



Extraction of organic materials from Green River, Wyoming oil shale
by Ronald H Johnson

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
© Copyright by Ronald H Johnson (1961)

Abstract:

This investigation is a continuation of a study being made at Montana State College on the air-oxidation and recovery of the organic material contained in Westvaco's • Green-River, Wyoming oil-shale. The study also has as one of its goals the identification of the oxidized organic components.

A stainless steel fluid-bed reactor was used, for the air-oxidation of the organic material. The oxidized organics were then extracted from the oil shale by boiling a water-shale mixture at atmospheric pressure under total reflux.

The study was made to determine the optimum condition for the air-oxidation of oil shale in a fluid-bed reactor. The first set of experimental runs was made to study the effect of temperature, pressure, and time on the yield obtained while using a shale size distribution of

-12, +100 mesh. A maximum yield of 11.17 per cent was obtained when the oil shale was oxidized at 240°C and 40.2 pounds per square inch absolute pressure for seven hours. The air velocity through the reactor remained at 0.55 feet per second for the entire study.

In an effort to shorten the oxidation time, a second study was made using a shale size distribution of -55, +150 mesh. In this study, a yield of 9.77 Per cent was reported when the shale was oxidized at 240°C and 40.2 pounds per square inch absolute for five hours. This was selected as the optimum operating condition for this investigation because of the shorter oxidation time.

It was found that a particle size distribution was needed to obtain desirable yields. From a charge having a size distribution of -35, +150 mesh and specific surface of 322 cm² per gram of shale, a yield of 9.77 per cent was obtained and from a similar charge of a single screen size (-65, +100 mesh) and a specific surface of 315 cm² per gram, a yield of only 5.6 per cent was obtained.

The identification study shows the oxidation products to be essentially highly complex acid polymers. Another result of this part of the study shows that the acid soluble portion of the product and an acetone extract of the acid insoluble portion have the same structural groups present.

EXTRACTION OF ORGANIC MATERIALS FROM
GREEN RIVER, WYOMING OIL SHALE

by

RONALD H. JOHNSON

A THESIS

Submitted to the Graduate Faculty

in

partial fulfillment of the requirements

for the degree of

Master of Science in Chemical Engineering

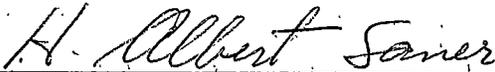
at

Montana State College

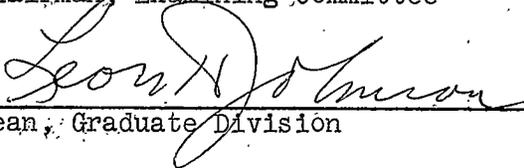
Approved:



Head, Major Department



Chairman, Examining Committee



Dean, Graduate Division

Bozeman, Montana
June, 1961

N378
J637
cop 2

TABLE OF CONTENTS

	Page
Abstract	3
Introduction	4
A. Oil Bearing Shales	4
B. Purpose of this Investigation	5
Procedure, Equipment, and Materials	7
A. Procedure and Equipment	7
1. Preparation of the Feed	7
2. Fluid-Bed Air-Oxidation	7
3. Extraction	15
4. Identification of the Organic Constituents	17
5. Simultaneous Air-Oxidation and Extraction	18
6. Large Quantity Air-Oxidation and Extraction	18
B. Materials	19
Discussion of Results	20
A. Air-Oxidation	20
B. Extraction of the Organic Material	28
C. Identification of Organic Material	29
D. Simultaneous Air-Oxidation and Extraction	30
Summary	32
Recommendations	34
Bibliography	35
Acknowledgment	36
Appendix	37

ABSTRACT

This investigation is a continuation of a study being made at Montana State College on the air-oxidation and recovery of the organic material contained in Westvaco's Green River, Wyoming oil shale. The study also has as one of its goals the identification of the oxidized organic components.

A stainless steel fluid-bed reactor was used for the air-oxidation of the organic material. The oxidized organics were then extracted from the oil shale by boiling a water-shale mixture at atmospheric pressure under total reflux.

The study was made to determine the optimum condition for the air-oxidation of oil shale in a fluid-bed reactor. The first set of experimental runs was made to study the effect of temperature, pressure, and time on the yield obtained while using a shale size distribution of -12, +100 mesh. A maximum yield of 11.17 per cent was obtained when the oil shale was oxidized at 240°C and 40.2 pounds per square inch absolute pressure for seven hours. The air velocity through the reactor remained at 0.55 feet per second for the entire study.

In an effort to shorten the oxidation time, a second study was made using a shale size distribution of -35, +150 mesh. In this study, a yield of 9.77 per cent was reported when the shale was oxidized at 240°C and 40.2 pounds per square inch absolute for five hours. This was selected as the optimum operating condition for this investigation because of the shorter oxidation time.

It was found that a particle size distribution was needed to obtain desirable yields. From a charge having a size distribution of -35, +150 mesh and specific surface of 322 cm² per gram of shale, a yield of 9.77 per cent was obtained and from a similar charge of a single screen size (-65, +100 mesh) and a specific surface of 315 cm² per gram, a yield of only 5.6 per cent was obtained.

The identification study shows the oxidation products to be essentially highly complex acid polymers. Another result of this part of the study shows that the acid soluble portion of the product and an acetone extract of the acid insoluble portion have the same structural groups present.

INTRODUCTION

A. Oil Bearing Shales

The name "oil shales" has been given to clayey or sandy deposits from which oil may be obtained by distillation and not by treatment with solvents (1). Oil shale has a gray to black appearance when it is mined due to the amount of kerogen present. Kerogen is the carbonaceous matter derived from plant or animal remains that has been deposited with the shale. Oil can be obtained from the kerogen by destructive distillation.

Oil from oil shale has the greatest promise of supplementing the supply of petroleum than any other source. First, because it yields products very similar to those made from petroleum, and second, because of the abundance of oil shale in the United States (1). The largest known deposits of oil shale are in Colorado, Utah, Wyoming, and Nevada. These oil shales contain considerable amounts of kerogen and may become commercially important when the more easily exploited petroleum deposits approach exhaustion. At the present time, it is not economically feasible to produce oil from the kerogen contained in the oil shale. Much attention has been given to the aspect of obtaining organic compounds from these shales or from the oil obtained therefrom which might warrant exploiting the oil shale deposits. This report is concerned with extraction of organic compounds from the Green River Oil Shale Formation at Green River, Wyoming.

B. Purpose of this Investigation

At Green River, Wyoming, Westvaco Division of the Food Machinery and Chemical Corporation has been producing a high grade soda ash (sodium carbonate) from trona. The trona, sodium sesquicarbonate, is a mineral composed of hydrous sodium carbonate and sodium bicarbonate. The trona is in a bed several hundred feet below the surface of the earth and is eight to ten feet thick. This trona lies between two layers of shale, both of which contain organic material in varying degrees. Because of its close proximity to the shale, the raw trona also contains small quantities of organic material which find their way to the processing liquors. Certain investigations made in connection with the problems encountered because of the presence of this organic material led Westvaco to consider the feasibility of recovering useful organic materials from the shale deposits. The work reported in this thesis is a continuation of a study made at Montana State College which was undertaken for the purpose of extracting and identifying the organic material from the shale deposits associated with the Green River trona (3 and 4).

Suiter (4) made a study of oxidizing the organic material by two methods. One was the simultaneous oxidation of the organic material by potassium permanganate and the extraction of the oxidation products with an alkaline water solution. He reported that 70 to 80 per cent of the available organic material was removed from the oil shale by using this above method. The removed oxidized material accounted for approximately 6.7 per cent of the shale weight. The other method he used was the air-

oxidation of the organic material in the shale. The oxidation was done by fluidizing the shale with air in a heated Pyrex glass column. In this part of the study, he reported recovering ten to twenty per cent of the available organic material. This part of his study, however, was very limited.

Erickson (3) continued the investigation of the fluid-bed air-oxidation of the organic material. For his investigation, he used a heated stainless steel reactor for the air-oxidation. Only the bottom or lower shale was used in his investigation. He reported a maximum yield of 10.13 per cent of the oxidized shale weight.

He also made a study of methods and conditions for extracting organic material from oxidized oil shale. In this part of his study, he concluded that boiling a shale-water mixture at atmospheric pressure under total reflux was the best method considered. The optimum extraction condition was boiling the mixture for one hour with a water to shale ratio of 10:1.

This investigation is a further study of the fluid-bed air-oxidation of oil shale in a heated stainless steel reactor. The effects of temperature, pressure, shale size, and oxidation time on yield were studied to find an optimum set of operating conditions. A limited study of a simultaneous air-oxidation and extraction method at atmospheric pressure was also made.

PROCEDURE, EQUIPMENT, AND MATERIALS

A. Procedure and Equipment

1. Preparation of the Feed

The oil shale obtained from Green River, Wyoming had to be ground and classified before it could be used in the reactor. The large chunks of shale were broken up by using a sledge hammer and then further reduced in size by a Montgomery Ward Model G hammer mill. After screening, the coarser material was further reduced in size by grinding in a ball mill. A series of Tyler screens was then used to classify all of the ground shale. The screens were shaken on a Roto-tap screen shaker. The shale from the various screens was then blended back in the proper ratios to give the desired size distribution for each experimental run.

2. Fluid-Bed Air-Oxidation

The organic matter in the oil shale was oxidized by fluidizing the shale in a stainless steel reactor (Figure 1, page 44). The reactor consisted of two parts: the preheat and reaction zone, and the expansion chamber. The head for the reactor included a wash chamber, a stainless steel screen, and a needle valve for adjusting the air rate. Following the needle valve was a manometer and a wet test flow meter to measure the air rate.

The reactor body was made of one-inch (inside diameter) stainless steel pipe four feet long. A stainless steel screen on a stand one foot from the bottom of the reactor was used as the bed support.

The section below the screen was filled with one-eighth inch metal helices. These, along with the screen, were used to disperse the air evenly over the cross-section of the pipe. This section was also used to preheat the incoming air. The reaction zone was the three-foot section of pipe above the screen. A six-inch length of two-inch black iron pipe was welded to the top of the reactor body to serve as an expansion chamber.

The body of the reactor was heated with three nichrome wire heating coils. This nichrome wire was encased in ceramic beads. One heating coil supplied heat to the air preheat section and the other two coils supplied heat to the reaction zone. Each nichrome wire heating coil was connected to a 110-volt Variac which was used to regulate the energy supply.

The reactor was insulated with approximately two inches of magnesia mud insulation and then covered with an aluminum sheet to reduce radiation of heat from the reactor. The reactor body was supported on a pivot so the reactor would rotate about its middle to facilitate dumping. A U-bracket at the bottom of the reactor held it in a vertical position.

The reactor head was connected to the top of the reactor body by a two-inch union. It was necessary to remove the head before loading and unloading the reactor. The reactor head was constructed of one-inch standard pipe except for a three-inch long section of one and three quarter-inch pipe which served as an expansion

chamber. The one-inch pipe was the wash chamber. It had valves at both ends to facilitate filling and draining the scrubber. A one-inch union was placed in the wash chamber so the head could be taken apart and cleaned. Following the expansion chamber was a pressure gauge (0-60 pounds per square inch) used for measuring the pressure in the reactor. Following the pressure gauge was a stainless steel screen and then a needle valve to control the air velocity through the reactor. The screen was used to keep the fine shale particles, that are carried completely through the system, from plugging the needle valve.

Air was used to fluidize the bed and also served as a source of oxygen for the oxidation of the organic material. The air was supplied, at 150 pounds per square inch gauge, by a laboratory compressor. The entering air passed through a pressure regulator which controlled the reactor pressure. The air entered the bottom of the reactor, passed through the preheat and reactor sections, and left through the scrubber. The air leaving the scrubber passed through the needle control valve that regulated the air flow rate. The air then went through an orifice, which was connected to an inclined air-water manometer, and finally to a wet-test meter. The meter was used to set the flow rate of air.

The temperatures in the reactor and preheat sections were measured with the aid of iron-constantan thermocouples connected to a Minneapolis-Honeywell "Electronik" temperature indicator. The

temperature in the air preheat section was measured three inches below the bed support. A moveable thermocouple was placed in the reaction zone to facilitate taking a temperature profile of the bed.

Erickson (3) found a maximum yield of 10.13 per cent when operating at the following conditions:

Air Velocity	0.55 fps
Temperature	200°C
Pressure	30.2 psia
Shale Size	-12, +100 mesh
Time	30.0 hrs
Bed Weight	200 grams

He reported that considerable difficulty was encountered during test runs because of an exothermic reaction taking place which would periodically cause the temperature to get out of control and rise from 200 to 500°C within seconds. At this temperature, retorting would occur and the run had to be discontinued. After reviewing Erickson's work, it seemed desirable to try to shorten the oxidation time by increasing the operating temperature and pressure. The problem, however, was to prevent runaway temperatures while operating at the more severe conditions. It was felt that if the bed temperature could be kept within very narrow limits and a very uniform efficient fluidization could be maintained to prevent any stagnation of particles, the possibility of any local overheating

would be minimized. It was hoped in this manner to keep the reaction in check and prevent the temperature from getting out of control. Before test runs were made, the reactor was taken apart and cleaned. In an effort to assure more uniform air dispersion across the entire cross-sectional area of the reactor, the metal helices in the air preheat section were replaced with new ones and a new bed support screen of fine mesh was installed.

Experience obtained during several test runs resulted in the following operating procedure. The empty reaction zone was heated with air flowing through it to ten or fifteen degrees centigrade below the operating temperature. At this time heat to the reaction zone was turned off and the charge was introduced to the reactor. Sufficient air flow was maintained to keep the bed fluidized while the head was connected and tightened. The reactor was then brought to operating pressure and the air velocity adjusted to approximately 0.55 feet per second (based on the empty reactor cross-section). The preheat air was maintained at all times about thirty-five degrees centigrade below the reaction zone temperature. This was done to prevent overheating in the very bottom of the reaction zone where fluidization is least efficient. When the temperature became stable after charging, heat was again applied and the reactor slowly brought up to reaction temperature. When the reactor reached operating temperature, the air velocity was again adjusted to 0.55 feet per second. With these precautions during the start-up and with careful

control during the run, it was possible to run at the desired conditions with a minimum of difficulty.

A series of runs (Runs B-1, -3, -5) was set up to study the effect of increasing the temperature on the yield while holding the other variables at the following conditions:

Air Velocity	0.55 fps
Pressure	30.2 psia
Shale Size	-12, +100 mesh
Time	7.0 hrs
Bed Weight	200 grams

The temperatures studied were 200, 220, 230, 240, and 250°C. The first run was made at 200 and the next at 220, etc. The reason for this was to find the highest operational temperature at the above conditions. Two runs were attempted at an operating temperature of 250°C. One of these runs was at a pressure of 30.2 psia and the other at atmospheric pressure (12.2 psia). All attempts to operate the reactor at these conditions failed because of the inability to keep the reaction in check and control the temperature.

A study of pressure effect was next undertaken. The effect of increasing the pressure from 30.2 psia to 50.2 psia at 200, 220, and 240°C was investigated. All other variables were held at the same values used for the temperature investigation. The highest pressure that could be maintained on the unit, with the source of air available, was 50.2 psia.

A series of runs (Runs B-11, -12, -13, -16) was also made to study the effect of time while operating at 240°C and 40.2 psia which appeared from the preceding investigation to be optimum.

One important factor that should be brought out at this point is the fact that the -12, +100 mesh shale used above had the following size distribution:

Retained on	12 mesh screen	0.0 per cent
"	" 20 "	2.4 " "
"	" 35 "	40.8 " "
"	" 48 "	21.8 " "
"	" 65 "	18.1 " "
"	" 100 "	16.9 " "

At this point it was decided to investigate shale particle size from the standpoint of its effect on reaction time at the following conditions:

Air Velocity	0.55 fps
Temperature	240°C
Pressure	40.2 psia

For this series of runs the size distribution was as follows:

Retained on	35 mesh screen	0.0 per cent
"	" 48 "	21.8 " "
"	" 65 "	18.1 " "
"	" 100 "	16.9 " "
"	" 150 "	43.2 " "

Runs were made at three, five, seven, and ten hours.

Since the effect of using the finer mesh material was to lower the reaction time necessary to reach optimum yield from seven to five hours, additional runs were set up at this point to again study the effect of temperature and pressure independently of the other variables.

To complete a study of the effect of shale size on yield, runs were made with the following size distributions at 240°C, five hours, 0.55 feet per second, and 40.2 psia:

Run B-15

Retained on 12 mesh screen	0.0 per cent
" " 20 " "	2.0 " "
" " 35 " "	34.1 " "
" " 48 " "	18.2 " "
" " 65 " "	15.0 " "
" " 100 " "	14.1 " "
" " 150 " "	16.6 " "

Run B-22

Retained on 48 mesh screen	0.0 per cent
" " 65 " "	21.6 " "
" " 100 " "	23.2 " "
" " 150 " "	55.2 " "

Run B-24

Retained on 12 mesh screen	0.0 per cent
" " 20 " "	2.9 " "

Run B-24 (continued)

Retained on	35 mesh screen	49.1 per cent
"	" 48 " " "	26.2 " "
"	" 65 " " "	21.8 " "

In order to determine if a range of particle sizes is desirable, runs were made where the whole reactor charge was taken from a single screen. These results were then compared to the yields obtained when a size distribution was used. The screen sizes used in this study were:

Run B-32	-35, +48 mesh
Run B-33	-48, +65 mesh
Run B-34	-65, +100 mesh

3. Extraction

Due to the previous work done on the extraction step by Erickson (3), no investigation was made of any of the extraction variables. The extraction procedure used throughout this investigation is shown schematically in Figure 2, page 45. The amount of oxidized organics in the oil shale was determined by the following procedure:

- a) Thirty grams of oxidized oil shale and three hundred milliliters of tap water were boiled, while being stirred, for one hour. This step was done at total reflux and atmospheric pressure. The extraction was done in a 600 ml Berzelius beaker. The apparatus is shown in Figure 3, page 46.

The stirrer shaft passed through a rubber stopper which was provided with a mercury seal. The mercury provided a seal between the shaft and the rubber stopper to keep the water vapor from escaping around the shaft. An adapter was inserted through the stopper and connected to a condenser for total reflux. The condenser was open to the atmosphere. A Bunsen burner supplied the heat and a Fisher "Fultork Laboratory motor" supplied power to the stirring shaft which contained a four-winged propeller.

b) The extraction mixture was then placed in a centrifuge for one hour to separate the shale from the aqueous solution containing the organic compounds.

c) The aqueous solution was decanted from the centrifuge containers and filtered to assure that all the shale particles were removed.

d) The liquid was acidified and the resulting precipitate was allowed to settle to the bottom of the beaker to facilitate filtering.

e) The mixture was filtered through a weighed filter paper and the dried precipitate was measured as part of the yield. It was called the acid insoluble portion.

f) The filtrate from (e) was evaporated to dryness. The organics on the salt were extracted with acetone.

g) The acetone was distilled from the organic-acetone solution in a distillation flask. The organic residue was again dissolved in acetone and filtered to remove any solid particles.

h) An infrared lamp was used to drive off the acetone from the second acetone-organic solution. The organic residue was weighed and recorded as the acid soluble portion.

i) The total per cent recovery of the oxidized organic material was based on the sum of the acid soluble and acid insoluble portions.

j) All the yields were reported as the grams of oxidized organics per one hundred grams of oxidized oil shale.

4. Identification of the Organic Constituents

Acetone extracts of the organic material, obtained from the shale oxidized at the following conditions.

Air Velocity	0.55 fps
Temperature	240°C
Pressure	40.2 psia
Shale Size	-35 _y +150 mesh
Time	7.0 hrs

were evaporated to dryness on a salt plate to be used in a Bechman IR-4 infrared spectrophotometer. The resulting infrared analysis charts were to be compared to the charts made by Sulter (4).

5. Simultaneous Air-Oxidation and Extraction

The equipment used in this part of the study was the same as that shown in Figure 3, page 46, except for two additions. The additions consisted of an air dispersion tube and a nichrome wire heater. The procedure consisted of boiling a shale-water mixture at atmospheric pressure while introducing a finely dispersed stream of air. Each run was accompanied by excessive foaming. The nichrome wire was uniformly stretched back and forth across the entire cross section of the beaker about one inch below the stopper and was used to control the foam by thermal shock. Only preliminary runs were made to see if the principle of thermal shock would disperse the foam. The test runs were of about twenty hours duration and met with only limited success.

6. Large Quantity Air-Oxidation and Extraction

The Food Machinery and Chemical Corporation requested about one pound of the oxidized organic material for further identification studies. The fluid bed reactor shown in Figure 1 was too small for this operation and therefore a small rotary kiln was used to oxidize the oil shale. The kiln was eight inches in diameter and four feet long. It was electrically heated. The oxidized organics were extracted in a steam heated copper kettle. The mixture was constantly

stirred and water was added periodically to maintain a constant volume during the five-hour extraction time.

B. Materials

Oil Shale: The oil shale used in this investigation was obtained from the lower shale bed at Green River, Wyoming. This shale contains approximately eight to ten per cent organic material.

Air: The air was supplied by a laboratory compressor at 150 pounds per square inch gauge.

Acetone: The acetone used was a commercial grade re-distilled at a 10:1 reflux ratio in a thirty theoretical plate packed column.

Hydrochloric Acid: Concentrated hydrochloric acid, made by Fisher, was used to acidify the extraction solution.

DISCUSSION OF RESULTS

A. Air-Oxidation

In an effort to find the optimum operating temperature, reaction temperatures of 200, 220, 230, and 240 degrees centigrade were studied. All of the air-oxidation data are tabulated in Table I, page 38. Several attempts were made to operate the reactor at 250°C and 30.2 pounds per square inch absolute (Run B-18), but all of them failed. All of the failures were due to the uncontrollable exothermic reaction taking place just after the shale had been charged to the reactor. Extreme care was taken during the start of the runs, but the temperature could not be controlled. During one attempted run the shale was in the reactor at 250°C and 30.2 psia for four hours and when it was removed, all of the organics had been burned off the shale. During this run, after the shale was charged, the heat to the reaction zone was shut off for approximately three of the four hours in order to maintain the temperature at 250°C. The necessary heat needed to maintain the operating temperature was generated in the reactor. Other runs were attempted at 250°C and atmospheric pressure (Run B-21). These runs also had to be discontinued. Runs at 250°C and higher pressures were not attempted because it was felt that if the runs could not be made at the lower pressures, there was no chance of completing them at higher pressures. For the shale used in this investigation, the highest operating temperature that could be maintained was 240°C.

The lower curve (30.2 psia) of Figure 4, page 47, shows the effect of increasing the temperature on the yield (Runs B-1, -3, -5) while the operating pressure was held at 30.2 psia, the air velocity at 0.55 feet per second, the oxidation time at seven hours and the shale size at -12, +100 mesh, (for size distributions, see page 13). The yield increased from 1.3 per cent to 9.5 per cent when the temperature was increased from 200°C to 240°C. The center curve (40.2 psia) of Figure 4 shows that the yield also increases with temperature over the range studied (Runs B-9, -10, -11) when the pressure is held at 40.2 psia. The yields obtained ranged from 2.1 per cent at 200°C to 11.17 per cent at 240°C. No experimental run was made at 40.2 psia and 250°C for the reason stated above. Due to lack of precise temperature control, no runs were made at 245°C. The top curve (50.2 psia) of Figure 4, (Runs B-6, -7, -8), shows the effect of increasing the temperature on the yield when the operating pressure is 50.2 psia. This curve shows the yield goes through a maximum as the temperature increases from 200°C to 240°C. The maximum yield of 9.58 per cent is obtained at the operating condition of 50.2 psia and 230°C. While this yield represents a maximum when operating at 50.2 psia and 230°C, the yield is lower than the maximum yield obtained when operating at 40.2 psia and 240°C.

The same series of experimental runs (B-1, -3, -5, -6, -7, -8, -9, -10, -11), as mentioned above, are plotted in Figure 5, page 48, showing the per cent yield versus the oxidation pressure with the oxidation temperature as the parameter. This was done to show the effect of oxidation pressure on the per cent yield more clearly than in Figure 4. The

lower and middle curves show an increase in yield accompanying an increase in pressure at 200°C. The top curve of Figure 5 shows that when the temperature is held at 240°C and the pressure is varied from 30.2 psia to 50.2 psia, the per cent yield obtained goes through a maximum. This maximum yield of 11.17 per cent occurred at 40.2 psia and 240°C. It is postulated that at some higher pressures the two lower curves would drop off the same as the top curve. With the available source of air, however, the reactor pressure could not be increased beyond 50.2 psia. Even if some experimental runs could have been made at some higher pressures, the maximum yield obtained would be somewhat lower than that obtained for the top curve.

This series of experimental runs indicates that the oxidation should be carried out at 240°C and 40.2 psia. Additional runs were therefore made at this temperature and pressure to determine the effect of reaction time on yield. Figure 6, (Run B-11, -12, -13, -16) page 49, shows a plot of the results of this test series. It is a plot of per cent yield versus oxidation time. The yield goes through a maximum when the time is varied from zero to ten hours. This maximum yield occurred in seven hours.

As shown in Figures 4 and 5, a decrease in yield resulted at 50.2 psia when the temperature was increased from 230°C to 240°C and also decreased at 240°C when the pressure was raised from 40.2 psia to 50.2 psia. In light of the fact that yield apparently decreases when reaction time exceeds certain limits (see Figure 6, page 49), it was postulated that the decreased yield at 240°C and 50.2 psia might be caused as a

result of exceeding the optimum reaction time for these conditions. As a result of this thinking, another time study (Runs B-8, -19, -20, -23) was made at the following conditions:

Air Velocity	0.55 fps
Temperature	240°C
Pressure	50.2 psia
Shale Size	-12, +100 mesh
Bed Weight	200 grams

The results are plotted in Figure 7, page 50. This time study showed that the maximum yield was obtained in seven hours. It should be pointed out that these runs were somewhat erratic and it was very difficult to keep the reaction in check and prevent the temperature from exceeding the desired value of 240°C. As a result, excessive decomposition of the organics probably occurred. It is quite apparent, at any rate, that reaction temperatures above 240°C and pressures above 40.2 psia are not practical. As a result of the investigation to this point, the optimum operating conditions were set at the following:

Air Velocity	0.55 fps
Temperature	240°C
Pressure	40.2 psia
Shale Size	-12, +100 mesh
Time	7.0 hours
Bed Weight	200 grams

It was believed that if the surface area were increased, the oxidation time might be shortened while still obtaining desirable yields. Additional charges of raw shale in the range of -35, +150 mesh were therefore prepared and a series of runs was designed to study the effect of temperature, pressure, and time on the per cent yield. On the basis of preceding results, a temperature of 240°C and a pressure of 40.2 psia were chosen while investigating the effect of reaction time. The results of these runs (B-14, -25, -26, -31) are plotted in Figure 8, page 51. The increase in surface area of the -35, +150 mesh charge (see page 13-15 for the actual size distribution) over the -12, +100 mesh material resulted in a reduction of optimum time from seven to five hours, although the maximum yield was only 9.77 per cent as compared to 11.17 per cent for the coarser grind. Using a reaction time of five hours, temperature and pressure effects were again investigated. Results of these runs (B-14, -27, -28, -29, -30) are plotted in Figures 9 and 10, pages 52-53, showing yield versus temperature and pressure, respectively. These results were similar to previous investigations and verified the use of 240°C and 40.2 psia as optimum values. From this study, using a size distribution of -35, +150 mesh, the optimum operating conditions were set as follows:

Air Velocity	0.55 fps
Temperature	240°C
Pressure	40.2 psia
Shale Size	-35, +150 mesh

Time	5.0 hours
Bed Weight	200 grams

The results of the two above studies, using different size distributions, indicate that the finer the average particle size, the shorter the oxidation time. As postulated, the increase in surface area shortened the oxidation time without appreciable sacrifice of yield. With the reactor used in this investigation, some difficulty was encountered when using fine shale particles (-100, +150 mesh) as part of the charge. In view of this, no shale particles smaller than minus 150 mesh were used in this study and no attempt was made to investigate finer grinds than -35, +150 mesh.

Since particle size and/or size distribution affected the yields and the oxidation time, it was decided to investigate this aspect in more detail. Runs B-13, -14, -15, -24, -32, -33, tabulated in Table III, page 43, were used for this study and the results were correlated on the basis of the specific surface of the charge. The specific surface is the total surface area of the particles divided by the weight of the charge. For this particular study, the shale was assumed to have properties similar to quartz and the data presented in Unit Operations by Brown (2) was used for determining the average specific surfaces of the various charges. Average diameters and specific surface for single screen sizes are presented in Table II, page 42. The specific surface of each charge, presented in Table III, is a weighted average based on the weight fractions retained on each screen and the specific surface of

the material retained on each screen. An example of the calculations follows:

<u>Shale Size</u>	<u>Wt. Fraction</u>		<u>Specific Surface</u>		
-48, +65 mesh	0.216	x	225	=	48.6
-65, +100 "	0.232	x	315	=	73.0
-100, +150 "	0.552	x	420	=	232.0
					<hr/>
					353.6 cm ² /gm.

All of these runs were made at the following conditions:

Air Velocity	0.55 fps
Temperature	240°C
Pressure	40.2 psia
Time	5.0 hrs

As discussed previously, an oxidation time of five hours was found to be optimum for the size distribution -35, +150 mesh used in Run B-14. Since the optimum time would be lowered with a finer grind and since yields decrease as this optimum time is exceeded, the size distributions for these runs were all chosen so that the specific surface was lower than the 322.3 cm² per gram for Run B-14. Therefore, the five-hour oxidation time would in no instance exceed the optimum. Figure 11, page 54, is a plot of per cent yield versus the specific surface of each charge. The upper curve represents the data from shale samples having a size distribution or fractions from several screen sizes. This curve shows that the per cent yield increases as the specific surface (cm² per gram of shale) increases. As the specific surface becomes large, the

per cent yield obtained levels off. The yield of Run B-24 is somewhat lower than might be expected when compared to the general pattern set by the other three points (Runs B-13, -14, -15). Here, however, the surface area is not the only factor affecting the yield. It is believed that the fluidization of the bed in the reactor is not as efficient because of the large fraction (52 per cent) of +35 mesh material present. Shale of this coarseness is difficult to fluidize.

The lower curve of Figure 11, page 54, shows the results when charges of shale from a single screen were charged to the reactor. The yield increases slightly with a large increase in specific surface. A comparison of the two curves shows the need of a charge with a size distribution in order to obtain desired yields. From a charge having a size distribution (-35, +150 mesh) and specific surface of 322 cm² per gram of shale, a yield of 9.77 per cent was obtained and from a similar charge having only one screen size (-65, +100 mesh) and a specific surface of 315 cm² per gram, a yield of only 5.6 per cent was obtained. It is postulated that fluidization is better when a size distribution is used than when the charge is from a single screen. There is very little difference in the yields obtained in Runs B-24 and B-32 even though B-24 had a particle size distribution. This, as stated earlier, may be due to poor fluidization of Run B-24. It is apparent, however, that size distribution is desirable and that more benefit is derived from the distribution of particle sizes at the higher specific surfaces than at the lower specific surfaces.

The per cent yield per specific surface was plotted versus the specific surface in Figure 12, page 55. The top curve is for charges having a size distribution and the lower curve for a charge having a single screen size. As the specific surface increases beyond 175 cm² per gram, the two curves are almost parallel. This figure also shows the need for a charge having a size distribution.

A word of caution is given here about interpreting the data in this part of the study. A limited study was made of the effect of particle size and only a few general conclusions can be drawn. Any attempt to set an optimum grind will require additional investigation.

B. Extraction of the Organic Material

Although a variable study was not made in this investigation, some reference will be made to the color of the products. The precipitate (acid insoluble portion of the product) was dark brown to black, depending upon how rigorous the oxidations conditions were. The amorphous precipitate turned very dark when it was dried and looked somewhat like a tar material but was hard and brittle. When all the acetone had been removed from the acid soluble portion, the resulting residue was a dark reddish brown tar-like material. The residue would not pour at room temperature. This residue would change color and become very dark with very little heat being applied. After all of the acetone had evaporated, under an infrared heat lamp, the residue was no longer entirely soluble in acetone. This would indicate the possibility of decarboxylation and/or polymerization taking place. The infrared analysis charts show the

presence of numerous carboxyl groups and also indicate that the residue is a polymer.

C. Identification of Organic Material

Due to previous work done on identification of the oxidation products, infrared analysis was chosen for trying to identify some of the structural groups present in the product obtained in this investigation. The identification work done in this investigation was compared to that done by Suiter (4). The infrared analysis chart for the acid soluble product (Figure 13, page 56) is almost identical to that made by Suiter. This indicates that the same products were obtained when the oil shale was air-oxidized in a fluid-bed and when oxidized by using potassium permanganate (by Suiter). The numbers listed below refer to the absorption peaks which are likewise numbered on the infrared analysis charts. Dr. Baker of the Chemistry Department at Montana State College made and interpreted all of the infrared analysis charts and the results follow:

1. Due to broad band spectra contribution of the OH in a carboxylic acid (-COOH) structure.
2. Due to aliphatic carbon-hydrogen bonding.
3. Broad band due to spectra contributions of carbonyl groups (i.e., aldehydes and ketones).
- 4-5. Broad band spectra characteristic of complex acid structures.

It should be noticed here that there is no peak at point 6 on Figure 13. There should be if there are acid dimers present. The fact that there is

no peak is not conclusive evidence to rule out the possibility of acid dimers. However, the broad bands are characteristic of polymers. Figure 13 is presumed to be of a product which is essentially a very complex acid. Figure 14, page 56, is an infrared analysis chart of the acetone fraction of the acid insoluble product. Again, this chart was compared to a similar one made by Suiter. The two were found to be just about the same. Figure 14 indicates the presence of the same groups as does Figure 13. However, there is still no peak at 10.6 microns to indicate the presence of acid dimers. Any unsaturation that might be present does not show because of the broad band contribution of the OH in the carboxyl groups and water.

It can be concluded that the acid soluble portion and the acetone fraction of the acid insoluble portion have essentially the same structural groups present. It is possible that the acid insoluble portion is more highly polymerized than the acid soluble portion. Both portions being essentially complex acids. Further work should be done on separating some of the components before another infrared analysis is made. This would give a more positive identification of the structural groups present.

D. Simultaneous Air-Oxidation and Extraction

Excessive foaming occurred during the initial runs. This foaming was detrimental to the operation of the test runs. The foam was dispersed by using a nichrome wire heating coil suspended above the aqueous mixture. In order for the wire heater to be effective, it had to be

"red hot". If the foam dried on the wire, the wire then became ineffective. The rate at which the foam could be dispersed dictated the air rate. The yields obtained were approximately 1.3 to 1.8 per cent. An oxidation time of twenty hours was required to obtain these yields. The yields indicate that some of the organic material can be removed by this process. Because of the low yield, the work on this phase of this investigation was discontinued.

SUMMARY

The maximum yield obtained in this investigation was 11.17 per cent.

The oxidation conditions were as follows:

Temperature	240°C
Pressure	40.2 psia
Air Velocity	0.55 fps
Shale Size	-12, +100 mesh
Time	7.0 hours
Bed Weight	200 grams

These operating conditions represent the optimum operating conditions when a shale size distribution of -12, +100 mesh was used.

The optimum operating conditions chosen for this investigation follow:

Temperature	240°C
Pressure	40.2 psia
Air Velocity	0.55 fps
Shale Size	-35, +150 mesh
Time	5.0 hours
Bed Weight	200 grams

At these optimum conditions, a yield of 9.77 per cent was obtained.

It was decided to select these as the optimum conditions because the oxidation time required was only five hours.

The results of this investigation show the need for a charge having a size distribution. From a charge having a size distribution and a specific surface of 322 cm^2 per gram of shale, a yield of 9.77 per cent was obtained, and from a similar charge having only one screen size and a specific surface of 315 cm^2 per gram, a yield of only 5.6 per cent was obtained. These two runs were made at the above operating conditions except that the particle size was changed.

The organic products, resulting from the oxidation of oil shale, are essentially highly complex acid polymers.

Yields of 1.3 to 1.8 per cent were obtained during the simultaneous air-oxidation and extraction. These yields were so low that the study was discontinued.

RECOMMENDATIONS

Further work could be done in continuation of this research project.

A complete study should be made of the effect of particle size and size distribution on the yield.

Also, the extraction step could be investigated to find out if any inorganic material is passing through the filter papers. This material might be in a colloidal state.

The results of this investigation could be compared with those obtained from Green River top shale and the Colorado shale.

When the oxidized organic material is identified, a study should be made to find the optimum conditions that give the most desirable product.

BIBLIOGRAPHY

1. Bell, H. S., Oil Shales and Shale Oils, D. Van Nostrand Company, Inc., New York, N.Y., 1948.
2. Brown, George G., Unit Operations, John Wiley & Sons, Inc., New York, N. Y., 1950.
3. Erickson, Larry L., Extraction of Organic Materials From Green River, Wyoming Oil Shales, M.S. Thesis, Montana State College, 1960.
4. Suiter, Raymond C., Extraction of Organic Materials From Green River, Wyoming Oil Shales, M.S. Thesis, Montana State College, 1959.

ACKNOWLEDGMENT

The author wishes to thank the Food Machinery and Chemical Corporation for sponsoring this research project. The author also wishes to thank Professor H. A. Saner and Research Fellow Raymond Porter of the Chemical Engineering Department, Montana State College, for their aid and suggestions on this project.

APPENDIX

	page
Table I	Air-Oxidation and Extraction Data 38
Table II	Specific Surface for Each Screen Size 42
Table III	Data for Figures 11 and 12 43
Figure 1	Air-Oxidation Fluid-Bed Reactor 44
Figure 2	Extraction and Analysis Flow Diagram 45
Figure 3	Open Boiling Apparatus 46
Figure 4	Effect of Oxidation Temperature on the Yield 47
Figure 5	Effect of Oxidation Pressure on the Yield 48
Figure 6	Effect of Oxidation Time on the Yield 49
Figure 7	Effect of Oxidation Time on the Yield 50
Figure 8	Effect of Oxidation Time on the Yield 51
Figure 9	Effect of Oxidation Temperature on the Yield 52
Figure 10	Effect of Oxidation Pressure on the Yield 53
Figure 11	Effect of Specific Surface on the Yield 54
Figure 12	Yield per Specific Surface versus Specific Surface 55
Figure 13	Infrared Analysis of Products 56
Figure 14	Infrared Analysis of Products 56

