



Air-oxidation and extraction of organic substances in oil shales  
by Raymond L Porter

A THESIS Submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering  
Montana State University  
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**Abstract:**

This research is a continuation of a study being conducted at Montana State College concerning the production of organic substances by air-oxidation of Green River, Wyoming oil shale in a fluid bed reactor, followed by extraction in alkaline water solution.

A study was made concerning the effect of specific surface area of reactor feeds on yield and on oxidation time. A maximum yield of 5.0 per cent was indicated when the optimum oxidation time was used for each specific surface. Previous investigators have reported higher yields than the above figure, but it was established that their products contained amounts of clay which filter paper could not remove. For this research the colloidal clay was eliminated from the products by filtering the water extract through a layer of diatomaceous silica. Optimum oxidation time decreases lineally with increase in specific surface.

In order to determine the effect of particle size on yield\* three series of tests were made holding specific surfaces of 170, 225, and 315 square centimeters per gram, respectively, constant. Oxidation time of five hours was kept constant, also. For each specific surface the yield increased as the average particle diameter increased when there was more than one screen size in the reactor feed.

Extraction tests indicated that the degree of acidity (pH) had little effect on the relative amounts of acid soluble and acid insoluble products produced.

A series of runs was also made with Colorado shale which showed that optimum reactor conditions of temperature and pressure, 240 degrees centigrade and 40.2 psia, were the same as those for Wyoming shale. Optimum oxidation time is longer for Colorado shale, however. A maximum yield of 11.5 per cent organics was obtained. Optimum extraction variables for Colorado shale were found to be: 20 grams of shale, 300 milliliters of water, 3 grams of sodium carbonate, and extraction time , of one hour.

Infrared spectral curves show Wyoming and Colorado acid soluble products to be structurally the same. Comparison of spectral curves of Wyoming acid soluble and acid insoluble organics indicate that these two products are similar. The main difference is that the acid insoluble product is probably more highly polymerized.

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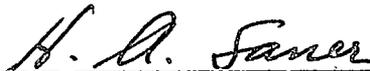
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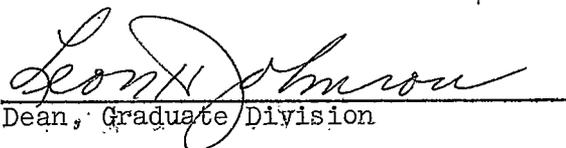
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Bozeman, Montana

August, 1961

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A study was made concerning the effect of specific surface area of reactor feeds on yield and on oxidation time. A maximum yield of 5.0 per cent was indicated when the optimum oxidation time was used for each specific surface. Previous investigators have reported higher yields than the above figure, but it was established that their products contained amounts of clay which filter paper could not remove. For this research the colloidal clay was eliminated from the products by filtering the water extract through a layer of diatomaceous silica. Optimum oxidation time decreases lineally with increase in specific surface.

In order to determine the effect of particle size on yield, three series of tests were made holding specific surfaces of 170, 225, and 315 square centimeters per gram, respectively, constant. Oxidation time of five hours was kept constant, also. For each specific surface the yield increased as the average particle diameter increased when there was more than one screen size in the reactor feed.

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## INTRODUCTION

### A. Oil Shales

Shale is a cleavable, fragile rock formed by the consolidation of clay, mud, or silt, and has a laminated structure. Oil shale contains organic substances which resulted from the slow decomposition of animal and vegetable matter within the rock strata over long periods of time. When this type of shale is pulverized and heated to above 250 degrees centigrade, condensable oil is produced which has properties similar to those of liquid petroleum found in underground wells. In fact, the word 'petroleum' is derived from two Latin words meaning 'rock oil'. This term was applied to oils distilled from rocks in England as early as the middle of the fourteenth century. Oil shale as mined is a dry rock of dark brown or gray-to-black color (1).

Oil shales are widely distributed throughout the world. Large deposits are found in the United States, England, Germany, South Africa, Russia, Peru, Burma, and New Zealand. In this country, the states with the largest oil shale resources are Colorado, Utah, Wyoming, Kentucky, and Indiana (1).

Colorado oil shales contain from 15 to 40 per cent\* organic matter, the amount depending on the vein from which it is mined. From 65 to 71 per cent of these organics are recoverable as petroleum (3). Green

\* All per cent figures given in this thesis are on a weight basis.

River, Wyoming bottom shale is known to contain from 8 to 10 per cent organics (6).

It is not economically profitable to produce synthetic fuels from oil shales on a commercial basis in the United States at the present time. Operating and equipment costs are too high to compete with petroleum crudes.

This research was done as part of an effort to chemically change most of the shale organics from water-insoluble compounds to compounds that dissolve in water by air-oxidation at sub-retorting temperatures. It is hoped that some of these extractable organic compounds might have economic value.

#### B: History of Project

This project was started early in 1959 and was sponsored until June 1960 by Westvaco Division of Food Machinery and Chemical Corporation. Westvaco produces a high grade soda ash (sodium carbonate) from trona at Green River, Wyoming. The trona, sodium sesquicarbonate, is a mineral composed of hydrous sodium carbonate and sodium bicarbonate. The trona lies between two layers of shale, both of which contain organic matter in varying degrees. Because of its closeness to the shale, the trona contains small amounts of organic matter which finds its way into processing liquors. Investigations into problems encountered because of the presence of this organic matter caused Westvaco to consider the feasibility of recovering organic substances

from the shale deposits (6).

The research work reported in this thesis is the fourth in a continued series of investigations at Montana State College concerning the oxidation of shale organics, and extraction and identification of the products. Colorado oil shale was included in this study to compare its characteristics with those of Wyoming shale.

Suiter (8), the first worker on this project, oxidized the oil shale organic matter by two different procedures. One method combined the oxidation and extraction operations by heating the shale and alkaline potassium permanganate solution to 200 degrees centigrade in a sealed Parr extraction apparatus. He reported a maximum yield of 6.7 per cent organic matter by a series of six extractions, each of 20 hours duration. Realizing this method was not commercially feasible, he built an electrically heated Pyrex glass column in which the fluid-bed principle was used to air-oxidize the shale organics. Subsequent extraction of the organics was done in the Parr extraction apparatus using sodium carbonate solution. Sodium carbonate was used to produce the alkalinity because it was available from Westvaco. Only two low temperature air-oxidation runs were made, and the maximum yield was 1.5 per cent. He reported two organic products, one that was insoluble in acid solution and one that was soluble. Suiter also made an identification study of his organic products with the aid of the Beckman IR-4 infrared spectrophotometer. He concluded that both were essentially

complex organic acids.

Erickson (4) carried on the air-oxidation studies in a larger, electrically heated, stainless steel, fluid-bed reactor. He reported a maximum yield of 10.1 per cent by air-oxidizing the oil shale for 30 hours at a temperature of 200 degrees centigrade and 30.2 psia pressure. He also optimized extraction conditions in an open boiling apparatus. He decided that the best method of extraction was to boil 30 grams of shale in 300 milliliters of water at total reflux for one hour. He concluded that it was not necessary to add sodium carbonate to the mixture. There was enough trona in the Green River shale to produce sufficient alkalinity to extract all of the oxidized organic matter.

Johnson (6) continued the air-oxidation research with the stainless steel reactor. He made studies at higher temperatures and pressures than the previous workers, and made preliminary investigations into the effects of shale surface area on yield. He reported that a maximum yield of 11.2 per cent organics was obtained using the oxidation conditions of seven hours, 240 degrees centigrade, 40.2 psia pressure, and a size distribution in the shale charge of -12, +100 mesh (Table III). Air velocity was kept at 0.55 feet per second for all runs. Temperature could not be controlled above 240 degrees centigrade. At higher temperatures, uncontrollable exothermic reactions occurred, probably due to rapid volatilization of organics from the shale charge and subsequent reaction with air. He also made an oxidation time versus yield study for

a size distribution of -35, +150 mesh (Table III) at optimum conditions, and reported a maximum yield of 9.8 per cent in five hours. This indicated that as the specific surface of the shale charge increased, optimum oxidation time decreased. Infra-red spectral curves made from air-oxidized products showed that these products were similar in structure to the potassium permanganate oxidized organic substances produced by Suiter.

#### C. Purpose of this Investigation

The objectives of this research were: to make a further study of the effect of specific surface on oxidation time; to investigate the effect of average particle size on yield; and to determine the optimum oxidation and extraction variables for Colorado shale. The effect of pH on relative amounts of acid-insoluble and acid-soluble products was studied, and an improved filtration procedure was devised to remove colloidal clay from the products.

## EQUIPMENT AND MATERIALS

### A. Fluid-Bed Reactor

The vertical reactor (Figure 1) consisted of two parts, the body and the head, which were joined by a union. The reactor body contained a pre-heat zone and an expansion chamber. The reactor head consisted of a wash chamber and a needle valve which was used for manual control of the air velocity. Air entered at the base of the reactor.

#### 1. Reactor Body

The reactor body consisted of a four-foot length of one-inch (inside diameter) stainless steel pipe welded at the top to a six-inch length of two-inch black iron pipe. The bottom one foot was packed with one-eighth-inch stainless steel helices and this section acted as the preheat zone. Atop the helices was a stainless steel screen which served as a bed support and an air disperser. The three-foot section above the screen was the reaction zone, and the two-inch pipe served as an expansion chamber. Three nichrome wire coils, insulated with ceramic beads, were wound around the outside of the pipes. Each coil was connected to a 110-volt Variac for manual control of the energy supply. One coil supplied heat to the preheat section and the other two heated the rest of the reactor body. The pipe and coils were covered with a two-inch thickness of magnesia mud insulation and the insulation was covered with aluminum sheet to reduce radiation heat losses. The reactor body was supported on a pivot so it could be easily inverted for dumping. It was held in

vertical position by a U-bracket at the base.

## 2. Reactor Head

A two-inch union connected the reactor head to the reactor body. The reactor was loaded and unloaded with the head removed. Starting from the union the pipe diameter was reduced to one-half inch. This pipe was topped by a one-half-inch tee, and through the straight-run section the thermocouple probe was inserted. Connected to the side of the tee was the U-shaped scrubbing chamber made of one-inch pipe. The one leg of the U contained a union for cleaning purposes and valves at both ends for filling and draining scrubbing water. At the upper end of the scrubber was a short section of one- and three-fourths-inch pipe which acted as an expansion chamber. After the expansion chamber was a pressure gauge (0-60 pounds per square inch) and then a needle valve. The gauge indicated the pressure inside the reactor and the valve was used for manual adjustment of the air velocity. Inserted into the inlet end of the valve was a stainless steel screen which removed shale dust that got through the scrubber.

## B. Accessories to Reactor

### 1. Air Supply

The air used to fluidize the shale bed and to furnish oxygen for the chemical reactions occurring within the bed was piped to the unit from a laboratory compressor at 105 pounds per square inch gauge. The air entered the reactor through a regulator valve where it was adjusted to the desired pressure.

2. Manometer and Wet-Test Meter

Following the needle valve after the wash chamber, the air flowed through an orifice which was connected to an inclined air-water manometer. From the manometer the air went through a wet-test meter and out into the room. The wet-test meter was used to set the air space velocity, which was adjusted with the needle valve. The manometer reading gave a continual check on the velocity.

3. Temperature Recorder

A Minneapolis-Honeywell Brown "Electronik" temperature recorder connected to iron-constantan thermocouples inside the reactor gave temperature readings in the preheat and reaction zones. In the air preheating zone the temperature was read three inches below the bed support. The temperature in the reaction zone was read approximately one foot above the bed support.

C. Extraction Equipment

1. Extraction apparatus (Figure 2) used to dissolve shale organics in alkaline water solution consisted of a 600-milliliter Berzelius beaker and rubber stopper; a Fisher "Fultork Labmotor" fitted with a one- and three-fourths-inch diameter, four-winged, propeller stirrer; a water-cooled condenser; an adapter fitted with rubber stopper; a support stand and screen; and a Bunsen burner. The stirrer shaft was inserted through the center of the wide stopper and a mercury seal was used to provide a vapor-tight fit. The extraction mixture was boiled and stirred in this apparatus. The condenser condensed all

leaving vapors so the liquid volume remained constant throughout the operation.

## 2. Centrifuge

An International Model H centrifuge was used to remove most of the finer shale particles from the extraction mixture after refluxing.

## 3. Miscellaneous Equipment

A Buchner funnel partial vacuum filtering apparatus was used for filtering the extract after centrifuging.

An electrically heated hot plate was used to evaporate the water from the extract.

A small laboratory distillation unit removed acetone from the redissolved organics.

A infra-red lamp dried the acid-soluble organic product from acetone solution.

## D. Materials

1. Oil Shale: Green River, Wyoming, lower bed; 22.3 gallons of 27.7 API gravity oil per ton; Colorado, 37.8 gallons of 27.0 API gravity oil per ton
2. Air: Gardner-Denver compressor supplied at 105 pounds psia
3. Water: Bozeman tap water
4. Sodium Carbonate: Westvaco light soda ash
5. Hydrochloric Acid: Fisher reagent grade, concentrated
6. Acetone: Commercial grade, redistilled at a reflux ratio of

10-1 in a 30-theoretical plate packed distillation  
column

7. Diatomaceous Silica: Johns-Manville "Super-Cel"

## PROCEDURE

### A. Air-Oxidation of Oil Shale

#### 1. Preparation of Feed

The oil shale was received in the form of large chunks. In order to use the shale in the fluid-bed reactor, the chunks had to be broken into particles of small diameter by a series of operations. The large pieces were first broken down into pieces of two inches in diameter or less by means of a sledge hammer. These pieces were reduced in size by putting them through a jaw crusher and then through a Montgomery Ward Model G hammer mill. Next, the shale was screened through a series of Tyler screens, and all plus 12 mesh material was ground smaller in the laboratory ball mill. All of the shale was then classified into screen size ranges by use of a set of Tyler screens and the Roto-tap screen shaker. The shale held by each screen was placed in a separate container and each reactor charge was blended into the size distribution desired. The analyses of the size distributions used in this research are given in Tables I and III.

#### 2. Operation of Reactor

The procedure outlined by Johnson (6) was followed in this research. With air flowing through it, the reaction zone was heated to a temperature approximately ten degrees below the desired operating temperature. The preheat section temperature was held about 35 degrees below that of the reaction zone. The heat to the

reaction zone was then turned off and the reactor head removed. The shale charge was added next, and just enough air was kept flowing to fluidize the charge but still keep it in the reactor body. The reactor head was then placed back on the body and the union tightened. The pressure regulator and the needle valve were adjusted until the reactor was at operating pressure and the air velocity was 0.55 feet per second (based on the empty reaction zone diameter). The heat to the reaction zone was again turned on and the reactor was slowly brought up to operating temperature. The air flow was readjusted to 0.55 feet per second. The preheat air was maintained from 50 to 100 degrees below that of the reaction zone during the run to help prevent uncontrollable exothermic reactions from starting. Fluidization efficiency was the lowest at the bottom of the reaction zone. Johnson (6) and Erickson (4) both reported overheating which they assumed occurred near the bed support. The overheating, they theorized, caused shale oil to vaporize and rapid exothermic reactions to occur.

Johnson reported optimum temperature and pressure for maximum yields of organic matter to be 240 degrees centigrade and 40.2 psia, respectively, for the Wyoming shale. Johnson had also established that optimum oxidation times for size distributions (Table III) of -12, +100 mesh (specific surface = 186 square centimeters of surface area per gram) and -35, +150 mesh (specific surface = 312 square centimeters of surface area per gram) were seven hours and five hours,

respectively. Since this indicated that optimum oxidation time decreased as specific surface increased, it was decided to make runs of three, four, and five hours at optimum conditions using a size distribution of -48, +150 mesh (specific surface = 354 square centimeters of surface area per gram) to see if optimum oxidation time decreased further.

Three series of runs were then designed to determine whether the varying of average particle diameter had any effect on yield of organics when the specific surface was kept constant. Studies were made with specific surfaces of 170, 225, and 315 sq. cm. per gm. Average particle diameter and specific surface for each Tyler screen range are listed in Table II (2). In this table -14, +20 mesh means that all of the particles went through the 14 mesh screen, but were retained on the 20 mesh screen. The average particle diameter is the arithmetic average of the lengths of openings in the two screens. The mesh number is the number of openings per linear inch, and for any given screen opening the mesh number varies with the diameter of wire used to make the screen. The specific surfaces were taken from data of average particle diameter versus specific surface given in Brown (2). No plot was available for shale so the one used was for quartz. Quartz has similar physical properties to shale. The following method was used to calculate the average particle diameter at constant specific surface:

Let: A = Specific surface of shale feed (sq. cm. of surface area per gm.)

a = Specific surface of shale particles of a particular screen size (sq. cm. per gm.) (Table II)

w = Weight fraction of shale particles of a particular screen size (gm. per gm. of feed)

d = Average diameter of shale particles of a particular screen size (cm.) (Table II)

D = Average diameter of shale particles in shale feed (cm.)

N = Average number of particles in one gram of shale feed

K = Average shape factor of particles in shale feed

I = Number of particular screen sizes used in shale feed

$$A = \sum_{i=1}^I (w_i)(a_i) = NKD^2 \quad (\text{Equation 1})$$

$$\sum_{i=1}^I \frac{(w_i)(a_i)}{d_i} = \frac{NKD^2}{D} = NKD \quad (\text{Equation 2})$$

$$D = \frac{\sum_{i=1}^I (w_i)(a_i)}{\sum_{i=1}^I \frac{(w_i)(a_i)}{d_i}} \quad (\text{Equation 3})$$

The specific surfaces for the size distributions listed in Table III were calculated using Equation 1, also.

Runs B-4 to B-20 (Table I), inclusive, were designed keeping the specific surface constant at 225 square centimeters per gram. The specific surface was kept constant at 170 for Runs B-21 through B-24, and constant at 315 for Runs B-25 through B-28.

In order to determine the maximum yield for a specific surface of 170 sq. cm. per gm., Run B-29 was run for seven hours, the optimum time reported by Johnson (6) for that specific surface. B-30 was an attempt to determine more closely the optimum oxidation time for a specific surface of 225. For Runs B-29 and B-30, shale feeds with optimum average particle diameters determined in previous runs were used.

Runs C-1 through C-5 (Table IV) were designed to determine the effect of oxidation time on yield using Colorado shale of size distribution -35, +150 mesh. Temperature and pressure were held constant at 240 degrees centigrade and 40.2 psia, respectively. Colorado shale Runs C-6 to C-14, inclusive, were designed to study the effects of temperature and pressure on yield. The oxidation time was held constant at seven hours, and a size distribution of -12, +100 mesh was used.

In an attempt to determine the approximate loss of organic carbon during a run, the exit air from the reactor was bubbled through calcium hydroxide solution for fifteen minutes during the latter part of Run B-29, and again during the first part of Run B-30.

Fifteen minutes was used because of the limited solubility of calcium hydroxide in water. Carbon dioxide reacts with calcium hydroxide to form insoluble calcium carbonate. After each bubbling operation the calcium carbonate was filtered from solution, dried, and weighed.

#### B. Extraction of Oxidized Organic Matter

The procedure used for the extraction of oxidized organics from Green River, Wyoming bottom shale was the same as that devised by Erickson (4), except for one filtration step. Since it was experimentally determined that products obtained by the old procedure contained clay, it was decided to filter the extract solution through a layer of diatomaceous silica to remove the colloidal particles that were going through the filter paper. The products were then free of clay. Extraction variables for Colorado shale were studied, and the change in the extraction procedure to remove these organics is given later in this section. The general outline of the extraction procedure is shown schematically in Figure 3.

##### 1. Wyoming Shale Procedure

(a) Thirty grams of oxidized shale was weighed on a two-pan balance. It was then mixed with 300 milliliters of tap water in a 600-milliliter Berzelius beaker and refluxed in the extraction apparatus (Figure 2) for one hour.

(b) The extraction mixture was then poured into four centrifuge flasks and was centrifuged for

one hour to settle most of the small spent shale particles. This operation aided the filtration operation.

- (c) The extraction solution was decanted from the centrifuge flasks into a Buchner funnel partial vacuum filtering apparatus, which removed more of the spent shale. The filter paper was then washed with water until the wash solution going into the filtrate was clear. The total volume of the filtrate varied with the amount of wash water needed.
- (d) The exact volume of the filtered mixture was measured. A 100- or 200-milliliter aliquot portion (Table I) of the mixture was then taken and filtered through a Buchner funnel apparatus. The filtering medium was a one-eighth-inch layer of washed diatomaceous silica on top of Whatman No. 42 fine grained filter paper.
- (e) The filtrate was then acidified with concentrated hydrochloric acid, and the precipitate that formed was allowed to settle.
- (f) The mixture was filtered through a weighed filter paper and the precipitate and filter paper were dried and weighed. The dried precipitate

was the acid insoluble product.

- (g) The filtrate from (f) was evaporated to dryness in a 400-milliliter beaker on the hot plate. The mixture was continually stirred when near dryness to prevent spattering and charring of the organics.
- (h) Acetone was added which dissolved the organics, but left most of the inorganic salts undissolved.
- (i) The acetone solution was filtered into a laboratory distillation unit and the acetone was distilled from the mixture.
- (j) The organic residue was again dissolved in acetone and filtered into a weighed beaker. The remaining inorganic salts were removed by this process.
- (k) An infrared lamp vaporized all of the acetone in an atmosphere of nitrogen gas, leaving the acid soluble product.
- (l) The beaker and product were weighed and the weight of the acid soluble product was recorded.
- (m) The per cent yield of organics was then calculated by the following method:

$$\frac{\text{Total Wt. of Products} (\text{Total Vol. of Extract}) (100)}{\text{Wt. of Shale Sample} (\text{Aliquot Vol. of Extract})}$$

## 2. Colorado Shale Procedure

This procedure was identical with that for Wyoming shale with the exception of Step (a).

- (a) Twenty grams of oxidized shale was weighed on a two-pan balance. It was then mixed with 300 milliliters of tap water and three grams of sodium carbonate in a 600-milliliter Berzelius beaker and refluxed in the extraction apparatus (Figure 2) for one hour.

## 3. Effect of pH

The effect of the degree of acidity on the relative amounts of acid insoluble and acid soluble products was studied. When hydrochloric acid is added to the filtered extraction solution, the acid insoluble product begins to precipitate at about a pH of three as determined by a Beckman pH meter. Two sets of analyses were done using a different extraction solution for each set.

## C. Identification of Products

Samples of Wyoming acid insoluble and acid soluble products, Colorado acid soluble product, and dried centrifuge mud were taken to the Chemistry Department. Graphs were made of these samples by the Beckman IR-4 infra-red spectrophotometer for comparison purposes. Nitrogen and sulfur analyses were run on the Wyoming acid insoluble and acid soluble products by research workers in the Chemical Engineering Laboratory.

## DISCUSSION OF RESULTS

### A. Air-Oxidation

Data for the air-oxidation runs using Green River, Wyoming shale are given in Table I, and the data for runs using Colorado shale are listed in Table IV. Runs concerning Wyoming shale are designated with the letter (B), and those concerning Colorado shale are designated with the letter (C).

Three oxidation tests (B-1, -2, -3), using a size distribution of -48, +150 mesh (specific surface = 354 square centimeters of surface area per gram), were made. The optimum time for maximum yield of organics was found to be about four hours (Figure 4). Johnson (6) had established that the optimum oxidation time for a specific surface of 186 was about seven hours, and that for a specific surface of 312 was approximately five hours. A plot of specific surface versus oxidation time (Figure 5) shows that optimum oxidation time decreases almost lineally with increase of specific surface in the specific surface range studied. Size distributions with specific surfaces greater than 354 would be almost impossible to run in the fluid-bed reactor because of the increased shale dust problems. Some of the dust gets through the scrubber and plugs the needle valve, which makes reactor conditions very hard to control. No attempt, therefore, was made at this time to use shale charges with specific surfaces larger than 354.

The relationship of average particle size to yield was studied next. This was done by preparing a number of charges each having the same specific surface but different average particle diameter. Each of these charges was oxidized for five hours under the same reactor conditions. The average particle diameter for each mixture was calculated by the use of Equation 3 given in the Procedure. Runs B-4 through B-20 were made keeping the specific surface constant at 225 sq. cm. per gm. Figure 6 is a plot showing the results. As the average particle diameter increases, the per cent yield tends to increase as long as the shale feed contains more than one screen size. The different symbols locating the points on the graph denote the number of particular screen sizes used to make the shale feed for the runs. The number of screen sizes used does not seem to affect the correlation, provided there is more than one used. As Johnson (6) reported in his work, the yield is always less for the same specific surface when feed from a single screen size is used. Johnson postulated that the reduction in yield was caused by less efficient fluidization within the bed. Run B-15 (average particle diameter = 0.0203 cm., yield = 5.0 per cent) does not correlate with the rest of the data, and no plausible explanation can be offered here. The vertical long dashed line on the graph indicates the maximum average particle diameter obtainable for the given specific surface. That diameter is always the one in which a single screen size makes up the feed. When two or more screen sizes are blended to produce a given specific surface, the total number of particles increases; so, consequently, the average par-

particle diameter decreases. Specific surface area is a function not only of the average particle diameter and the shape factor, but also of the number of shale particles. Four runs (B-21 through B-24), keeping the specific surface constant at 170 sq. cm. per gm., and four runs (B-25 through B-28), keeping the specific surface constant at 315 sq. cm per gm., were then made to see if the same correlation existed as in the previous series. Figures 7 and 8 show the results of these two series of runs. The graphs show the same trend as was indicated when the specific surface was held constant at 225 sq. cm. per gm. The yields varied directly with the average particle diameters when the feed contained more than one screen size. The reason theorized for this increase in yield with increase in average particle diameter is that the feed having a smaller average particle diameter must contain a larger weight portion of coarser particles than the feed with a larger average particle diameter. For example, compare Runs B-13 and B-6 which have average particle diameters of 0.0233 cm. and 0.0221 cm., respectively. The feed for B-13 contained 37.9 per cent -65, +100 mesh and 62.1 per cent -35, +48 mesh. In B-6, although the -65, +100 mesh fraction was increased to 51.4 per cent, the remaining 48.6 per cent of the feed now consisted of -20, +35 mesh shale. This much larger increase in weight of harder-to-oxidize coarse material more than offsets the increase in fines, and consequently the yield of organics decreased when the average particle diameter decreased. Similar comparisons can be made between all runs in which specific surface is held constant.

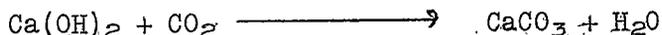
Figure 9, which was plotted from results of Runs B-3, B-28, B-29, and B-30, indicated that a maximum yield of approximately five per cent of the shale weight can be produced from Green River, Wyoming lower bed shale for feed of any given specific surface. This requires that the optimum oxidation time and optimum average particle diameter be used for the given specific surface. Each of these runs employed an oxidation time very close to the optimum, as indicated by Figure 5, and the average particle diameter of the feed, in each case approached the maximum for the specific surface in question.

From the foregoing discussion it can be concluded that, in order to produce a maximum yield, shale feed of a particular specific surface should contain more than one screen size, have an average particle diameter as high as possible, and be oxidized for the optimum length of time.

Colorado shale, Runs C-1 to C-5, inclusive, showed that the optimum oxidation time for a size distribution of -35, +150 mesh was approximately seven hours (Figure 10). This time is somewhat longer than for the Wyoming shale and might be explained by the fact that the Colorado shale is much more dense. The maximum yield obtained was 11.5 per cent. All runs were made at 240 degrees centigrade, 40.2 psia, and an air velocity of 0.55 feet per second. Runs C-6 through C-14 were a temperature and pressure study keeping oxidation time at seven hours, air velocity at 0.55 feet per second, and using a size distribution of -12, +100 mesh.

Figure 11 shows that the yield increased as the reactor temperature increased for the constant pressures used. Highest yields were obtained at a temperature of 240 degrees centigrade. Temperatures above this figure could not be maintained accurately because of the rapid exothermic reactions that occurred. These results are the same as were found for the Wyoming shale. Figure 12 shows the effect that reactor pressure has on yield and indicates that the optimum pressure was 40.2 psia. Johnson (6) reported that the per cent yield of oxidized organics from Wyoming shale also decreased when the reactor pressure was increased from 40.2 to 50.2 psia at 240 degrees centigrade.

In an attempt to determine the approximate loss of carbon during a run, which would give an indication of the amount of organic matter lost to the air stream, three tests were made by bubbling the exit reactor air through calcium hydroxide solution. Carbon dioxide, formed by the exothermic chemical reaction of carbon compounds in the oil shale and the oxygen in the air, reacts with calcium hydroxide in solution as shown by the following chemical equation:



The calcium carbonate formed was very insoluble in water and was filtered from solution, dried, and weighed. Three fifteen-minute tests were made: one during the latter part of Run B-29; the second during the early part of Run B-30; and the last at identical reactor conditions, but without shale in the reactor to determine the amount of carbon dioxide in the air itself. The weights of calcium carbonate produced were 0.169 gram,

0.385 gram, and 0.041 gram, respectively. Calculations show that, after subtracting 0.041 gram from each of the calcium carbonate weights obtained from the shale test runs and averaging, the average carbon loss was 0.0283 gram per fifteen minutes. Assuming that 200 grams of shale feed contains ten per cent organic matter, the average loss of carbon was 2.8 per cent, on an organic matter basis, during a five-hour run. These tests, though rather incomplete, show that the loss of organic matter is appreciable and helps to explain why the per cent yield of oxidized organics decreases when optimum oxidation time is exceeded (Figures 4 and 10).

B. Extraction of Oxidized Organic Matter

The extraction procedure used in this research to extract oxidized organic matter from Green River, Wyoming oil shale was determined experimentally by Erickson (4). One addition was made, however. After burning a quantity of acid insoluble product, produced using the old procedure, in a muffle furnace, considerable ceramic-appearing ash remained in the crucible. This ash was assumed to be clay which was apparently not being removed by the filter paper during the filtration operation. Analyses with the infrared spectrophotometer verified this assumption. To remove the finely divided clay particles, therefore, a method was devised whereby the extraction solution was filtered through an approximate one-eighth-inch thickness of washed diatomaceous silica on top of Whatman No. 42 filter paper in a Buchner funnel apparatus. After burning a quantity of product, produced using this step in the extraction procedure, there was no ash except that from the filter paper which held the product.

At this point it should be emphasized that this clay removal is responsible for the yields reported in this research being lower than those reported by previous investigators on this project. Analyses run on a composite of acid insoluble products produced by Johnson (6) showed an average ash content of 45.5 per cent by weight. This amount is sufficient to account for the higher yields that he reported.

The extraction variables for Colorado shale were studied and that data is compiled in Table V. The extraction solution containing ten grams of sodium carbonate was very hard to dry on the hot plate, and there were some inorganic salts in the acid soluble product, which gave a high yield figure. From the study it was decided to use 20 grams of shale, 300 milliliters of water, 3 grams of sodium carbonate, and reflux the mixture for one hour.

The effect of pH on the relative amounts of acid insoluble and acid soluble products was investigated. The pH at which the precipitate comes out of solution upon acidification was determined to be between three and two. Two different extraction solutions were each divided into two equal parts. The four solutions were then acidified to different pH values, and the regular analysis procedure was used to determine the amounts of acid insoluble and acid soluble products formed. The results are given in the table below.

<u>Extraction Solution.</u>	<u>pH</u>	<u>Wt. of Acid Insoluble (gm.)</u>	<u>Wt. of Acid Soluble (gm.)</u>
1	2.00	0.488	0.177
1	0.75	0.505	0.175
2	2.10	0.134	0.163
2	0.70	0.122	0.167

From the above data it can be seen that there is no appreciable effect on relative amounts of products when the pH is changed.

### C. Identification of Products

The acid soluble product is a gummy, semi-solid and is brown-to-black in color. The acid insoluble product is a black solid.

Infrared spectrographs (Figures 13, 14, 15, 16) were made and interpreted by Dr. G. Baker of the Montana State College Chemistry Department. Comparison of Figures 13 and 14 show that the Wyoming and Colorado acid soluble products are almost identical. The broad band near 3000 Kaysers indicates multiple hydroxyl (OH) stretching, such as from carboxyl acids or alcohols in conjunction with acids. The relatively broad band at 1730 Kaysers is suggestive of carbonyl (C=O) stretch, such as in esters and/or ketones. The band between 1200 and 1300 Kaysers indicates carbon and oxygen single bond (C-O) stretch, such as in acids and/or esters. It was difficult to get a good film of the acid insoluble product on the salt plate to run on the infrared spectrophotometer. Even though the structures are diffuse, however, the graph (Figure 15) indicates that

similar structures to those that are in the acid soluble product are present in the acid insoluble product. It is possible that both products are essentially acid polymers, the main difference being that the acid insoluble product contains higher molecular weight compounds. The degree of oxidation might also be a possible difference.

Johnson (6) reported that the infrared spectrographs made from air-oxidized organic substances were similar to the infrared graphs made of products which had been oxidized by potassium permanganate by Suiter (8). Robinson, Cummins, and Stanfield (7) reported that by chemically transforming the two products of potassium permanganate oxidation of Colorado oil shale organic matter into n-butyl esters, the products were characterized. Although the conditions under which they carried out their oxidation was quite different from those used by Suiter, it is interesting to note that one product was characterized by dicarboxylic acids of the alkane series, oxalic to adipic. The other product contained cyclic higher molecular weight dicarboxylic acids which were not identified.

The infrared spectrograph of the centrifuge mud (Figure 16) shows that it is clay (5). This sample was taken from the settlings in one of the centrifuge flasks after centrifuging one of the extraction solutions. This spectrograph was included in the Appendix because a comparison of it and the infrared spectrograph of the acid insoluble product in Johnson's thesis (6) show similar low points at 2900, 1470, 1380, and 735 Kaysers, which indicates that clay was in the product.

Sulfur and nitrogen determinations were made on the Wyoming acid insoluble and acid soluble products by Research Fellows L. Orr and K. Cox, using analysis apparatus available in the Chemical Engineering Department Research Laboratory. The results are given below:

	<u>Acid Insoluble</u>	<u>Acid Soluble</u>
Sulfur	1.60%	1.31%
Nitrogen	2.54%	1.94%

This compares to sulfur and nitrogen analyses of 0.91 per cent and 1.66 per cent, respectively, for the oil retorted from this same shale, and 1.30 per cent sulfur and 2.60 per cent nitrogen found in the kerogen of a Colorado shale (7).

SUMMARY

A maximum yield of organic matter equal to approximately five per cent of the shale weight can be obtained by air-oxidizing Green River, Wyoming lower bed oil shale in the fluid-bed reactor. In addition to the optimum reactor conditions of 240 degrees centigrade, 40.2 psia, and an air velocity of 0.55 feet per second, the shale feed should be of optimum size for the oxidation time used. As specific surface area of the feed increases, the optimum oxidation time decreases. Also, for feed of a given specific surface, the average particle diameter should be as high as possible and the feed should contain more than a single screen size.

By bubbling the exit air from the reactor through calcium hydroxide solution, the amount of carbon loss during a five-hour run was estimated to be 2.8 per cent of the organic matter that was originally present.

The optimum fluid-bed reactor conditions for the air-oxidation of Colorado oil shale were found to be 240 degrees centigrade and 40.2 psia, using an air velocity of 0.55 feet per second. A maximum yield of 11.5 per cent was obtained at these conditions when using shale feed with a size distribution of -35, +150 mesh and an oxidation time of seven hours.

Colloidal clay was eliminated from the products by filtering the centrifuged extraction mixture through a layer of diatomaceous silica.

A pH of between three and two is required in the acidification of the extraction solution to precipitate the acid insoluble product. However, excess acidity does not affect the relative amounts of acid insoluble and acid soluble products formed.

Extraction variables for Colorado shale were determined to be 300 milliliters of tap water, 3 grams of sodium carbonate, 20 grams of oxidized shale, and a refluxing time of one hour.

Infrared graphs of Wyoming and Colorado acid soluble products show them to be structurally very similar. Comparison of infrared graphs made from Wyoming acid insoluble and acid soluble products indicates that both are acid polymers. The acid insoluble product is assumed to contain higher molecular weight compounds because it is a solid at room conditions, and the acid soluble product is a semi-solid.

RECOMMENDATIONS

At this point, it seems that any further work on this particular project should be directed toward the identification of the extractable organic substances and/or breaking down and isolating of the individual compounds of the mixtures obtained.

Once a clearer concept of what chemicals are available is obtained, further work on the oxidation and extraction steps might be warranted from the standpoint of determining conditions that will lead to the maximum yield of specific compounds.

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ACKNOWLEDGMENT

The author wishes to thank the Montana State College Engineering Experiment Station for sponsoring this research project. The author also wishes to thank Professor H. A. Saner for his helpful suggestions, along with former Research Fellow Ronald H. Johnson for his instructions concerning the operation of the equipment.

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TABLE I. AIR-OXIDATION AND EXTRACTION DATA -- GREEN RIVER, WYOMING, BOTTOM SHALE

For the Runs listed below, the oxidation conditions held constant were: temperature - 240°C; pressure - 40.2 psia; air velocity - 0.55 ft. per sec.; weight of shale charge - 200 gm. The extraction conditions held constant were: shale sample weight - 30 gm; time - 1 hr; temperature - 96°C. Mesh sizes are referred to as follows: -14, +20 = 20; -20, +35 = 35; -35, +48 = 48; -48, +65 = 65; -65, +100 = 100; -100, +150 = 150.

Run No.	Size (Mesh)	Size Fract.	Ave. Part. Dia. x 10 <sup>2</sup> (cm.)	Spec. Surf. (cm <sup>2</sup> /gm)	Oxid. Time (hr.)	Total Ext. Vol. (ml.)	Aliquot Vol. (ml.)	Acid Insol. (gm.)	Acid Sol. (gm.)	Per Cent Yield
B-1	65	0.216	1.45	354	5	442	100	0.276	0.055	4.9
	100	0.232								
	150	0.552								
B-2	65	0.216	1.45	354	3	542	200	0.357	0.092	4.1
	100	0.232								
	150	0.552								
B-3	65	0.216	1.45	354	4	465	100	0.267	0.061	5.1
	100	0.232								
	150	0.552								
B-4	35	0.3275	2.03	225	5	598	200	0.212	0.097	3.1
	48	0.3275								
	100	0.1725								
	150	0.1725								
B-5	35	0.2725	2.26	225	5	520	200	0.379	0.082	4.0
	48	0.2725								
	100	0.455								
B-6	35	0.486	2.21	225	5	540	200	0.252	0.130	3.4
	100	0.514								

TABLE I - cont.

Run No.	Size (Mesh)	Size Fract.	Ave. Part. Dia. x 10 <sup>2</sup> (cm.)	Spec. Surf. (cm <sup>2</sup> /gm)	Oxid. Time (hr.)	Total Ext. Vol. (ml.)	Aliquot Vol. (ml.)	Acid Insol. (gm.)	Acid Sol. (gm.)	Per Cent Yield
B-7	48	0.353	2.40	225	5	515	200	0.408	0.093	4.3
	65	0.431								
	100	0.216								
B-8	48	0.722	2.14	225	5	527	200	0.284	0.106	3.4
	100	0.139								
	150	0.139								
B-9	65	1.0	2.52	225	5	480	100	0.158	0.065	3.6
B-10	48	0.248	2.44	225	5	460	200	0.468	0.114	4.5
	65	0.600								
	100	0.152								
B-11	48	0.124	2.48	225	5	470	100	0.212	0.062	4.3
	65	0.800								
	100	0.076								
B-12	48	0.062	2.50	225	5	420	100	0.263	0.063	4.6
	65	0.900								
	100	0.038								
B-13	48	0.621	2.33	225	5	535	100	0.190	0.053	4.3
	100	0.379								
B-14	35	0.673	1.83	225	5	472	100	0.168	0.042	3.3
	150	0.327								
B-15	48	0.78	2.03	225	5	495	100	0.244	0.062	5.0
	150	0.22								

TABLE I - cont.

Run No.	Size (Mesh)	Size Fract.	Ave. Part. Dia. x 10 <sup>2</sup> (cm)	Spec. Surf. (cm <sup>2</sup> /gm)	Oxid. Time (hr.)	Total Ext. Vol. (ml.)	Aliquot Vol. (ml.)	Acid Insol. (gm.)	Acid Sol. (gm.)	Per Cent Yield
B-16	35	0.269	2.09	225	5	483	100	0.150	0.063	3.4
	48	0.373								
	100	0.227								
	150	0.131								
B-17	35	0.1345	2.21	225	5	452	100	0.153	0.066	3.3
	48	0.497								
	100	0.303								
	150	0.0655								
B-18	35	0.168	2.26	225	5	490	100	0.162	0.069	3.8
	48	0.155								
	65	0.500								
	100	0.095								
	150	0.082								
B-19	35	0.0673	2.26	225	5	480	100	0.187	0.068	4.1
	48	0.5590								
	100	0.3410								
	150	0.0327								
B-20	20	0.020	2.05	225	5	490	100	0.125	0.059	3.0
	35	0.341								
	48	0.182								
	65	0.150								
	100	0.141								
	150	0.166								
B-21	48	1.0	3.56	170	5	495	100	0.145	0.038	3.0

TABLE I - cont.

Run No.	Size (Mesh)	Size Fract.	Ave. Part. Dia. x 10 <sup>2</sup> (cm.)	Spec. Surf. (cm <sup>2</sup> /gm)	Oxid. Time (hr.)	Total Ext. Vol. (ml.)	Aliquot Vol. (ml.)	Acid Insol. (gm.)	Acid Sol. (gm.)	Per Cent Yield
B-22	20	0.029	3.40	170	5	505	100	0.165	0.056	3.7
	35	0.384								
	48	0.262								
	65	0.325								
B-23	35	0.289	3.48	170	5	525	100	0.163	0.049	3.7
	48	0.500								
	65	0.211								
B-24	35	0.600	3.26	170	5	465	100	0.159	0.064	3.5
	48	0.125								
	65	0.175								
	100	0.100								
B-25	100	1.0	1.78	315	5	515	100	0.135	0.078	3.7
B-26	48	0.208	1.55	315	5	513	100	0.146	0.082	3.9
	65	0.181								
	100	0.169								
	150	0.442								
B-27	48	0.125	1.63	315	5	515	100	0.168	0.079	4.2
	65	0.109								
	100	0.500								
	150	0.266								
B-28	48	0.0625	1.70	315	5	565	100	0.180	0.070	4.7
	65	0.0545								
	100	0.750								
	150	0.133								

TABLE I - cont.

Run No.	Size (Mesh)	Size Fract.	Ave. Part. Dia. x 10 <sup>2</sup> (cm.)	Spec. Surf. (cm <sup>2</sup> /gm)	Oxid. Time (hr.)	Total Ext. Vol. (ml.)	Aliquot Vol. (ml.)	Acid Insol. (gm.)	Acid. Sol. (gm.)	Per Cent Yield
B-29	35	0.289	3.48	170	7	455	100	0.277	0.074	5.3
	48	0.500								
	65	0.211								
B-30	48	0.062	2.50	225	6	480	100	0.218	0.074	4.7
	65	0.900								
	100	0.038								

TABLE II

Specific Surface For Each Screen Size

<u>Screen Size (mesh)</u>	<u>Average Part. Dia. (cm.)</u>	<u>Specific Surface (cm<sup>2</sup>/gm)</u>
-14, +20	0.1010	87
-20, +35	0.0607	130
-35, +48	0.0356	170
-48, +65	0.0252	225
-65, +100	0.0178	315
-100, +150	0.0126	420

TABLE III

Screen Analyses of Shale Charges

<u>Size Distribution (mesh)</u>	<u>Screen Size (mesh)</u>	<u>Fraction of Charge</u>	<u>Specific Surface of Charge</u>
-12, +100	-12, +20	0.024	186 cm <sup>2</sup> /gm
	-20, +35	0.408	
	-35, +48	0.218	
	-48, +65	0.181	
	-65, +100	0.169	
-35, +150	-35, +48	0.218	312 cm <sup>2</sup> /gm
	-48, +65	0.181	
	-65, +100	0.169	
	-100, +150	0.432	
-48, +150	-48, +65	0.216	354 cm <sup>2</sup> /gm
	-65, +100	0.232	
	-100, +150	0.552	

TABLE IV. AIR-OXIDATION AND EXTRACTION DATA -- COLORADO SHALE

For the Runs listed below, the oxidation conditions held constant were: Air Velocity - 0.55 ft. per sec.; Wt. of Charge - 200 gm. Extraction conditions held constant were: Wt. of Sample - 20 gm.; Wt. of Sodium Carbonate - 3 gm.; Time - 1 hr.; Temperature - 96°C.

Run No.	Size Dist, (Mesh)	Oxid. Time (hr)	Oxid. Temp. (°C)	Oxid. Press. (psia)	Total Ext. Vol. (ml.)	Aliquot Vol. (ml)	Acid Insol. (gm)	Acid Sol. (gm)	Per Cent Yield
C-1	-35,+150	1.5	240	40.2	545	200	0.160	0.061	3.0
C-2	-35,+150	7	240	40.2	565	200	0.724	0.095	11.5
C-3	-35,+150	5	240	40.2	540	200	0.567	0.102	9.0
C-4	-35,+150	10	240	40.2	557	200	0.667	0.113	10.9
C-5	-35,+150	3	240	40.2	501	200	0.231	0.096	4.1
C-6	-12,+100	7	200	30.2	463	200	0.029	0.008	0.4
C-7	-12,+100	7	200	40.2	455	200	0.029	0.013	0.5
C-8	-12,+100	7	200	50.2	438	200	0.019	0.022	0.5
C-9	-12,+100	7	220	30.2	447	200	0.059	0.069	1.4
C-10	-12,+100	7	220	40.2	460	200	0.148	0.065	2.4
C-11	-12,+100	7	220	50.2	473	200	0.080	0.052	1.6
C-12	-12,+100	7	240	30.2	490	100	0.179	0.045	5.5
C-13	-12,+100	7	240	40.2	515	100	0.404	0.042	11.5
C-14	-12,+100	7	240	50.2	473	100	0.207	0.044	6.0
C-15	-12,+100	7	230	40.2	500	100	0.335	0.049	9.6

TABLE V. COLORADO SHALE EXTRACTION DATA

<u>Run No.</u>	<u>Wt. of Shale (gm)</u>	<u>Vol. Water (ml)</u>	<u>Wt. of Sodium Carbonate (gm)</u>	<u>Reflux Time (min)</u>	<u>Per Cent Yield</u>
C-1	15	300	0.3	60	0.3
C-1	15	300	0.5	60	1.2
C-1	15	300	1.0	60	2.2
C-1	15	300	3.0	60	3.0
C-1	15	300	5.0	60	3.0
C-1	15	300	10.0	60	3.7
C-1	15	300	3.0	60	3.0
C-1	20	300	3.0	60	2.9
C-1	30	300	3.0	60	2.9
C-2	30	300	3.0	30	10.5
C-2	30	300	3.0	60	11.5
C-2	30	300	3.0	120	11.6

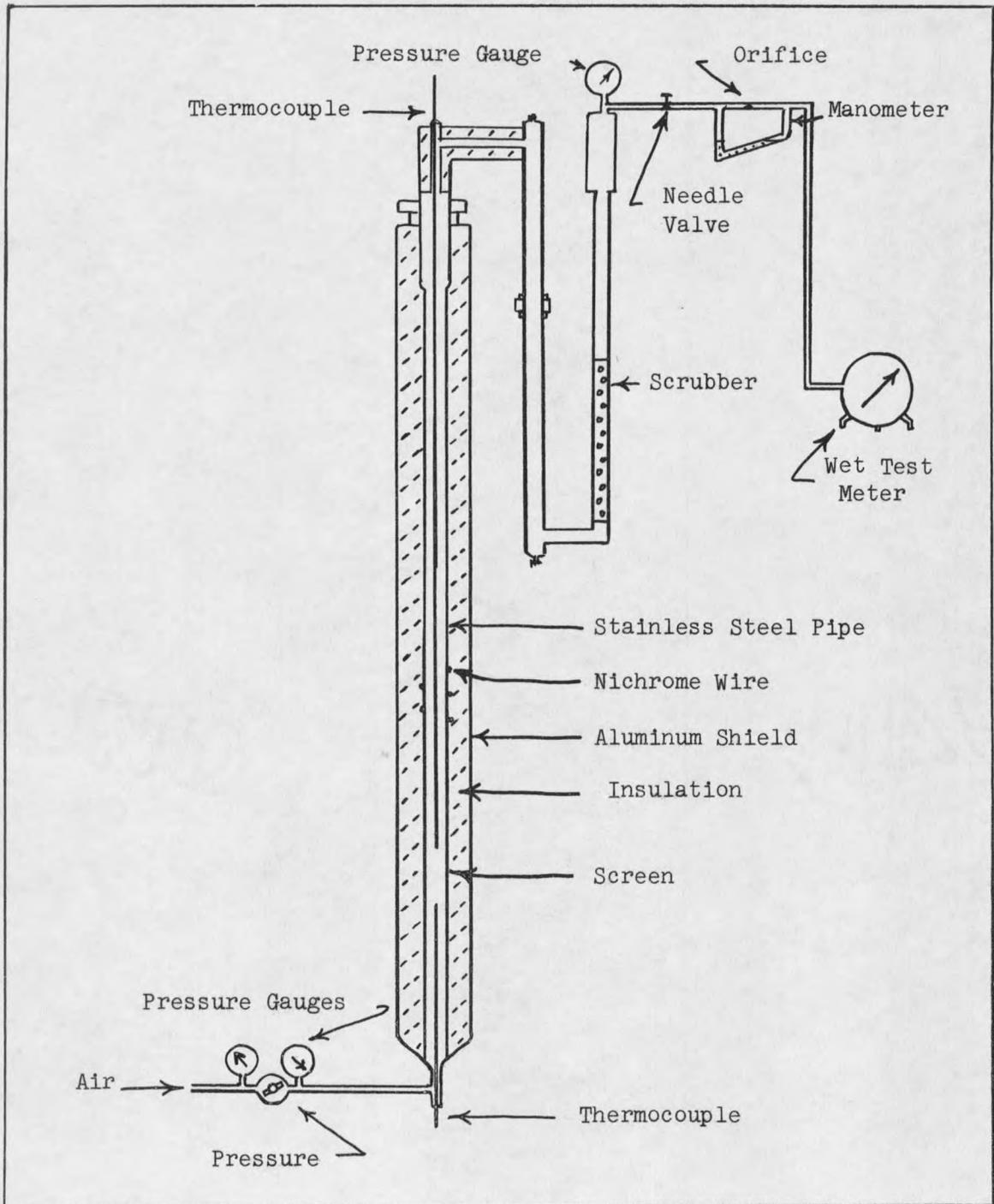


Figure 1. Fluid-Bed Reactor

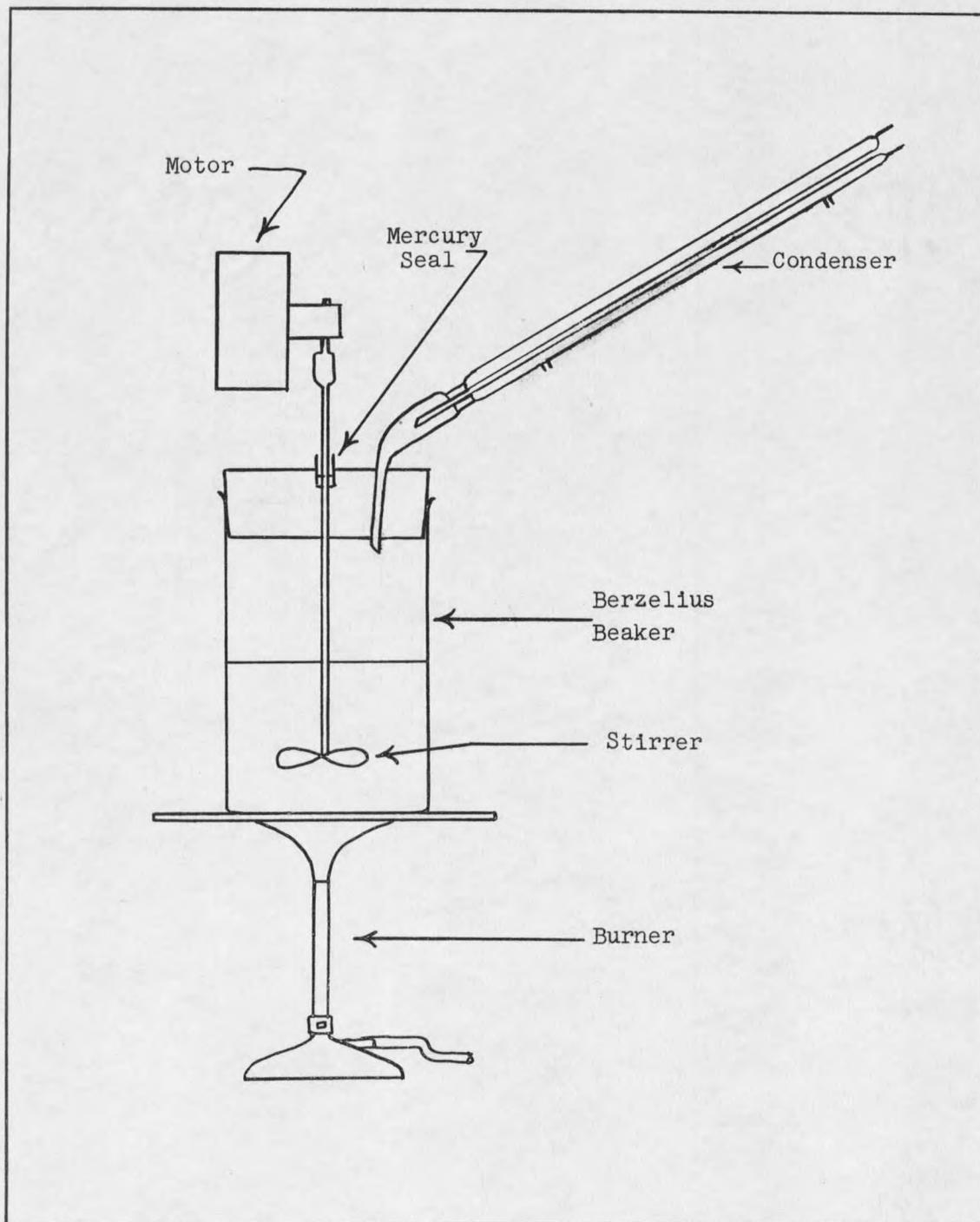


Figure 2. Extraction Apparatus

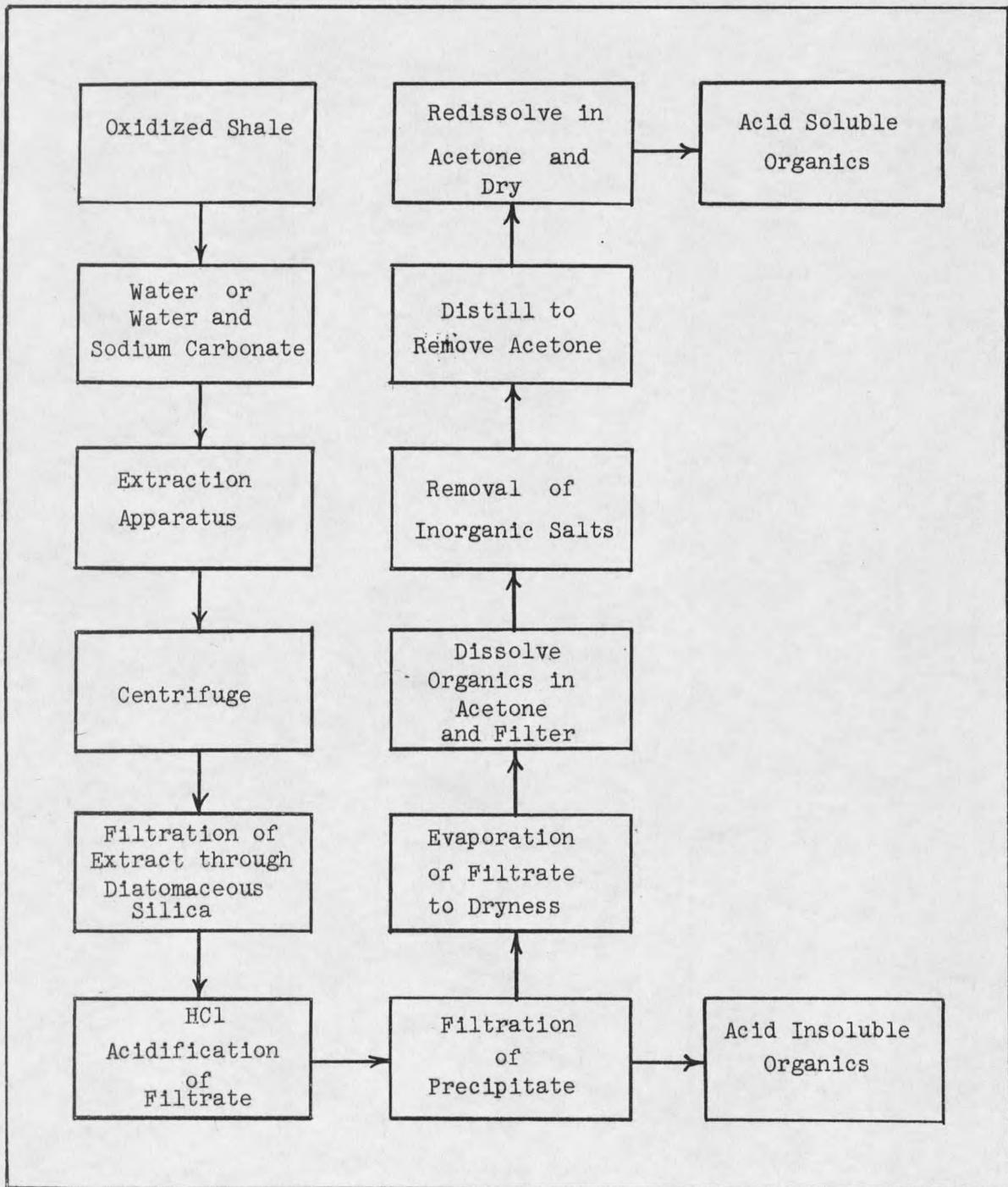


Figure 3. Extraction and Analysis Flow Diagram

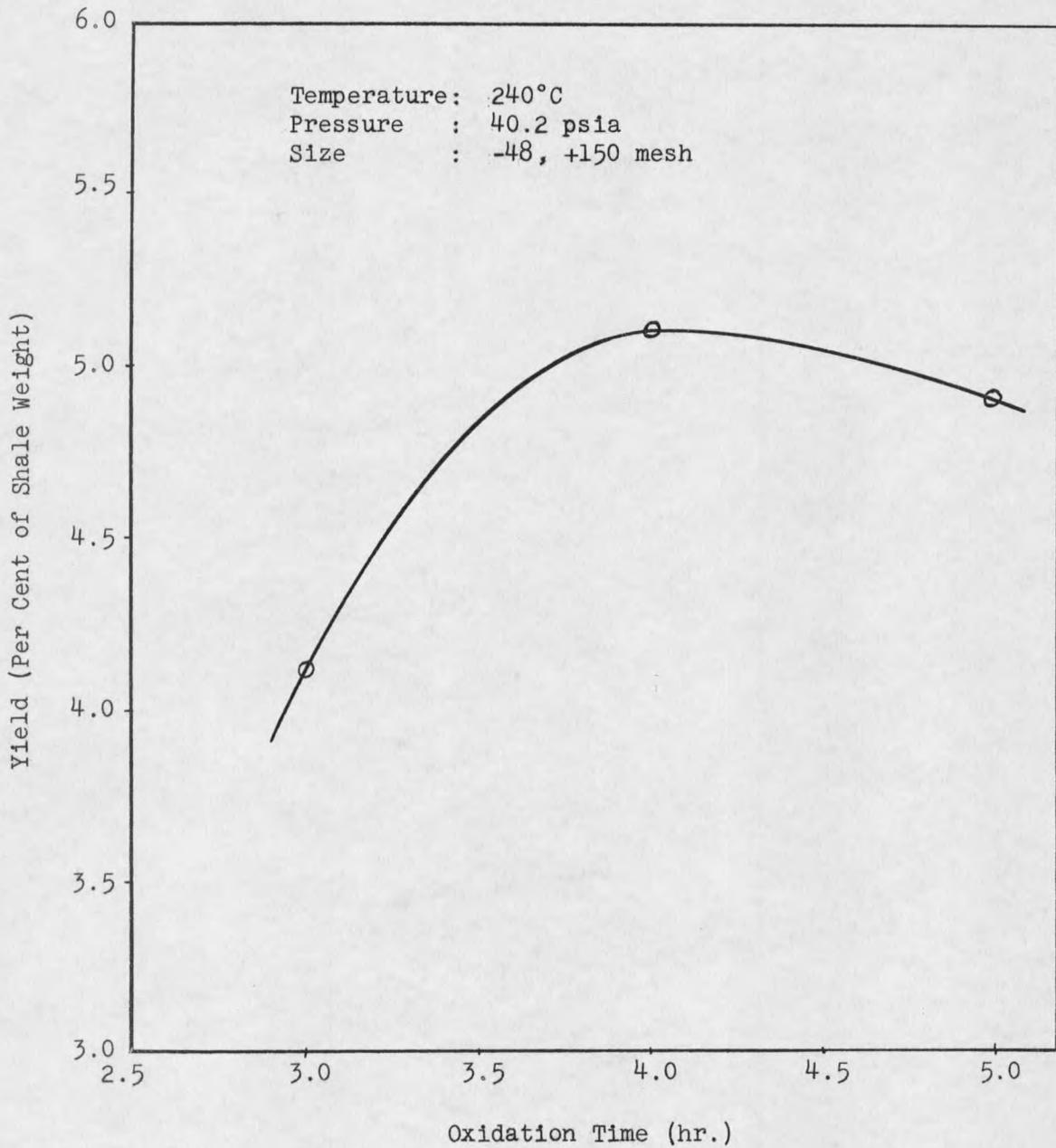


Figure 4. Effect of Oxidation Time on Yield

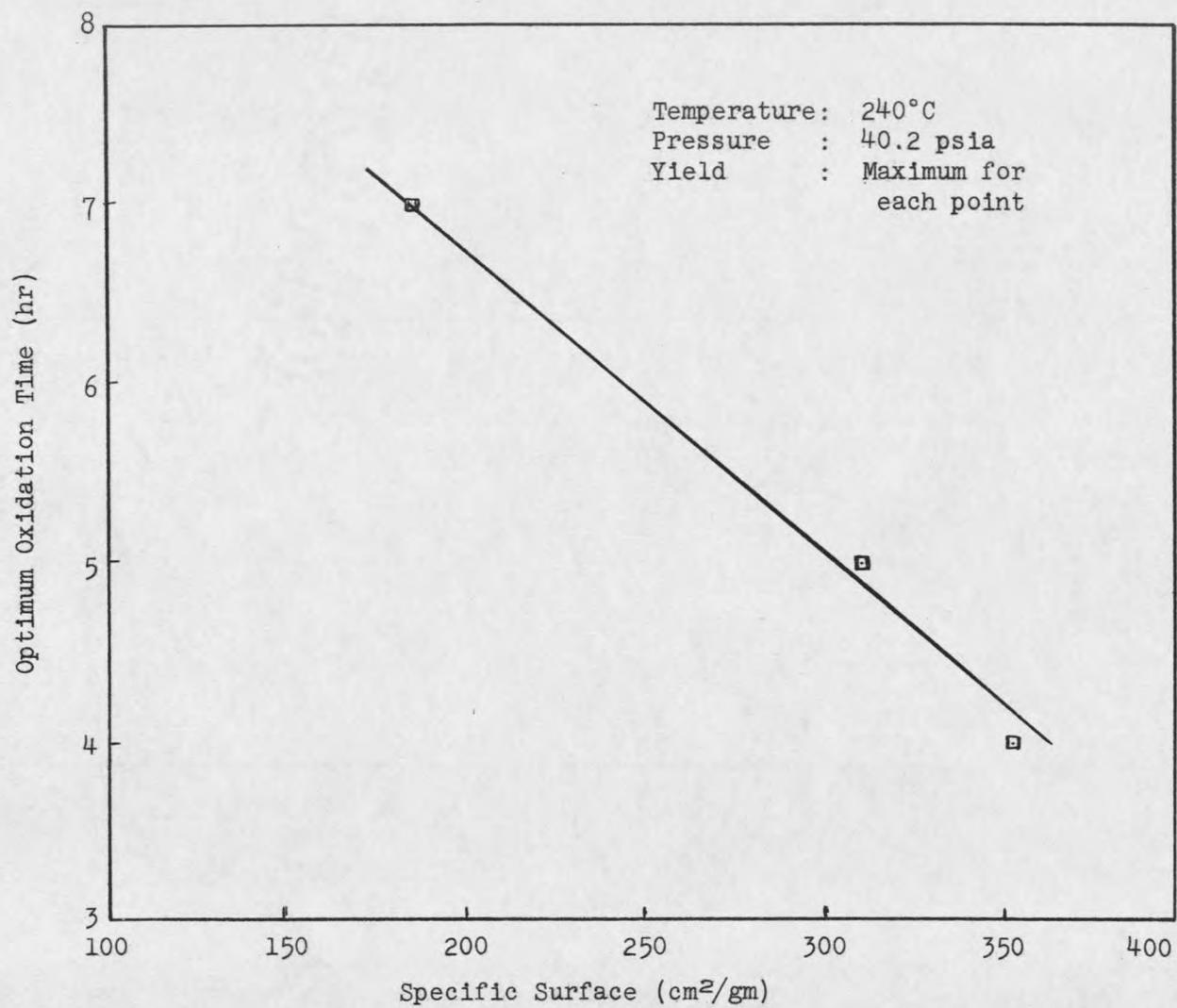


Figure 5. Effect of Specific Surface on Optimum Oxidation Time

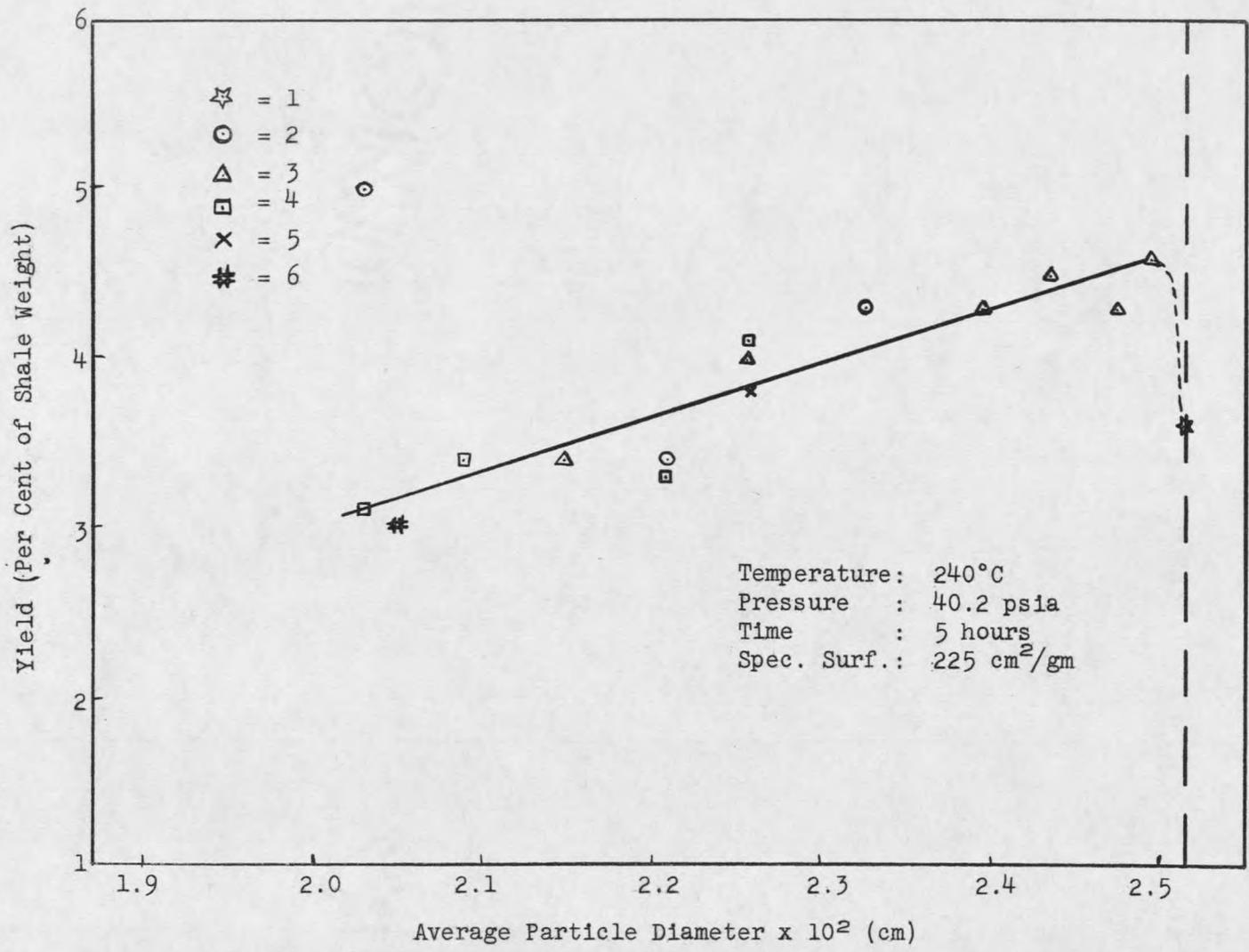


Figure 6. Effect of Average Particle Diameter on Yield

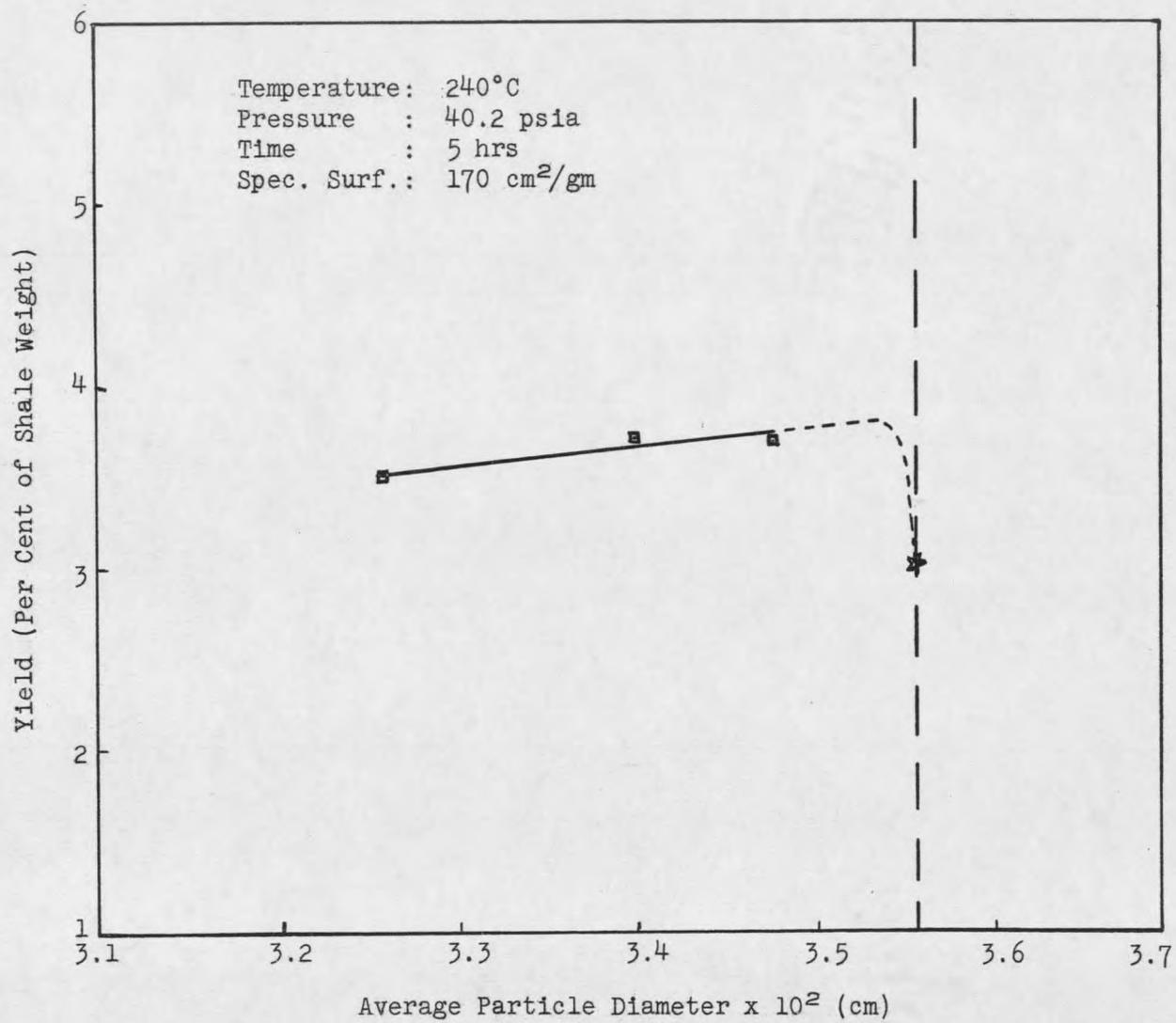


Figure 7. Effect of Average Particle Diameter on Yield

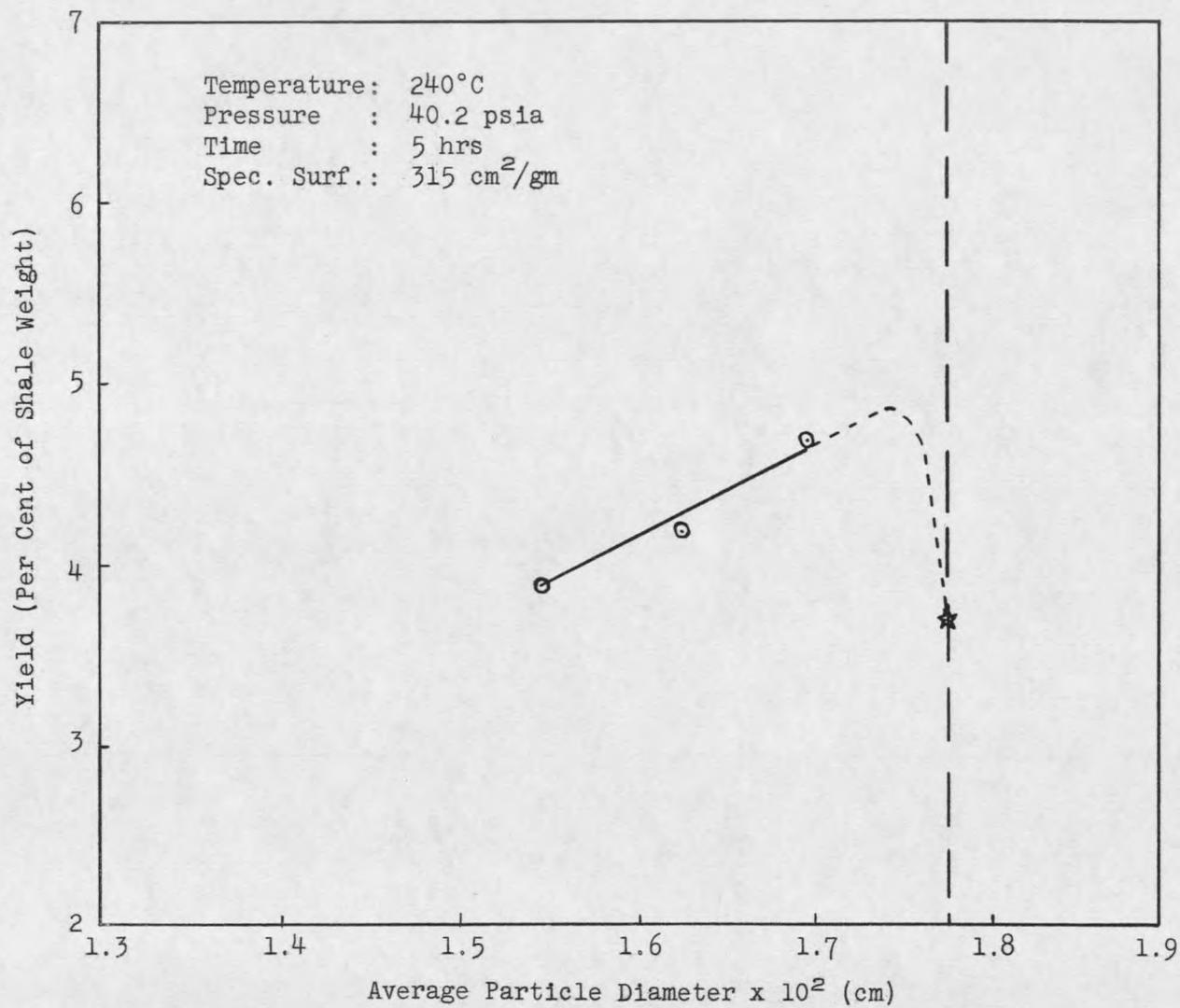


Figure 8. Effect of Average Particle Diameter on Yield

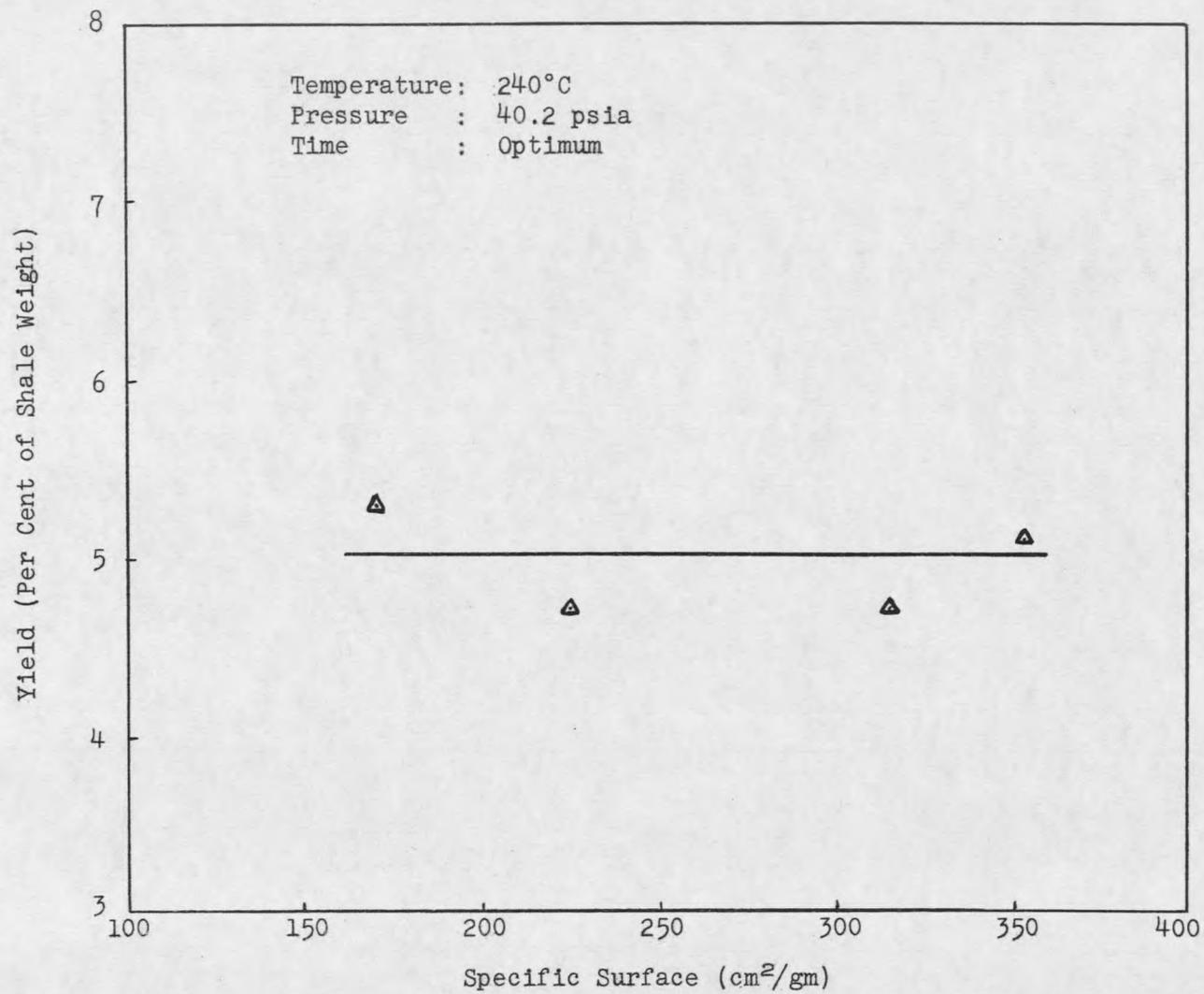


Figure 9. Effect of Specific Surface on Maximum Yield

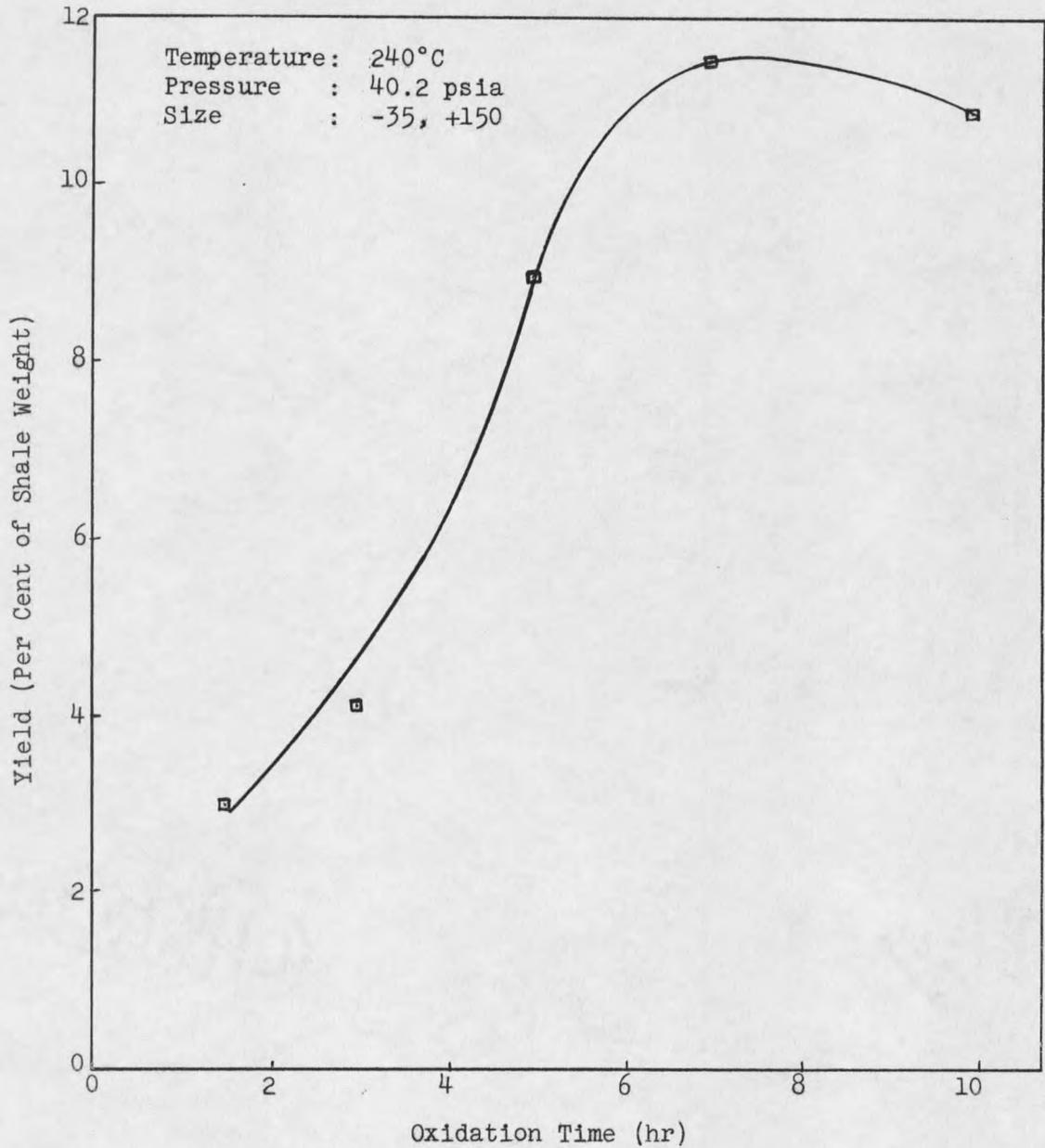


Figure 10. Effect of Oxidation Time on Yield -- Colorado Shale

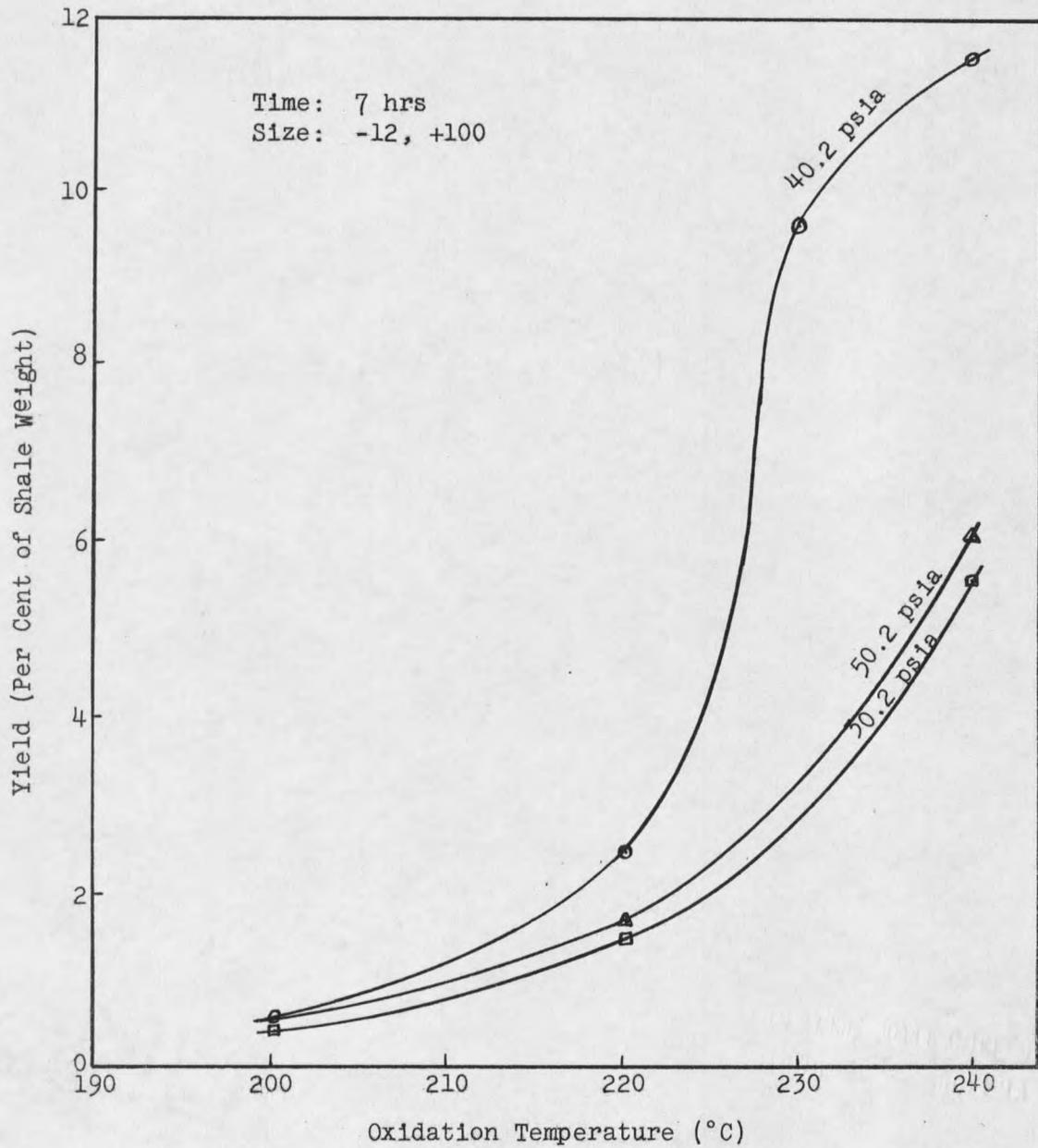


Figure 11. Effect of Oxidation Temperature on Yield -- Colorado Shale

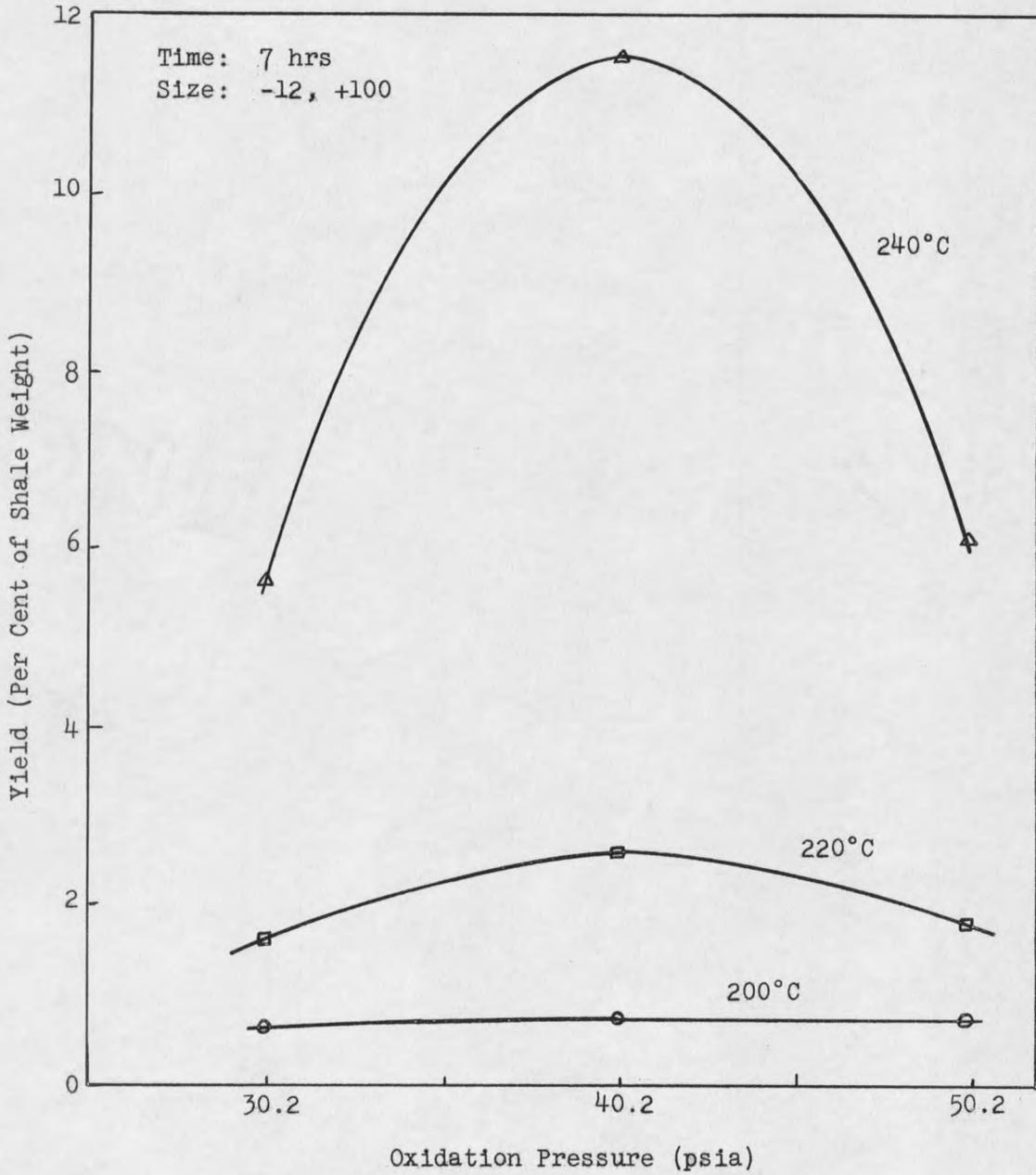


Figure 12. Effect of Oxidation Pressure on Yield -- Colorado Shale

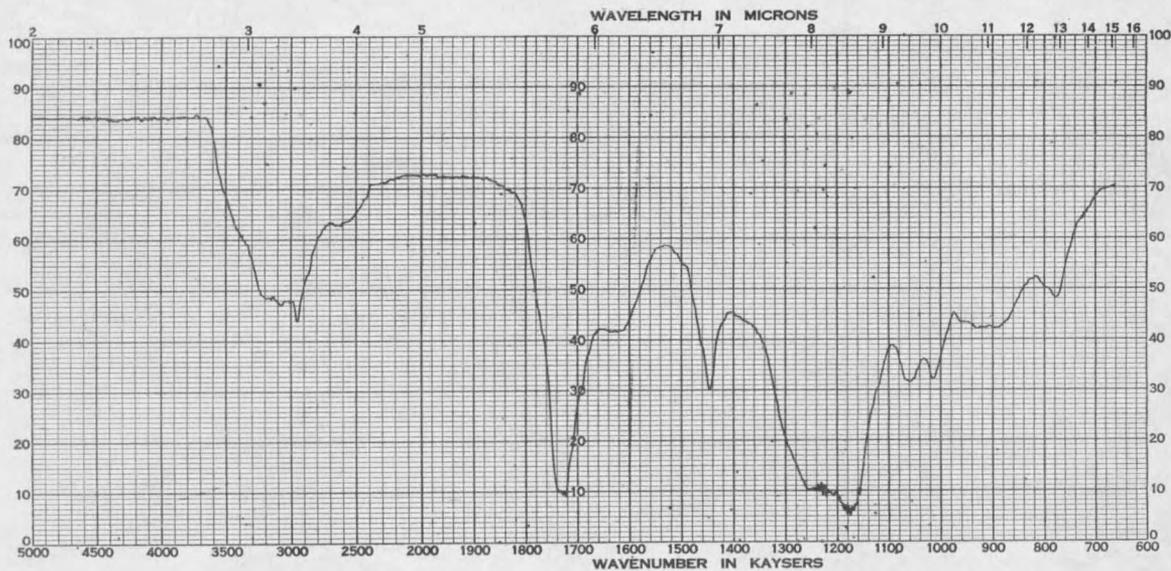


Figure 13. Infrared Spectrograph of Wyoming Acid Soluble Product

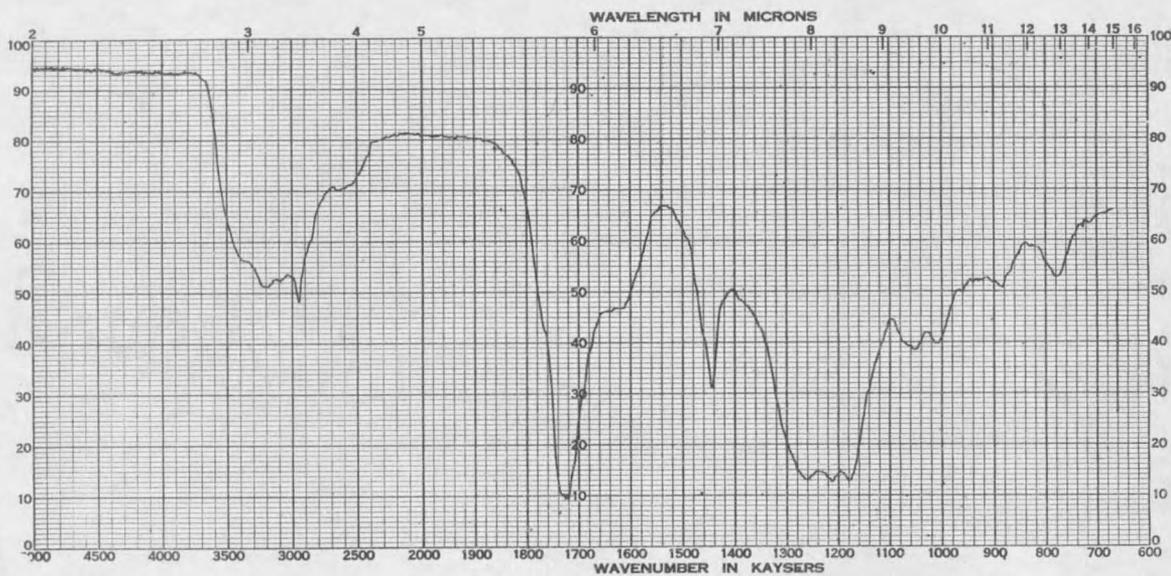


Figure 14. Infrared Spectrograph of Colorado Acid Soluble Product

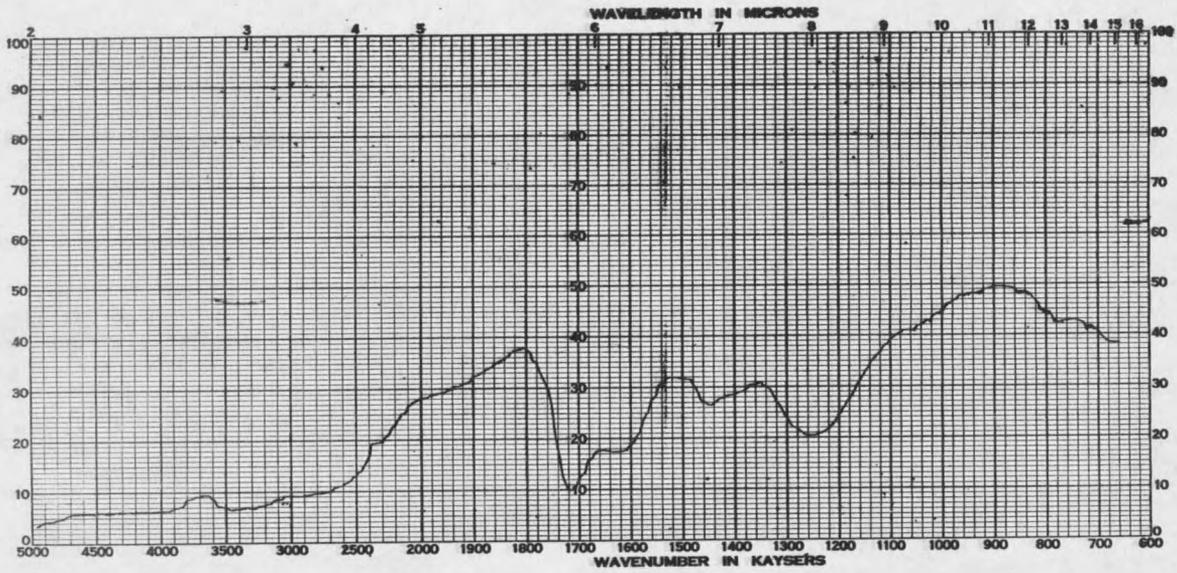


Figure 15. Infrared Spectrograph of Wyoming Acid Insoluble Product

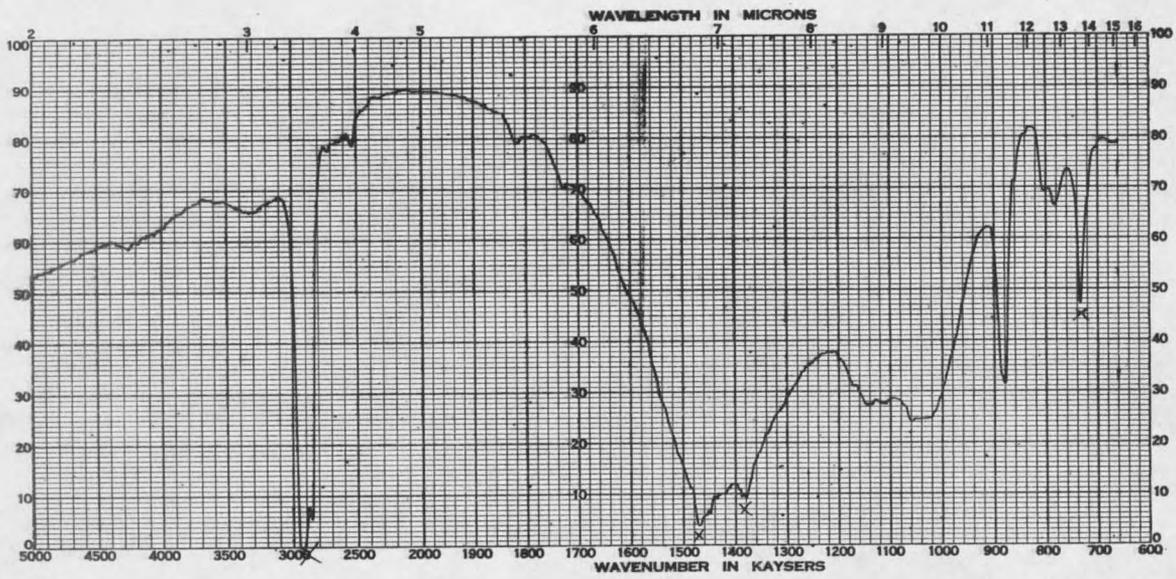


Figure 16. Infrared Spectrograph of Centrifuge Mud

