EXTRACTION OF POTENTIAL POLLUTANTS
FROM OHIO COAL BY
SYNERGISTIC USE OF SUPERCRITICAL FLUIDS

Final Report
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I. EXECUTIVE SUMMARY

A novel clean coal process has been developed and its process feasibility has been demonstrated using a semi-batch extraction process unit. This process is based on the emerging separation technology called supercritical extraction. However, this specific process is different from all other supercritical extraction process, in that a mixture of physically and chemically outstanding fluids at supercritical conditions is used in order to attain process synergism as well as highly selective extraction efficiencies.

The process was found to be effective in selectively cleaning organic sulfur from Ohio coals. The optimal case involved a mixture of CO_2 , H_2O , and CH_3OH and the removal of organic sulfur typically ranged from 35%-55% for Ohio coals. Thus, most Ohio coals containing less than 2 wt% of organic sulfur can be cleaned to less than 1 wt% of organic sulfur. Once combined with the pyrite and mineral matter removal by gravitational separation (a well defined technology), the resultant coals would have approximately 20%-30% increased heating values per pound and their SO_2 emission when combusted would be down to 1.2-1.5 pounds per million BTU. Thus, Ohio coals could meet the requirements of compliance coal by this precleaning route.

Even though the process economic study has not been fully conducted for this novel technology, the estimated cleaning cost including the pyrite removal step is in the range of 25 to 45 dollars per ton. Since the cost of solvents involved is relatively inexpensive and their recycle is rather easily facilitated, the most important cost factor involves the operation at high pressures.

The anticipated next step for the process development involves: (a) design of a 10 kg/hr continuous pilot plant, (b) research on solid processing at high pressure, and (c) secondary treatment of recovered organic sulfur waste. For this research, Electric Power Research Institute (EPRI), Midwest Ore Processing Co. (MOPC), Ohio Edison, and Centerior Energy have shown some interest. The University of Akron is also substantially committed to this project and has provided great support.

II. INTRODUCTION

(II.1) Problem Statement and Background

The United States has approximately forty percent of the world's coal reserves. Midwestern states, including the state of Ohio, have a substantial amount of these coal deposits. However, coals in these states contain large amounts of sulfur, typically ranging from three to seven percent by mass. Combustion of these coals presents a serious environmental problem, which is most frequently publicized as "acid rain" or the " SO_x/NO_x problem".

Sulfur in coal can be classified as organic and inorganic sulfur. Inorganic sulfur can be further classified as pyritic and sulfatic sulfur. Pyritic sulfur (FeS_2) accounts for approximately half of the total sulfur content, and can be rather easily cleaned via physical cleaning methods which utilizes gravitational separation techniques. Sulfatic sulfur in coal, especially in fresh, nonoxidized coal, accounts for only a very small percentage of the total sulfur and its removal is not of major concern.

The removal of organic sulfur has long been a problem, and to date there has not been an efficient, commercially viable process for the selective removal of organic sulfur. If the philosophy of pre-combustion cleaning of coal is adopted, then the cost-effective removal of organic sulfur becomes crucially important.

Compounding the problem is the fact that the chemistry of organosulfur in coal is very poorly understood. Historically, people have studied this subject using model compounds including a species like dibenzothiophene. However, practically no general agreement among the researchers has been attained in regard to the compositions of organosulfur compounds in coal. Even the analytical method for forms of sulfur by ASTM Standards (ASTM D-2492) determines the content of organic sulfur by taking differences between the total and the inorganic sulfur. The determination procedure is not only tedious and lengthy, but also prone to error. Therefore, better understanding of the chemistry of organic sulfur in coal is essential for successful development of coal cleaning processes.

This project was proposed in order to develop a novel coal cleaning process using an emerging separation technology known as "supercritical extraction" as well as to develop a better understanding of the critical issues of coal cleaning, extraction processes, and forms of sulfur.

(II.2) Project Objectives

The principal objective was to develop a novel process that selectively removed organosulfur from high-sulfur Midwestern coals by use of an emerging process separation known as "supercritical extraction".

The secondary objectives were targeted towards (a) optimization of the process, (b) understanding of organic sulfur in coal and its metamorphism, and (c) understanding of properties and behavior of supercritical fluids.

Since the proposed project had never been demonstrated or proven on any scale by other investigators, a fair amount of range-finding experiments were to be involved in the project. Therefore, the specific objectives of the work performed under the project included the following:

- (a) Initial conceptual feasibility
- (b) Experimental system fabrication

- (c) Preliminary range finding experiments
- (d) Statistical design of experiments
- (e) Process feasibility study of binary supercritical mixtures
- (f) Process feasibility study of ternary supercritical mixtures
- (g) Optimization of the process
- (h) Process feasibility study of consecutive supercritical treatments
- (i) Characterization of extracted organosulfur compounds
- (j) Test of other fluid combinations
- (k) Conceptual design of pilot-scale plant
- (l) Preliminary economic analysis

(II.3) Involvements of Co-Sponsors

This project was co-sponsored by the Ohio Coal Development Office (OCDO) and the University of Akron (UA). Two thirds of the project cost was funded by the OCDO and the remaining third was supported the the UA. Another clean coal technology project supported by the Electric Power Research Institute (EPRI) has also aided this project directly and indirectly, by supplying additional scientific and technological understanding as well as some of the necessary coal samples.

III. TECHNICAL DISCUSSION

(III.1) Description of Process

(III.1.1) Fundamentals of the Supercritical Extraction Process

Fluids exhibit exceptional solvent powers at their supercritical conditions. The term "supercritical" comes from the fact that the temperature and pressure are beyond the critical ones (i.e., higher than the critical values). In such a region, fluid is neither vapor nor liquid, and it is not right to call this a mixture. Most interestingly, fluids at supercritical conditions behave in both a "vapor-like" and a "liquid-like" manner. In other words, the fluids at supercritical conditions have excellent viscosity and diffusivity while keeping high density. This is why exceptional solvent power is expected of such a fluid.

In fact, supercritical extraction has been successfully applied to various food processes such as decaffeination of coffee. Most of the prior work in any area of application has involved a single fluid component, usually carbon monoxide or water. Very few attempts at supercritical extraction have been made in the fuel technology area. There is a serious dearth of research data regarding supercritical extraction of coal even with pure components.

One of the major advantages of the process is that it can very easily be combined with a physical cleaning process in order to facilitate the removal of pyritic sulfur as well. A float sink process utilizing water as a medium is nicely compatible with the current process, since the two processes utilize the same liquid, i.e., water. The process does not involve any carcinogens and does not leave any harmful residues in the treated coal. Furthermore, the process can be very effectively utilized for preparation of a clean coal-water slurry for advanced internal combustion engines as well as for other purposes.

(III.1.2) Types of Solvents Considered for the Research

Carbon dioxide (CO_2) is an outstanding candidate for various supercritical extraction processes, due to its nontoxicity, low critical temperature (88 F), and relatively low critical pressure (1072 psi). Exceptional solvent power can be obtained by CO_2 at low temperature and pressure.

Water (H_2O) is also an outstanding candidate for various supercritical extraction applications, as it is the best polar solvent inexpensively available. Due to their quadrupole moments, polar solvents under supercritical conditions exhibit far stronger solvent powers than their nonpolar counterparts. The disadvantage is that the critical temperature and pressure of water are very high ($T_c = 705$ F and $P_c = 3209$ psi), thereby making the commercialization somewhat more difficult.

Because it shows good solubility toward many organic substances, methanol (CH_3OH) is known as one of the best organic solvents. Critical properties of methanol are in between the cases of carbon dioxide and water, ($T_c = 462$ F and $P_c = 1156$ psi).

The organosulfur compounds in coal involve a great many types of compounds, which are believed to be in aliphatic sulfur, aromatic sulfur, and heterocyclic sulfur. Thiols, polysulfides, sulfonic and sulfinic acids, and thiophenes are typical examples of such compounds. Thus, a single solvent may not be able to attack most of these different types of compounds.

The novelty of the process developed here is in the way it achieves a perfect chemical ensemble among the key solvents at their supercritical conditions. In other words, a ternary system of CO_2 - H_2O - CH_3OH involves all of nucleophilic, polar, inorganic, and organic solvents in a single mixture. Furthermore, the critical points for such a mixture are lower than that for pure water and can be varied by changing the mixture compositions. When such a synergistic hybrid solvent system is used, many different types of organosulfur forms can be attacked. Thus, the developed process optimizes not only the chemical system but also the physical properties of the resultant mixture.

(III.2) Approaches Taken to Meet the Project Objectives

(III.2.1) Fabrication of Experimental Unit

A bench-scale, supercritical extraction unit was designed, fabricated and operated. The process unit is based on a semi-batch operation in which the solid coal is stationary and fluids are continuously passing through. The system involves four pressure vessels, of which one is the main extractor, and the other three are for compressed fluids (viz., CO_2 , H_2O , and CH_3OH). Figure 1 shows a schematic of the experimental system fabricated for this project.

Good pressure control was achieved by the use of manually controlled back-pressure regulators. The temperature of the system was closely controlled to ensure stability. Single-point axial measurements of the coal bed and extractor wall temperature were used for the control. A fast-response single-zone high-density heater was used to ensure that the coal bed was maintained under near-isothermal conditions. Rupture discs with axial vents were used for safety.

A Milton-Roy high-pressure pulseless duplex pump system was installed for feeding the solvent streams of methanol, water, or mixtures thereof. The delivery of carbon dioxide to the extractor was achieved by the use of the controlled pressure-bomb source shown in Figure 2.

The condensables in the gaseous product from the reactor were separated and collected by condensing in receptacles maintained at 0 C. Zero dead-volume sampling valves and low-dead-volume tubing were used to ensure intrinsic safety and to allow waste disposal advantages.

The entire extraction system was housed in a stainless-steel enclosure that added to the enhanced process safety measures. Since all the valves, indicators, and switches were installed on the front panel of the system, there was absolutely no need for an operator to work inside the enclosure during experimental runs.

The unique feature of our experimental system can be summarized as follows:

- (a) good pressure control
- (b) fast heating rate and good control of temperature
- (c) capability of handling different fluids at wide ranges of conditions
- (d) accurate flow measurement and control
- (e) capability of handling a wide range of particle sizes
- (f) quick separation of fluids and solids
- (g) versatility for some other applications
- (h) capability of handling mixture fluids
- (i) capability of handling a relatively large amount of samples.

Figure 1. Supercritical Extraction System.

Figure 2. Internal Details of the Supercritical Extraction Unit

(III.2.2) Coal Samples Used for This Investigation

Most Ohio coal manufacturers were contacted for supply of coal samples; however, no definite answers were obtained from any of them. This may be attributed to their potential fear that some of the investigation results might be used against their marketing and production, even though our true intention was clearly stated in our letter.

All the coal samples were obtained through out-of-state assistance. Ohio 5/6 coals were obtained from Hydrocarbon Research, Inc. (HRI); Ohio 6 coal was obtained from UE&C-Catalytic, Inc.; Illinois No. 6 coal was obtained from Illinois Geological Survey; and Indiana No. 5 coal was supplied by Midwest Ore Processing Co.

Even though the original project scope included only Ohio coals for the process investigation, other midwestern state coals were also tested, because of their diversely different organic sulfur compositions. In order to establish a set of reproducible and reliable data, standardization of each kind of coal sample and storage of this standardized sample were crucially important. Grinding, riffing, mixing, sifting, and storing in an inert, sealed environment were carried out in our laboratory.

(III.2.3) Analysis

Both raw and extracted samples were analyzed by proximate analysis, ultimate analysis, heating value measurements, forms of sulfur analysis, N content measurement, etc. Certain selected samples were examined by N_2 BET surface area as well as by scanning electron microscopy, in order to investigate potential changes in coal morphological structure due to the extraction.

(III.2.4) Prediction of Thermodynamic Properties of Supercritical Solvent Mixtures

In order to devise a supercritical extraction process, thermodynamic properties of involved fluids, especially near the critical region, are essential. When a single component is used, the critical properties are readily available in the literature. However, when a multi-component system of supercritical fluid is used, prediction of critical properties for the mixture system becomes a very difficult task, unless the system is guaranteed to behave like an ideal mixture. (This assumption is nearly impossible to expect in most cases.)

The Redlich-Kwong equation of state modified by Soave was used to predict the supercritical physical properties of the extraction solvent mixtures. Details on the development and applicability of this equation of state are given elsewhere (Daubert, T.E., Chemical Engineering Thermodynamics, McGraw Hill, New York, 1985), and will not be repeated here. The computer program needed for the calculation of the thermodynamic properties given by Elliot and Daubert was slightly modified for

our application. This program, based on the Scave equation, has proven to be the best in correlating and predicting thermodynamic properties near critical points. Another computer program was written in APL to calculate the supercritical solvent mixture densities.

(III.2.5) Statistical Design of Experiments

In order to carry out an experimental investigation on a new process, the technique of statistical experimental design is very useful. For binary solvent mixture cases (CO₂-methanol; water-methanol; CO₂-water) and ternary solvent mixture cases (CO₂-methanol-water), a factorial design of experiments was set up.

Initially, a four-factor experimental system was considered where, temperature, pressure, composition of species 1, and composition of species 2 were the designated factors. At two levels for each factor a 2⁴ factorial design would have been needed for a full-scale investigation, requiring sixteen experiments. This experimental design was rejected in favor a central composite design. Although the central composite design requires 29 experimental runs (2⁴ design points, (4 x 2) outer layer points, 3 to 5 replication points), this design is far superior to 2⁴ factorial design since the design involves five levels for each variable, instead of only two. The central composite design is a powerful tool for process optimization studies.

Table 1 shows a list of coded variables (or factors) and illustrates a central composite design for four-factor cases of ternary extraction system.

The coded variables in Table 1 were termed x₁, x₂, x₃, and x₄. The following equations give the formulae for calculating the values of the coded variables:

$$x_1' = \frac{\text{mole fraction of methanol } (x_1) - 0.40}{0.05}$$

$$x_2' = \frac{\text{mole fraction of CO}_2 \text{ } (x_2) - 0.15}{0.05}$$

$$x_3' = \frac{\text{extraction temperature } (x_3) - 585}{10}$$

$$x_4' = \frac{\text{extraction pressure } (x_4) - 210}{10}$$

It may be readily observed from this table that with only 29 experiments a total of five levels was incorporated for each variable (factor). Accordingly, nonlinearity of the response as

Table 1
Optimization Study on Ohio 5/6 Coal

Design Matrix of the Experiments and
the Response of the System

#	Run #	x_1	x_2	x_3	x_4	y
1	1	0.35	0.10	575	200	45.07
2	2	0.45	0.10	575	200	41.65
3	15	0.35	0.20	575	200	36.52
4	11	0.45	0.20	575	200	36.02
5	23	0.35	0.10	595	200	56.35
6	3	0.45	0.10	595	200	54.05
7	13	0.35	0.20	595	200	49.87
8	20	0.45	0.20	595	200	46.20
9	8	0.35	0.10	575	220	37.92
10	17	0.45	0.10	575	220	42.73
11	4	0.35	0.20	575	220	43.28
12	19	0.45	0.20	575	220	37.45
13	24	0.35	0.10	595	220	60.43
14	5	0.45	0.10	595	220	49.51
15	22	0.35	0.20	595	220	52.48
16	10	0.45	0.20	595	220	57.24
17	6	0.40	0.15	585	210	44.22
18	12	0.40	0.15	585	210	47.10
19	18	0.40	0.15	585	210	40.25
20	28	0.40	0.15	585	210	40.77
21	29	0.40	0.15	585	210	43.13
22	25	0.30	0.15	585	210	42.72
23	7	0.50	0.15	585	210	47.40
24	14	0.40	0.05	585	210	51.57
25	26	0.40	0.25	585	210	42.84
26	9	0.40	0.15	565	210	27.54
27	27	0.40	0.15	605	210	53.68
28	16	0.40	0.15	585	190	42.84
29	21	0.40	0.15	585	230	45.41

x_1 = mole fraction of MeOH

x_2 = mole fraction of CO₂

$1-x_1-x_2$ = mole fraction of H₂O

x_3 = temperature, °K

x_4 = pressure, atm

y = organic sulfur removal in percent

well as standard error estimation can be handled in a direct, rigorous way.

(III.3) Procedures

(III.3.1) Coal Samples

The coal samples used in this study were bituminous coals from Ohio (Ohio 5/6 coal) and Indiana (Indiana 5 coal). The particle size distribution of the coal was 80 wt% - 200 mesh coal, and 20 wt% - 180+200 mesh coal. The proximate and ultimate analyses of these coals are given in Table 2.

(III.3.2) Experimental Procedures

The experiments were initiated by charging a pre-weighed sample of coal into the extractor. The methanol and/or water solvent was delivered to the extractor at the rate of 70 ml/h with the exit from the reactor closed to permit build-up of the desired supercritical reaction temperature and pressure. The extraction pressure was controlled by a controlled exit purge from the extractor. After the required extraction time, the extractor pressure was relieved by entraining the solvent. The experiments were termed semi-batch, since the coal sample was not fed into the reactor continuously. The vapor hourly space velocity for the typical run ranged from 1-2 ml/ml/h.

(III.3.3) Analysis of Clean Coal and Supercritical Extract

The extracted coals were analyzed for total sulfur content and elemental composition. The forms of sulfur analysis was based on the ASTM standard method ASTM D-2492 while the total sulfur content was measured using a LECO SC 132 Sulfur Analyzer. The proximate analysis was carried out on a Fisher Proximate Analyzer, Model No. 490. Ultimate analysis and N analysis were conducted on a LECO CHN-600 Analyzer. The nitrogen BET areas for coal samples were measured using a Quantasorb Jr. Surface Analyzer. The heating value of coals before and after the extraction was measured using a Parr Adiabatic Oxygen Bomb Calorimeter. Liquid samples obtained from the extraction runs were analyzed by a Hewlett Packard GC-5890/MS-5970. An ultracapillary column of 0.2 mm diameter and 12.5 m length was used for product separation.

Table 2
Proximate and Ultimate Analysis of
Ohio 5/6 and Indiana 5 Coal Samples
(wt% dry basis)

	Ohio 5/6	Indiana 5
Proximate Analysis		
Volatile Matter	37.5	35.49
Ash	8.2	40.42
Fixed Carbon	54.2	42.43
Ultimate Analysis		
Carbon	69.4	46.45
Hydrogen	5.4	4.18
Nitrogen	1.8	0.79
Total Sulfur	3.3	6.95
Pyritic Sulfur	1.1	3.28
Organic Sulfur	1.9	2.20
Sulfate Sulfur	0.3	1.48
Oxygen	20.1	41.63
Calorific Value (BTU/lb)	11,997	8,339

(III.4) Problems or Breakthroughs Encountered During the Course of the Project

A major breakthrough was that we were able to obtain a definite process synergism in the solvent power, by using a ternary mixture of carbon dioxide, methanol, and water for the supercritical extraction of coal. This has never been achieved by other investigators.

(III.5) Results and Discussions

(III.5.1) Single Component Supercritical Extraction

Samples of Ohio 9 coal were chosen for the semi-batch extraction experiments using carbon dioxide, methanol, and water as pure-component supercritical fluids. The amounts of total and organic sulfur in the original sample were 3.075 wt% and 1.582 wt% respectively. The major results of the pure component extractions have been summarized in Table 3 and interpreted as follows:

(a) There was very little reduction of sulfur when CO₂ alone was used as a supercritical solvent. Since the critical temperature of CO₂ is only 31 C (88 F), the extraction temperature was kept low, thereby slowing the kinetic rate.

(b) Water and methanol as single components were found to be excellent solvents for the extraction of sulfur. In addition to sufficient extraction of organic sulfur, supercritical extraction with water also yielded a large amount of tar. Formation of tars and release of volatile matters from coal are normally considered negative in coal processing because of the loss in heating value as well as the operational difficulties. This is because the conditions required for supercritical extraction using pure water alone are very severe and because tar starts to vaporize in high amounts near 530 F or higher. This is why the strong extractability of water cannot be fully exploited if used alone.

(c) Sufficient amounts of sulfur were extracted in the methanol runs. It was found that increasing extraction time resulted in only a small increase in the amount of sulfur extracted. However, it is believed that a fully continuous contacting mode would increase the percent extraction significantly due to the ever-fresh solvent power.

(III.5.2) Binary Solvent Mixture at Supercritical Extraction

There are three different systems for binary mixtures, viz., carbon dioxide-methanol, methanol-water, and carbon dioxide-water. Based on the thermodynamic calculations, methanol-water system is slightly off from the ideal, while carbon dioxide-water is very strongly nonideal. In a strongly

Table 3. Results of batch supercritical coal extraction experiments.

Solvent	T (°F)	P (psig)	Solvent Feed Rate (ml/h)	Extraction Time (h)	Percent Reduction in Organic Sulfur
CO ₂	300	2500	6000	12	4.04
CH ₃ OH	509	2500	22	5	28.57
CH ₃ OH	509	3000	22	8	31.60
H ₂ O	765	3500	22	2	35.20
CH ₃ OH/ H ₂ O [*]	550	2000	22	3	34.21
CH ₃ OH/ H ₂ O [*]	550	2500	22	3	35.90

Note: ^{*}; a 50% v/v solution of methanol.

nonideal mixture system, the fluids are not easily miscible near their critical conditions and, therefore, significantly high critical temperature and pressure conditions are required in order to attain homogeneity. This, however, does not mean that supercritical extraction requires such high temperatures and pressure. Figures 3, 4, and 5 show the critical properties for binary mixtures of $\text{H}_2\text{O}-\text{CH}_3\text{OH}$, $\text{CO}_2-\text{H}_2\text{O}$, and $\text{CO}_2-\text{CH}_3\text{OH}$ systems.

Semi-batch experiments were conducted to assess the relative extraction powers of the supercritical solvents CO_2 , H_2O , and CH_3OH , especially in the binary cases. Thirty five extraction runs were performed on Ohio 5/6 coal with supercritical solvent mixtures. The extraction conditions for these runs are given in Tables 4, 5, 6, 7, and 8.

These experiments were carried out at fixed values of T_r (reduced temperature) = 1.1, and P_r (reduced pressure) = 1.3 for all the solvent systems.

Figure 6 shows the extent of sulfur extraction as a function of the molar composition of the water-methanol solvent mixture. Also shown is reactor temperature as a function of solvent composition. Artificially high sulfur contents caused by the removal of volatiles from the coal during processing can downgrade the calculated efficiency of the sulfur removal technique. Although the raw coal basis may seem to be more appropriate for computing extent of desulfurization, to avoid this ambiguity, the more appropriate basis of weight of sulfur per million BTU was used. The figure shows that the reduction of sulfur goes through a definite minimum as the mole fraction of water increases. The minimum in the sulfur reduction value occurs at water mole fraction of 0.1 and 0.2. However, the extraction conditions at these mixture compositions are more severe than that for the pure method. Since the solvent power of a particular solvent depends on the density of a solvent, this kind of behavior suggests that the extraction may also be governed by chemical forces. As both water and methanol are polar solvents, the attractive forces between these two solvents may contribute to this rather interesting effect. It is seen that increasing the concentration of water at concentrations higher than 40 mole percent increases the extraction of sulfur drastically. However, using a high concentration of water is also not advisable, since the extraction conditions tend to be commercially prohibitive.

Figure 7 shows sulfur extraction and extractor pressure as a function of the molar composition of the water- CO_2 solvent mixture. Figure 8 shows the extent of desulfurization and extractor pressure as a function of extraction temperature for the same set of runs. The results clearly show that water- CO_2 mixtures do not extract sufficient amounts of sulfur although water by itself proved to be an excellent solvent.

Figure 9 shows extent of sulfur extraction and extractor pressure as a function of the molar composition of the methanol- CO_2 solvent mixture. Figure 10 shows the same ordinates plotted as function of extraction temperature. As expected, the methanol/ CO_2 solvent mixtures proved to be poorer desulfurization agents than water/ CO_2 mixtures.

Figure 3.

Figure 4

Figure 5.

Table 4. Results of semi-batch supercritical coal extraction experiments at $T_r=1.1$, $P_r=1.3$.

Run	Solvent	T (°F)	P (psig)	Extraction time (h)	% Reduction in Total Sulfur	Heating Value (Btu/lb)
1	CH ₃ OH	555	1525	2	23.46	12,550
2	CH ₃ OH/H ₂ O ⁺	570	1800	2	17.25	12,952
3	CH ₃ OH/H ₂ O [*]	580	2000	2	18.92	13,021
4	CH ₃ OH/H ₂ O ^{**}	640	2325	2	30.12	12,260
5	CH ₃ OH/H ₂ O [#]	660	2575	0.5	25.25	12,952
6	CH ₃ OH/H ₂ O [#]	660	2575	2	38.84	12,835
7	CH ₃ OH/H ₂ O ⁺⁺	690	2900	2	44.54	12,999

⁺ Methanol:water mole ratio is 9:1.

^{*} Methanol:water mole ratio is 4:1.

^{**} Methanol:water mole ratio is 1:1.

[#] Methanol:water mole ratio is 2:3.

⁺⁺ Methanol:water mole ratio is 3:7.

Table 5. Results of semi-batch experiments on Ohio 5/6 coal at constant solvent density (5 g/mol/L) at 650 K.

Run No.	Solvent	P (psig)	Extraction time (h)	% Reduction of Total Sulfur	Heating Value (Btu/lb)
1	CH ₃ OH-H ₂ O ⁺	3030	2	42.03	13,129
2	CH ₃ OH-H ₂ O [*]	2965	2	38.20	13,153
3	CH ₃ OH-H ₂ O [#]	2780	2	37.73	12,733
4	CH ₃ OH-H ₂ O ⁺⁺	2725	2	40.26	13,072
5	CH ₃ OH-H ₂ O ^{**}	2625	2	40.11	12,574
6	H ₂ O	2550	2	43.37	13,157

⁺ Methanol-water mole ratio is 9:1.

^{*} Methanol-water mole ratio is 4:1.

[#] Methanol-water mole ratio is 1:1.

⁺⁺ Methanol-water mole ratio is 2:3.

^{**} Methanol-water mole ratio is 1:4.

Table 6.
Results of semi-batch supercritical coal extraction experiments at Tr=1.1, Pr=1.3 using water/carbon dioxide mixtures.

Run	Solvent	T (°F)	P (psig)	Extraction time (h)	% Reduction in Total Sulfur (Raw basis)	Solvent Density g/ml
1	Water	822	4150	2	50.60	0.1390
2	Water/CO ₂ [*]	686	3605	2	19.40	0.1660
3	Water/CO ₂ ^{**}	550	3050	2	6.25	0.2340
4	Water/CO ₂ ⁺	482	2775	2	10.95	0.2025
5	Water/CO ₂ ⁺⁺	414	2500	2	10.95	0.2137
6	Water/CO ₂ [#]	278	1950	2	11.56	0.2350
7	CO ₂	143	1390	2	1.88	0.2490

* Water:CO₂ mole ratio is 4:1.

** Water:CO₂ mole ratio is 7:3.

+ Water:CO₂ mole ratio is 1:1.

++ Water:CO₂ mole ratio is 2:3.

Water:CO₂ mole ratio is 1:4.

Table 7. Results of semi-batch supercritical coal extraction experiments with methanol/water mixtures at $Tr=1.1$, $Pr=1.3$.

Run	Solvent	T (°F)	P (psig)	Extraction time (h)	% Reduction in Total Sulfur (Btu basis)	Heating Value (Btu/lb)
1	CH ₃ OH	555	1525	2	17.28	12,103
2	CH ₃ OH/H ₂ O ⁺	575	1650	2	15.75	12,372
3	CH ₃ OH/H ₂ O [*]	589	1775	2	12.00	12,354
4	CH ₃ OH/H ₂ O ^{**}	623	2100	2	24..21	12,055
5	CH ₃ OH/H ₂ O [#]	640	2325	2	29.32	12,412
6	CH ₃ OH/H ₂ O ^{##}	660	2575	2	38.54	12,481
7	CH ₃ OH/H ₂ O ⁺⁺	690	2900	2	38.10	12,210
8	CH ₃ OH/H ₂ O ^o	742	3360	2	38.60	12,285
9	H ₂ O	822	4150	2	41.57	10,140

⁺ Methanol:water mole ratio is 9:1.

^{*} Methanol:water mole ratio is 4:1.

^{**} Methanol:water mole ratio is 3:2.

[#] Methanol:water mole ratio is 1:1.

^{##} Methanol:water mole ratio is 2:3.

⁺⁺ Methanol:water mole ratio is 3:7.

^o Methanol:water mole ratio is 1:4.

Table 8. Results of semi-batch supercritical coal extraction experiments at $Tr=1.1$, $Pr=1.3$ using methanol/carbon dioxide mixtures.

Run	Solvent	T (°F)	P (psig)	Extraction time (h)	% Reduction in Total Sulfur (Btu basis)	Solvent Density g/ml
1	MeOH	555	1525	2	11.56	0.110
2	MeOH/CO ₂ [*]	530	1750	2	7.19	0.123
3	MeOH/CO ₂ ^{**}	512	1985	2	3.12	0.168
4	MeOH/CO ₂ ⁺	492	2250	2	3.45	0.199
5	MeOH/CO ₂ ⁺⁺	466	2535	2	1.56	0.236
6	MeOH/CO ₂ [#]	206	2165	2	0.30	0.392
7	CO ₂	143	1390	2	1.88	0.249

* Methanol:CO₂ mole ratio is 9:1.

** Methanol:CO₂ mole ratio is 4:1.

+ Methanol:CO₂ mole ratio is 7:3.

++ Methanol:CO₂ mole ratio is 3:2.

Methanol:CO₂ mole ratio is 1:9.

Figure 6. Percent of total sulfur removal by supercritical extraction of Ohio 5/6 coal with water-methanol mixtures. Reaction temperature is also plotted with mole fraction water as abscissa.

Figure 7.

Figure 8

Figure 9.

Figure 10.

Figure 11 shows the extent of sulfur extraction and extraction conditions as a function of the molar composition of the water-methanol solvent mixture. The figure shows that, in general, the reduction of sulfur increases as the mole fraction of water increases. Based on our results, we may say that methanol/water mixtures are better solvents for coal desulfurization than methanol/CO₂ or water/CO₂ mixtures.

Figure 12 shows the effect of solvent density on the extraction of sulfur from coal. As seen from this figure, density does not appear to be an important governing variable in the desulfurization process. This implies that chemical effects may also be involved in the desulfurization process. Figure 13 shows the alteration in calorific value of the coal as a function of extraction conditions. It can be seen that the methanol/water mixtures did not significantly alter the BTU content of the coal. However, the water extraction run reduced the BTU content of the coal drastically. This implies that there is an optimum methanol/water mixture composition that removes the most sulfur for the least reduction in BTU.

(III.5.3) Analysis of Cleaned Coal and Supercritical Extract for Binary Solvent Mixtures

Figure 14 gives the proximate analyses of coals extracted by methanol/water mixtures. The data in general show a greater reduction in volatile content with increasing severity of processing conditions. Obviously, a reduction in volatile matter content is accompanied by an increase in the fixed carbon content in terms of its percentage. This indicates that some hydrogen-rich fractions are extracted from the coal structure. Such a loss of volatile matter (VM) is generally considered undesirable, since the coal loses some of its original heating value. Figure 15 gives the ultimate analyses of the coal samples after supercritical extraction with the methanol/water mixtures. The more severe the extraction conditions, the higher is the C/H ratio plot given in Figure 16.

An interesting observation from the supercritical water runs was that the extract-containing aqueous-phase was an almost clear and pungent-smelling liquid. The methanol and methanol/water extracts on the other hand were yellow in color and turbid.

Liquid samples from the extraction experiments were analyzed using GC/MS and FTIR. Figures 17 through 19 show typical TICs for the supercritical extracts. Figure 20 shows a typical FTIR trace for a supercritical extract.

The TICs for the supercritical extracts showed peaks of sulfur compounds like 4-hydroxybenzene sulfonic acid, 2-methyl phenyl methane sulfonic acid, ethane 1,1-bis (methylthio-), 1-(methylthio)ethyl methyl disulfide, and methyl ether 2-mercapto benzoic acid. Other typical non-sulfurous compounds detected were 1,2 diphenyl-ethanediol, 2,5-dimethyl phenol, and naphthalene (methylated substitutes). The identification of the disulfides and sulfonic acids appears to be a very crucial

Figure 11.

Figure 12.

Figure 13.

EFFECT OF SUPERCRITICAL EXTRACTION ON THE
PROXIMATE ANALYSIS OF OHIO 5/6 CCOAL

Figure 14.

EFFECT OF SUPERCRITICAL EXTRACTION ON
ULTIMATE ANALYSIS OF OHIO 5/6 COAL

Figure 15.

EFFECT OF SUPERCRITICAL EXTRACTION ON
C/H RATIO OF OHIO 5/6 COAL

Figure 16.

Figure 17. TIC of supercritical extract obtained from a run with 1:1 mole ratio methanol-water solvent.

Figure 18. TIC of supercritical extract obtained from a run with methanol as solvent.

Figure 19. TIC of supercritical extract obtained from a run with water as solvent.

Figure 20. FTIR of a supercritical extract obtained from a run with methanol as solvent.

achievement, since it gives some invaluable information regarding the chemistry of organic sulfur.

(III.5.4) Sequential Treatment at Supercritical Conditions

Ohio 5/6 coal was sequentially treated in the following manner. The reactor was charged with approximately 35 grams of preweighed coal. The first supercritical fluid (designated as run A) was passed through the reactor. A small amount of the treated coal was removed from the reactor for testing. The remaining coal was subjected to treatment by a second supercritical fluid (designated as run B). The conditions for each of the runs are listed in Table 9. The results of these runs are listed in Tables 10 through 12. In general, sequential treatments were not as effective as mixture treatments, as somewhat expected.

(III.5.5) Ternary System Experiment Results and Discussion

Based on our experimental results on mixtures and sequential treatments using methanol-water-CO₂ system, we have found the optimal operating process conditions. This conclusion was based on 98 Ohio 5/6, 16 Indiana 5, and 14 Illinois 6 experimental runs and the results were compared on the organic sulfur reduction per 10⁶ BTU. Table 13 shows the optimal process operation conditions and the extraction results shown are for Ohio 5/6 coal (50-50 blend of Ohio 5 and Ohio 6 coals, supplied by Hydrocarbon Research, Inc.). As can be seen in the table, all the operating conditions recommended are for the mixture mode of extraction. No sequential treatment resulted in higher than 35% reduction in organic sulfur, which was achieved in methanol and carbon dioxide sequential treatments. Furthermore, the sequential treatments require approximately double the effort, time, and energy costs to complete the job, yet result in significantly poorer extraction results. Therefore, the best synergism can be obtained when the ternary system mixtures are used together.

(III.5.6) Alternative Fluids at Supercritical Conditions

An additional study, beyond the scope of the contracted project, was done to determine if another solvent, or combination of solvents, would be more effective. The candidate chemical species considered to replace the methanol-water-carbon dioxide system were ethanol and toluene. The choice of these chemicals was based on the following rationale:

(a) Ethanol is similar to methanol in many regards and is very miscible with water at both room and supercritical conditions.

Table 9
SEQUENTIAL TREATMENT OF
OHIO 5/6 COAL

RUN	FLUID	TIME	CONDITIONS
1A	Methanol	1 hr	T = 510 °F P = 1500 psi Flow = 150 cc/hr
1B	Water	1/2 hr	T = 762 °F P = 4165 psi Flow = 120 cc/hr
2A	Water	1/2 hr	T = 762 °F P = 4165 psi Flow = 130 cc/hr
2B	Methanol	1 hr	T = 510 °F P = 1500 psi Flow = 110 cc/hr
3A	Methanol	1 hr	T = 510 °F P = 1500 psi Flow = 110 cc/hr
3B	Carbon Dioxide	2 hr	T = 115 °F P = 1393 psi
4A	Carbon Dioxide	2 hr	T = 115 °F P = 1393 psi
4B	Water	1/2 hr	T = 762 °F P = 4165 psi Flow = 110 cc/hr
5A	Carbon Dioxide	2 hr	T = 115 °F P = 1393 psi
5B	Methanol	1 hr	T = 510 °F P = 1500 psi Flow = 110 cc/hr
6A	Water	1/2 hr	T = 762 °F P = 4165 psi Flow = 110 cc/hr
6B	Carbon Dioxide	2 hr	T = 115 °F P = 1393 psi

Table 10
 PROXIMATE ANALYSIS OF
 SEQUENTIALLY TREATED
 OHIO 5/6 COAL

SAMPLE	% MOISTURE	% VOLATILES	% ASH	% FIXED CARBON
OHIO 5/6	3.95	37.14	5.05	57.81
1A (m)	0.97	35.47	6.90	57.63
1B (w)	0.93	16.71	11.74	71.55
2A (w)	1.47	16.05	7.11	76.84
2B (m)	0.83	16.58	15.74	67.68
3A (m)	13.72	35.43	4.73	59.84
3B (c)	6.82	34.96	4.94	60.10
4A (c)	4.91	37.12	4.92	57.96
4B (w)	0.77	32.66	20.23	47.11

(m) - methanol extraction
 (w) - water extraction
 (c) - carbon dioxide extraction

Table 11.
CHN ANALYSIS AND HEATING VALUE OF
SEQUENTIALLY TREATED
OHIO 5/6 COAL

SAMPLE	% CARBON	% HYDROGEN	% NITROGEN	HEATING VALUE
OHIO 5/6	71.91	5.70	1.51	14,145
1A (m)	73.74	4.92	1.54	13,914
1B (w)	75.78	3.47	1.55	13,275
2A (w)	77.35	4.03	1.58	13,859
2B (m)	76.14	3.68	1.57	13,480
3A (m)	69.19	6.35	1.23	14,133
3B (c)	69.04	5.60	1.31	13,656
4A (c)	69.41	5.51	1.34	13,662
4B (w)	75.06	4.13	1.60	13,600

(m) - methanol extraction
(w) - water extraction
(c) - carbon dioxide extraction

Table 12.
SULFUR ANALYSIS OF
SEQUENTIALLY TREATED
OHIO 5/6 COAL

SAMPLE	TOTAL SULFUR	SULFATIC SULFUR	PYRITIC SULFUR	ORGANIC SULFUR
OHIO 5/6	3.74	0.49	1.30	1.95
1A (m)	3.40	0.30	1.31	1.79
1B (w)	2.50	0.02	0.10	2.38
2A (w)	2.71	0.05	0.26	2.40
2B (m)	3.05	0.07	0.34	2.64
3A (m)	3.25	0.32	1.19	1.74
3B (c)	3.50	0.28	1.17	2.05
4A (c)	3.68	0.40	1.18	2.10
4B (w)	3.00	0.10	0.44	2.46
5A (c)	3.41	0.19	1.29	1.93
5B (m)	3.66	0.36	1.35	1.95
6A (w)	2.61	0.07	0.32	2.22
6B (c)	2.53	0.06	0.05	2.42

(m) - methanol extraction
(w) - water extraction
(c) - carbon dioxide extraction

Table 13
Optimal Conditions for
Synergistic Supercritical Desulfurization Process

Methanol	Water	Carbon Dioxide	T F	P atm	mode	% Org. Sulfur Reduction
35%	55%	10%	595	200	mixture	56.35
35%	55%	10%	595	220	mixture	60.43
45%	35%	20%	595	220	mixture	57.24

(b) Toluene has good solvent power as well demonstrated in various applications (soil analysis and polypropylene dissolution), and is still relatively inexpensive.

Ethanol and toluene supercritical properties were predicted using a modified Soave equation, which has been proven to be the best for correlating such properties near critical conditions. More details about this thermodynamic prediction procedure have been reported in earlier reports for the methanol-water, methanol-carbon dioxide, and water-carbon dioxide systems.

Figures 21, 22, and 23 show the $P_c - X_i$ plot, the $T_c - P_c$ plot, and the T_c vs. X_i plot, respectively for the binary system of ethanol and toluene. As can be seen in the plots, the binary ethanol-toluene system is fairly ideal, i.e., the interactive effects are insignificant. Therefore, the miscibility of these two components is excellent at supercritical conditions.

(III.5.7) Analysis of Cleaned Coal for the Alternative Fluids at Supercritical Conditions

In order to find the individual solvent behaviors of the aforementioned solvents, we conducted supercritical experiments on Ohio 5/6 coal at $Tr = 1.1$, and $Pr = 1.3$. The results are shown in Table 14. It is interesting to note that toluene as an individual component gives good total sulfur reduction, while organic sulfur was not reduced. All of the samples for the experiments were ground and standardized in the same batch, thereby ensuring the same compositions for each run.

Table 15 shows supercritical extraction results using methanol, ethanol, and toluene as single components. To facilitate unbiased comparison between the results, the reduced temperature and pressure were kept at 1.1 and 1.3, respectively.

Interestingly, toluene again extracted pyritic sulfur. It has to be mentioned that no particulate was recovered from the experiments. In certain cases, the organic sulfur content was found to have increased rather than decreased due to reaction. This may be explained by the fact that all three solvents act as very strong organic solvents at the extraction conditions, and extract other valuable hydrocarbons from coal. In particular, toluene and ethanol are strong enough to break the macromolecular coal structure at supercritical conditions.

Binary pairs of ethanol-water and acetone-water systems at supercritical conditions have also been studied on Indiana # 5 coal and their results are shown in Table 16.

Table 17 shows the results of CHN analysis of raw and treated samples. As shown, hydrogen contents are most affected by supercritical extraction. This proves that hydrogen-rich volatile matters have been removed from coal along with pollutant. For all cases, the nitrogen contents were relatively unaffected.

Based on the preliminary runs using toluene, ethanol, acetone, and binary mixtures, we can conclude that the binary pairs of acetone-water and ethanol-water are not as effective as

ETHANOL / TOLUENE CRITICAL PROPERTIES

P_c vs. X_1

Figure 21.

ETHANOL / TOLUENE CRITICAL PROPERTIES

Figure 22.

ETHANOL / TOLUENE CRITICAL PROPERTIES

Tc vs. X₁

Figure 23.

Table 14
Supercritical Extraction of Ohio 5/6 Coal
 $T_r = 1.1$ $P_r = 1.3$

Run#	Component	% Total Sulfur	% Pyritic Sulfur	% Sulfatic Sulfur	% Organic Sulfur
11	methanol	2.910	1.118	0.185	1.607
12	ethanol	2.705	1.230	0.250	1.230
13	toluene	2.455	0.421	0.007	2.028
raw		3.7	1.3	0.421	1.979

Table 15
Supercritical Extraction of Illinois #6 Coal
 $T_r = 1.1$ $P_r = 1.3$

Run#	Component	% Total Sulfur	% Pyritic Sulfur	% Sulfatic Sulfur	% Organic Sulfur
14	methanol	3.85	1.97	0.181	1.699
15	ethanol	3.83	1.56	0.160	2.110
16	toluene	3.27	1.15	0.191	1.929
raw		4.34	2.42	0.266	1.654

Table 16
Binary Systems at Supercritical Conditions
(Alternative Fluid Systems)
for Indiana # 5 Coal
 $T_r = 1.124$ $P_r = 1.3$

System	Mole %	% Total Sulfur	% Pyritic Sulfur	% Sulfatic Sulfur	% Organic Sulfur
Raw		7.10	3.99	1.30	1.81
Acetone/ water	65/35	6.73	3.08	0.67	2.98
Ethanol/ water	65/35	7.04	3.37	1.12	2.55
Ethanol/ water	65/35	6.77	3.59	0.78	2.40
Methanol/ water	65/35	5.70	3.87	0.49	1.34
Ethanol/ water	100/0	6.95	2.89	0.99	3.06

Table 17
CHN Analysis Data for Alternative
Fluid Extraction on Indiana # 5 Coal

Treatment	mole %	% C	% H	% N	% O
raw		54.48	6.08	1.04	31.30
acetone/water	65/35	61.68	4.91	1.19	25.50
ethanol/water	100/0	60.85	5.31	1.09	25.81
methanol/water	65/35	61.36	4.52	1.16	27.27
methanol/water	80/20	58.80	4.76	1.16	28.64

methanol-water and that it does not appear to be a good idea to replace methanol with toluene in a ternary mixture.

III.6 Conclusions

(III.6.1) Effects of Different Solvent on the Extraction Process

Different solvents extract different compounds, as shown in the liquid extracts analyzed on the Hewlett Packard GC- 5890/MS- 5970.

When methanol is present in a substantial amount, both aromatic and aliphatic hydrocarbons were extracted. The types and kinds were dependent upon the coal types and ranks. Typically, naphthalene, phenanthrenes, triphenylene, hexadecanes, etc. are obtained along with thiols (mercaptans). It is quite interesting to note that -SH is extracted in the alcohol medium.

When water is present in the supercritical mixture, the high temperature required causes volatile matters to be devolatilized. Organosulfurs obtained are typically sulfonic acids, sulfinic acids, benzenesulfonic acids, etc. Also, phenols or derivatives are obtained instead of naphthalene, phenanthrenes, etc. This, in comparison to the methanol case on the same coal, proves that the process not only involves physical phenomenon of supercritical extraction, but also involves chemical reactions, such as hydrolysis.

When toluene is used in the mixture, the strong solvent nature toward polymeric structure extracts larger and late-boiling materials. Measurable amounts of aromatic and large molecular hydrocarbons are extracted. Organosulfur compounds in these extracts are not easily detectable from the GC/MS.

When carbon dioxide is used in the mixture, light molecular weight organosulfurs such as dimethyl disulfide are extracted. Other organic matter removal is less active.

(III.6.2) Advantages of the Supercritical Extraction Process

The advantages of our novel, synergistic supercritical extraction process are summarized below:

(1) It uses a mixture of inexpensive fluids, namely, water, carbon dioxide, and methanol.

(2) It provides an excellent chemical ensemble by incorporating the various types of solvent powers at supercritical conditions. Water is an excellent supercritical fluid with high polarity, but it requires very high temperatures and pressures which may result in large amounts of volatile matter being lost if it is used alone. Methanol is an excellent organic solvent that has moderate critical temperature and pressure. Carbon dioxide has the best physical properties including very low critical temperature and pressure, and is a good nucleophilic solvent. Therefore, by combining these three

in a synergistic manner, one can obtain all of the polar solvent, organic solvent, and nucleophilic solvent properties at the same time, while having far better control of the operating pressure and temperature.

(3) The solvent used does not have to be stripped by steam or air at the end of the process. Furthermore, it is ideal for cleaning the coal if a clean coal-water slurry is to be made.

(4) The cleaned coal can be sent to the next stage in which pyritic sulfur is removed by a float sink type of gravitational separation.

(5) The organic sulfur can be cleaned by 40%-60% based on the million BTU, which is excellent since very few chemical processes are targeted on the removal of organic sulfur. Rather well-studied physical cleaning of pyritic sulfur can add to the process, boosting its total sulfur cleaning efficiency near 80%, if both are combined.

IV. MARKETING/COMMERCIALIZATION DISCUSSION

(IV.1) Market for the Process Technology

The process is classified under pre-combustion clean coal technology, in which sulfur forms from coal are extracted before final combustion. In order to make the process commercially viable, the process must be incorporated with physical cleaning of pyritic sulfur by gravitational separation or washing. The market for cleaned coal is vast, covering utilities and highly energy-intensive industries.

(IV.2) Marketplace Adoption Rate

The results in terms of selective organic sulfur removal are very encouraging and no other processes were able to achieve that. However, the use of high pressure systems affects the system design as well as the process economics. As a result, the equipment cost may be on the high side. However, the space requirement and the solvent amount need not be high, since the compressed fluid phase is highly dense. The solvent-to-coal ratio of less than one can be adopted for this process, while other solvent processes require a ratio of 2.5 to 10. The process requires preground coal of preferably -140 mesh, and this may require that existing technological structures at power plants be modified.

At this moment, the scientific value of better understanding the coal extraction process and supercritical fluid extraction technology is great. More research work is strongly recommended for capitalizing such scientific and technological benefits at a commercial scale. The pilot, continuous flow process unit would be ideal as the first step.

(IV.3) Near-Term Increased Use of Ohio Coals

The study shows that Ohio coals can be cleaned of organic sulfur by supercritical extraction. The characterization of organic sulfur extract show that Ohio coals do not contain any abnormally toxic or hazardous organic sulfur compounds in them. The effect of these results on near-term use of Ohio coals is rather minimal. However, it will benefit the long-term use of Ohio coals. Quantification of the increased use of Ohio coals can be made after the completion of a detailed process economic study.

(IV.4) Cost per Processed Ton of Ohio Coals

The project was aimed at development of a novel clean coal process using an emerging separation technology. In order to make a cost analysis of the process, pilot plant data for the process would be needed. It is estimated at \$25-45/ton of coal for cleaning both organic and pyritic sulfur by this process in combination with a physical cleaning method.

(IV.5) Next Steps

We will be investigating into the continuation of the project. The next project will be aimed at design and operation of a 10 kg/hr of continuous treatment pilot plant. This pilot plant will enable us to obtain the data necessary to address issues such as moisture and disposal of extracted sulfur compounds that were beyond the scope of the initial project. In this regard, we plan to have a project assessment/evaluation meeting with OCDO managers.

V. FINAL BUDGET SUMMATION

At the moment of this reporting, the official, final budget information is not available. The following is the tentative information, and it will be revised as soon as the final numbers are available.

(V.1) Total Program Budget by Major Category

	OCD0	UA *
Personnel (including fringes)	\$76,200	\$51,090
Supplies	13,000	
Equipment	15,000	
Indirect Cost	37,464	21,458
TOTAL	\$141,664	\$72,548

* The University of Akron

(V.2) Expenditures of OCD0 Funds for the Project

Personnel	\$75,133
Supplies	16,002
Equipment	13,447
Indirect Cost (42% of total direct cost)	36,621
TOTAL	\$141,203

Note: This information is not final. If this is in discrepancy with the accounting office report, please disregard this information.

APPENDIX A
TEMPERATURE AND PRESSURE CONVERSIONS

Temperature	
K	F
300	80
400	260
500	440
600	620
700	800

Pressure	
atm	psi
50	735
100	1470
150	2205
200	2940
250	3675
500	7350
1000	14700
1500	22050
2000	29400
2500	36750
3000	44100
3500	51400

END

**DATE
FILMED**

8/19/93