (*17) COPPER CUP WITH POROUS SS PLATE
72     (*13)      YES     (*17) SS CUP WITH ?

69      (*2)      YES     (*17) COPPER CUP WITH ? SCREEN
       (*20)       NO     (*17) GLASS CUP IN SS RETAINER RING.
       (*18)      YES     (*17) COPPER CUP #5

       (*12)      YES     (*17) ETHANOL INJECTED AT DIFFERENT TEMPERATURES
       (*19)      YES     (*17) FRESHLY GROUND COAL.. GAS DELIVEDED BY PUMPING.
       (*19)      YES     (*17) FRESHLY GROUND COAL. GAS DELIVERED BY PUMPING WITH

89     (*19)      YES     (*17) FRESHLY GROUND ILL.COAL.NO GAS PUMP.
85     (*18)      YES     (*17) COPPER TURNINGS AND COPPER SCREEN ON SS SCREEN
       (*14)       NO     (*17) 2 HRS CONDITIONING W/50 ML/M He+0.5% NO

       (*13)      YES     (*17) STAINLESS STEEL CUP AND SCREEN
       (*13)       NO     (*17) STAINLESS STEEL CUP AND SCREEN
       (*13)       NO     (*17) STAINLESS STEEL CUP AND SCREEN

       (*13)       NO     (*17) FRESHLY GROUND COAL,PRECONDITIONED SS CUP & SCREEN
       (*13)       NO     (*17) PRECONDITIONED STAINLESS CUP AND SCREEN
86     (*13)       NO     (*17) PRECONDITIONED SS CUP & SCREEN, SEQUENTIAL ADDITIO

      (*14)        NO    (*17)  MONEL CUP PRECONDITIONED
63    (*12)       NO     (*17)  PRESULFIDED CU CUP AND PRECONDITIONING
      (*12)       NO     (*17)  PRESULFIDED CU CUP BUT NO PRECONDITIONING

      (*12)       NO     (*17)  CU CUP, PRECONDITIONED
      (*12)       NO     (*17)  CU CUP, ETHANOL BEFORE AND AFTER 0.5% NO
13    (*12)       NO     (*17)  CU CUP, PRECONDITIONED, QUICK HEATING,3 PORTIONS E

      (*19)      YES     (*17)  NEW CU CUP & SCREEN,BLAASTED,PRECONDITIONED 1 HR @
      (*19)      YES     (*17)  CU CUP ARTIFICIALLY SULFIDED WITH H2S
      (*21)       NO     (*17)  BRASS CUP SULFIDED W/H2S,CONDITIONED W/He+0.5% NO

15    (*14)       NO     (*17)  MONEL CUP,SULFIDED W/H2S,PRECONDITIONED W/He + 0.5
17    (*21)      YES?    (*17)  BRASS CUP,NATURALLY SULFIDED,NO PRECONDITIONING
      (*21)       NO     (*17)  BRASS CUP, NATURALLY SULFIDED,PRECONDITIONED

19    (*21)       NO     (*17)  BRASS CUP, POST CONDITIONED,3 PORTIONS ETHANOL
17    (*21)       NO     (*17)  BRASS CUP, POST CONDITIONED"BRASS CUP,POST CONDITI
17    (*14)       NO     (*17)  MONEL CUP,SULFIDED W/H2S,PRECONDITIONED
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RUN NUMBER	DATE	APPARENT % S REMOVED	% S in PRODUCT	REAL % S REMOVED	% S IN RAW COAL	COAL OHIO #6	MESH SIZE	ACTIVATOR	CARRIER GAS	RATE ml/min	TEMP C	
178	8/ 4/92	32.6	2.38	49.6	3.53	PSOC1518	-60	1.5% O2	He	30	450	
179	8/ 6/92	54.3	1.64	65.3	3.37	PSOC1518	-60	0.5% NO	He	30-70	475	
180	8/10/92	59.9	1.35	70	3.37	PSOC1518	-100	0.5% NO	He	30-100	465	6
181	8/11/92	36.2	2.44	52.4	3.82	PSOC1518	-100	0.5% NO	He	30	480	
182	8/13/92	36.8	2.3	52.8	3.64	PSOC1518	-100	0.5% NO	He	30-60	480	
183	8/14/92	34.1	2.4	51.1	3.64	PSOC1518	-100	0.5% NO	He	30-70	480	
184	8/17/92	32.8	2.46	48.4	3.66	PSOC1518	-100	0.5% NO	He	30-100	475	6
185	8/19/92	66.8	1.27	75.1	3.83	?	-100	0.5% NO	He	30-90	480	
186	8/21/92	56.9	1.57	67.9	3.64	PSOC1518	-80	0.5% NO	He	40-80	480	5
187	8/26/92	53	1.65	63.3	3.51	PSOC1518	-100	0.5% NO	He	30-80	480	
188	8/28/92	49.2	1.82	62	3.58	PSOC1518	-100	0.5% NO	He	30-80	480	5
189	9/ 2/92	58.2	1.52	69.2	3.64	PSOC1518	-100	0.97% NO	He	30-80	470	
190	9/ 4/92	63.6	1.31	73.3	3.6	PSOC1518	-100	0.97% NO	He	30-80	480	6
191	9/ 9/92	63.7	1.35	72	3.72	PSOC1518	-100	0.97% NO	He	30-80	480	
192	9/10/92	26.1	1.98	41	2.68	PSOC1518	-100	0.97% NO	He	30-80	475	
193	9/25/92	42.6	2.3	60.3	4.01	OHIO 4A	-100	0.97% NO	He	30-80	480	
194	9/30/92	46.6	2.07	63.5	3.85	OHIO 4A	-20	0.97% NO	He	30-80	480	
195	10/ 2/92	22.4	3.08	46.3	3.97	OHIO 4A	-20	0.97% NO	He	70	480	
196	10/ 6/92											
197	10/ 8/92	36.7	2.38	57.7	3.76	OHIO 4A	-20	NONE	N2	30-60	480	
198	10/12/92	37.7	2.43	59.2	3.9	OHIO 4A	-20	0.97% NO	H2	20	480	
199	10/15/92	50	2.04	62.9	3.83	OHIO 4A	-100	0.97% NO	He	30	480	
200	10/20/92	58	1.69	69.6	3.72	OHIO 4A	-100	.97% NO	He	20	480	
201	10/22/92	50	1.86	62.2	3.72	OHIO 4A	-100	.97% NO	He	20	480	
202	10/24/92	73.1	.98	82.4	3.64	OHIO 4A	-100	0.97% NO	He	70	500	80
203	10/26/92											
204	10/28/92	67.6	.78	76.3	2.41	OHIO #11	-20	.97% NO	He	20	480	
205	10/30/92	67	.8	75.5	2.41	OHIO #11	-20	.97% NO	?	20	480	
206	12/ 3/92	74.2	.98	82.7	3.8	OHIO 4A	-100	0.97% NO	He	30	500	60
207	12/10/92	58.9	1.57	74.3	?	OHIO 4A	-100	0.97% NO	He	80	525	60
208	12/14/92	72.9	1.01	81.5	3.73	OHIO 4A	-100	0.97% NO	He	15-30	500	60
209	12/16/92	85.5	.55	90.4	3.73	OHIO 4A	-100	0.97% NO	He	?	525	65
210	12/18/92	72.6	1.02	81.45	3.72	OHIO 4A	-100	NONE	H2	30	525	30
211	1/ 6/93	73.6	.99	83.2	3.75	OHIO 4A	-100	0.97% NO	He	10-20	500	50
212	1/18/93	81.6	.71	87.9	3.86	OHIO 4A	-100	0.97% NO	He	30	500	50
213	1/20/93	77	.87	85	3.79	OHIO 4A	-100	0.97% NO	He	0-10	500	70

RATE ml/min	TEMP C	PRESS psig	ml ETOH	RATIO ETOH	ETHANOL RATE	ml WATER	HOURS IN AUTOCLAV	WEIGHT RAW COAL	GMS.COAL RECOVERY	SAMPLE HOLDER	GLASS BEAD BLAST	OPERATOR NUMBER	
30	450	75	7	1.4ml/gm	3.5ml/min		4	10	7.49	(*12)	YES	(*17)	TH
0-70	475	75	8	1.6ml/gm	1ml/min		4	5	3.58	(*12)	YES	(*17)	CL
0-100	465	60-85	10	2/ml/gm	1/ml/min		3	5	3.75	(*12)	NO	(*17)	CU
0	480	80	9	1.8ml/gm	1ml/min		3.5	5	3.75	(*14)	YES	(*17)	CL
0-60	480	75	9.5	1.9ml/gm	1ml/min		3	5	3.74	(*14)	NO	(*17)	MO
0-70	480	70	9	1.8ml/gm	1ml/min		2.5	5	3.7	(*14)	NO	(*17)	MO
0-100	475	60-80	9.5	1.9ml/gm	0.5ml/min		2.5	5	3.85	(*14)	NO	(*17)	MO
0-90	480	80	9	1.8ml/gm	0.5ml/min		4	5	3.75	(*12)	NO	(*17)	CU
0-80	480	55-80	9	1.8ml/gm	1ml/min		4	5	3.73	(*12)	NO	(*17)	CU
0-80	480	75	8	1.6ml/gm	1ml/min		5	5	3.93	(*12)	NO	(*17)	CU
0-80	480	50-80	7.5	1.5ml/gm	1ml/min		4	5	3.73	(*18)	NO	(*17)	CU
0-80	470	65	9.5	1.9ml/gm	1ml/min		3.5	5	3.7	(*18)	NO	(*17)	CU
0-80	480	60-80	9	1.8ml/gm	1ml/min		5	5	3.7	(*18)	NO	(*17)	CU
0-80	480	80	8.5	1.7ml/gm	1ml/min		5	5	3.85	(*18)	NO	(*17)	CU
0-80	475	75	9.5	1.9ml/gm	1ml/min		3.5	5?	3.98	(*18)	NO	(*17)	PS
0-80	480	80	9	1.8ml/gm	1ml/min		5	5	3.46	(*22)	NO	(*17)	NE
0-80	480	60	10	2ml/gm	1ml/min		5	5	3.43	(*22)	NO	(*17)	CU
70	480	60	N	NONE	0		3	5	3.46	(*22)	NO	(*17)	RE
										(*22)	NO		RU
0-60	480	60	10	2ml/gm	1ml/min		6.5	5	3.34	(*22)	NO	(*17)	RU
20	480	35	NO	NONE	NA		4.5	5	3.27	(*22)	YES	(*17)	HY
30	480	80	9.5	1.9ml/gm	1ml/min		5.5	5	3.51	(*22)	YES	(*17)	SU
20	480	70	13.	2.7ml/gm	1ml/min		4	5	3.6	(*22)	NO	(*16)	CU
20	480	65	13.	2.7ml/gm	.1ml.min		5.5	5	3.7	(*22)	NO	(*16)	CU
70	500	80-130	10	2ml/gm	.9ml/min	8	4	5	3.26	(*22)	NO	(*17)	SU
										(*22)			RE
20	480	80	13.	2.7ml/gm	1ml/min	0	4	5	?	(*22)	NO	(*16)	CU
20	480	80	13.	2.7ml/gm	1ml/min	0	6	5	3.7	(*22)	YES	(*16)	CU
30	500	60-145	5	1/ml/gm	.5ml/min	2.5	5	5	3.36	(*22)	NO	(*17)	ETH
80	525	60-125	6	1.2ml/gm	.5ml/min	2.5	4	5	3.31	(*22)	NO	(*17)	ETH
5-30	500	60-150	4	.8ml/gm	.5ml/min	8	5	5	3.43	(*22)	NO	(*17)	WAT
?	525	65-170	9	1.8ml/gm	.5ml/min	NONE	4	5	3.31	(*22)	NO	(*17)	ETH
30	525	30-120	NO	0	NA	?	4	5	3.47	(*22)	NO	(*17)	HYD
0-20	500	50-150	5	1ml/gm	1ml/min	5?	3.5	5	3.16	(*22)	NO	(*17)	ETH
30	500	50-200	5	1ml/gm	.8ml/min	5	3.5	5	3.27	(*22)	NO	(*17)	WAT
-10	500	70-250	5	1ml/gm	.5ml/min	4.5	3	5	3.3	(*22)	NO	(*17)	ETH

SAMPLE HOLDER	GLASS BEAD BLAST	OPERATOR NUMBER	NOTES (*)
(*12)	YES	(*17)	THOROUGH GLASS BEAD CLEANING OF ENTIRE AUTOCLAVE.
(*12)	YES	(*17)	CLEAN CU CUP TO GET NATURAL SULFIDIZATION FOR NEXT
(*12)	NO	(*17)	CU CUP, PRECONDITIONED, NATURALLY SULFIDED, OLD PS
(*14)	YES	(*17)	CLEAN MONEL CUP, NO PRECONDITIONING
(*14)	NO	(*17)	MONEL CUP, NATURALLY SULFIDED, PRECONDITIONED
(*14)	NO	(*17)	MONEL CUP, NO PRECONDITIONING ,3 PORTIONS ETHANOL
(*14)	NO	(*17)	MONEL CUP,SULFIDED, PRECONDITIONED 1.5 HR @ 4540 C
(*12)	NO	(*17)	CU CUP, PRECONDITIONED, NATURALLY SULFIDED
(*12)	NO	(*17)	CU CUP, PRECONDITIONED, NATURALLY SULFIDED, NEW PS
(*12)	NO	(*17)	CU CUP, CLEANED, AIR-OXIDIZED
(*18)	NO	(*17)	CU CUP #5,AIR OXIDIZED, NATURALLY SULDIDED
(*18)	NO	(*17)	CU CUP,ACTIVATED,ROASTING,REDUCTION,NOT SULFIDED
(*18)	NO	(*17)	CU CUP #5,PRECOMDITIONED, NATURALLY SULFIDED
(*18)	NO	(*17)	CU CUP #5,PRECONDITIONED
(*18)	NO	(*17)	PSOC1518 SAMPLE CONTAINED 1% CU AS CU2CO3
(*22)	NO	(*17)	NEW CU AND ACTIVATION,2HR AIR @ 380 C + 2HR H2 @ ?
(*22)	NO	(*17)	CU CUP SULFIDED & PRECONDITIONED
(*22)	NO	(*17)	REPEAT EXPERIMENT WITHOUT ETHANOL
(*22)	NO		RUN ABORTED
(*22)	NO	(*17)	RUN WITHOUT ACTIVATOR GAS, CU CUP PRECONDITIONED
(*22)	YES	(*17)	HYDROGEN REPLACED ETHANOL,ACTIVATION OF CU CUP,2HR
(*22)	YES	(*17)	SULFIDING THE CU CUP
(*22)	NO	(*16)	CU CUP ACTIVATED AND SULDIDED
(*22)	NO	(*16)	CU CUP PRECONDITIONED-ETOH PUMPED CONTINUOUSLY,2HR
(*22)	NO	(*17)	SUCCESSIVE ETHANOL - WATER TREATMENT
(*22)			REACTOR REGENERATION
(*22)	NO	(*16)	CU CUP REGENERATED W/AIR AND H2
(*22)	YES	(*16)	CU CUP CLEANED W/GLASS BEADS
(*22)	NO	(*17)	ETHANOL-WATER-ETHANOL INJECTION
(*22)	NO	(*17)	ETHANOL-WATER-ETHANOL,REACTOR CONDITIONED
(*22)	NO	(*17)	WATER-ETHANOL-WATER INJECTION,REACTOR CONDITIONED
(*22)	NO	(*17)	ETHANOL-ETHANOL INJECTION, REACTOR CONDITIONED
(*22)	NO	(*17)	HYDROGEN + WATER,REACTOR RECONDITIONED
(*22)	NO	(*17)	ETHANOL-WATER, NON-SULFIDED REACTOR
(*22)	NO	(*17)	WATER-ETHANOL, REACTOR CONDITIONED @ 500 C.
(*22)	NO	(*17)	ETHANOL-WATER, CONDITIONING 2HR @ 500 C.

RUN NUMBER	DATE	APPARENT % S REMOVED	% S in PRODUCT	REAL % S REMOVED	% S IN RAW COAL	COAL OHIO #6	MESH SIZE	ACTIVATOR	CARRIER GAS	RATE ml/min	TEMP C	PRESS psig	ml ETOH	RATIO ETOH	ETHANOL RATE	ml WATER	HOURS IN AUTOCLAV	WEIGHT RAW COAL	GMS.COAL RECOVERY	SAMPLE HOLDER	GLASS BEAD BLAST	OPERATOR NUMBER	NOTES (*)
214	1/28/93	64.9	1.36	78.3	3.87	OHIO 4A	-100	0.97% NO	He	30-50	500	50-420	NO	NA	1ml/min	3.8	3.5	5	3.1	(*22)	NO	(*17)	WATER + HYDROGEN GAS,REACTOR CONDITIONED
215	2/ 1/93	73.3	1.02	82.7	3.82	OHIO 4A	-100	0.97% NO	He	90-150	500	60-240	5	1/ml/gm	1ml/min	5	4	5	3.2	(*22)	NO	(*17)	WATER-ETHANOL,REACTOR CONDITIONED @ 550 C.
216	2/ 5/93	59.8	1.55	73.8	3.85	OHIO 4A	-100	0.97% NO	He	0-150	500	70-300	10	.5ml/gm	1ml/min	10	3.5	20	13.1	(*22)	NO	(*17)	WATER-ETHANOL, 20 GM COAL, REGENERATED REACTOR
217	2/ 9/93	20.6	5.17	28.7	6.51	PETR.COKE	-20	0.97% NO	He	0-150	560	70-170	10	1ml/gm	1ml/min	NONE	3	10	8.96	(*22)	NO	(*17)	PETROLEUM COKE WITH ETHANOL
218	2/13/93	44.2	2.17		3.89	OHIO 4A	-100	0.97% NO	He	50	490	60-230	12	1.2ml/gm	?	NONE	5	10	6.66	(*22)	NO	(*16)	RUN WITH ETHANOL ONLY
219	2/17/93	58.8	1.57	72.7	3.81	OHIO 4A	-100	0.97% NO	He	0-80	525	60-450	10	.5ml/gm	1ml/min	10	3.5	20	13.25	(*22)	YES	(*17)	WATER-ETHANOL,REACTOR REGENERATED
220	2/19/93	79.3	1.28		3.89	OHIO 4A	-100	0.97% NO	HE	60-150	500	60-160	12	0.6ml/gm	?	6	5.5	10	6.9	(*22)	NO	(*16)	WATER THEN ETHANOL
221	2/22/93	69.1	.5	76.6	1.62	KY COAL	-20	0.97% NO	He	0-150	525	60-290	6	.5ml/gm	1ml/min	6	2.5	10	7.57	(*19)	NO	(*17)	KY COAL, WATER-ETHANOL, REGENERATED REACTOR
222	2/24/93	64.2	2.32	69.3	6.48	PETR.COKE	-20	0.97% NO	He	0-150	660	330	10	1ml/gm	1ml/min	NONE	3	10	6.44	(*14)	NO	(*17)	PETROLEUM COKE WITH ETHANOL, SULFIDED
223	2/25/93	63.3	2.38	69	6.48	PETR.COKE	-20	0.97% NO	He	0-150	670	75-330	11	1.1ml/gm	1ml/mimn	NONE	3.5	10	6.75	(*22)	NO	(*17)	PETROLEUM COKE, CU CUP
224	2/27/93	71.1	1.11		3.84	OHIO 4A	-100	0.97% NO	He	60-150	500	60-250	0			12	5.5	10	6.56	(*22)	NO	(*16)	WATER ONLY
225	3/ 2/93	78.9	.79	86.9	3.75	OHIOI 4A	-100	0.97% NO	He	0-150	580	80-380	6	.6ml/gm	?	6	5	10	6.23	(*22)	NO	(*17)	ETHANOL THEN WATER
226	3/ 4/93	81.4	.81	86.7	4.35	Ill #6	-100	0.97% NO	He	0-150	550	60-345	6	.6ml/gm	?	6	4	10	7.2	(*22)	NO	(*17)	ETHANOL AND WATER WITH ILLINOIS COAL

(*1) COAL SAMPLE HOLDER =1/2 " x 3" dia.
brass cup w/ 325 mesh stainless screen
(*2) " = 4" X 3" dia. copper cup
w/ 325 mesh stainless screen.-CUP #1
(*3) " = ditto w/ furnace cement
to repoair damage.
(*4) " = 4" x 3" dia. copper cup
w/ 200 mesh stainless screen.-CUP #2
(*5) Operator was Dr. Pan
(*6) Operator was Dr. Savage
(*7) Samples collected top to bottom
(s = 0.48% to 0.29%). Ave. = 0.36%
(*8) H2S added to carrier gas.
(*9) Low sulfur treated coal charged to
autoclave.
(*10) Negative removal (resulfurization)
resulted from H2S in carrier gas.

(*11) N.D. sample holder, brass cup
below screen.
(*12) New copper cup from shop.-CUP #2
(*13) New stainless cup & screen -CUP #3
(*14) New monel cup from shop.-CUP #4
(*15) Glass cup w/ glass fiber filter and
beaker in bottom of autoclave
(*16) Operator was Naresh Kumar.
(*17) Operator was Dr. Lazarov.
(*18) NEW COPPER CUP FROM PHYSICS SHOP.-CUP #5
(*19) NEW COPPER CUP FROM PHYSICS SHOP.-CUP #6
(*20) GLASS CUP WITH SS RETAINER RING.
(*21) BRASS CUP FROM SHOP,-CUP #7
(*22) NEW CU EQUIPMENT W/CU GAS CHAMBER-CUP #8
resulted from H2S in carrier gas.

END

DATE
FILMED
5/13/94