

REPORT OF
RESEARCH ON SASKATCHEWAN AND MANITOBA OIL SHALES

By
Richard W. Ince

RECOVERY RESEARCH

May, 1966

MANITOBA AND SASKATCHEWAN
OIL SHALES RESEARCH

During the past year, Sun Oil Company has been involved in extensive research programs pertaining to the oil shales of Manitoba and Saskatchewan. The research areas include the development of assaying techniques, the analysis of shale oil obtained from retorting the Canadian shales, the analysis of the gas produced from retorting the shales, the development of batch retorts for producing large samples of oil, the analysis of spent Canadian shale for fixed carbon heating value, and the development of a retorting process which might be economically attractive for use in a commercial venture in producing synthetic fuels from oil shale. A detailed economic study of commercial possibilities for the Manitoba and Saskatchewan oil shales was also made.

The results of date of these research activities are presented in this report. Most of the activities described herein are being continued, and new research projects in oil shales are planned for the future.

OIL SHALE ASSAY RESEARCH

The Fischer assay has long been the standard assay tool for oil shales. The Production Service Laboratory of Sun Oil Company found this apparatus very cumbersome and time consuming for running numerous samples. Standard downdraft core retorting equipment appeared to contain most of the essentials necessary to yield proper results of oil shale assays. A research project was initiated to determine whether or not the downdraft retort would adequately assay the large number of core samples which were anticipated from the Saskatchewan and Manitoba oil shale deposits.

The study included an evaluation of the following variables:

- 1 Retort design
- 2 Retort lid gasket materials
- 3 Rate of heating
- 4 Cooling bath temperatures
- 5 Sample size
- 6 Sample preparation
- 7 Methods of sampling
- 8 Oil and water collection apparatus
- 9 Oil hold-up in condenser tube

The assay equipment which was developed from the study is shown in Figure 1. A detailed drawing of a single retort with adapter is shown in Figure 2. The equipment is briefly described as follows:

Retort - The retort body, 5 inches long and 1-1/2 inches in diameter, is constructed of stainless steel. A 1/4 inch diameter by 9 inches long stainless steel tube is welded to the retort body. A screw cap and gasket assembly at the top assure a leak-free system. The retort will hold 100 grams of crushed oil shale.

Furnace - The furnace consists of four 1000 watt heater strips affixed to a metal support. The metal support also positions twelve retorts in the furnace. The entire assembly is insulated against heat loss. A temperature sensing and controlling unit is provided.

Collection System - The oil and water vapors are condensed in a 15 milliliter centrifuge tube which is immersed in a 32°F water bath. Since all of the vapor and mist is not totally collected in the tube, an adapter has been designed so that any oil particles not trapped in the centrifuge tube must pass through a column of glass beads before escaping. The volumes of oil and water collected are read directly from the centrifuge tube.

The procedure for assaying is as follows. The cores are slabbled lengthwise, and half of the core (usually one foot in length) is crushed to a size of 1/4 inch or less. The crushed material is "coned and quartered" to a sample of about 110 grams. This sample is oven dried at 110°C for 16-24 hours. The retort is charged with 100 grams of the dried sample and placed in the furnace. The adapter and centrifuge tube are connected, and the ice bath is positioned. Heat is applied so that a temperature of 500°C can be attained in less than an hour. Once maximum temperature is attained, it is maintained for at least thirty minutes more. This retorting time is sufficient to complete the kerogen decomposition. The centrifuge tube is removed, allowed to come to room temperature, and after centrifuging is read to the nearest 0.1 milliliter. The gain in weight of the adapter is determined, and the volume of oil and water this weight represents is calculated and added to that volume in the centrifuge tube. Finally, the appropriate calculations are made to convert the assay results to gallons of oil and water per ton of oil shale.

The research study resulted in many runs in order to determine the effect of each variable. A large number of cores were crushed, combined, and thoroughly mixed. The resulting aggregate was then "coned and quartered" to obtain duplicate samples of approximately 110 grams. Six samples were tested each time against one variable. Table I is a summary of the test work.

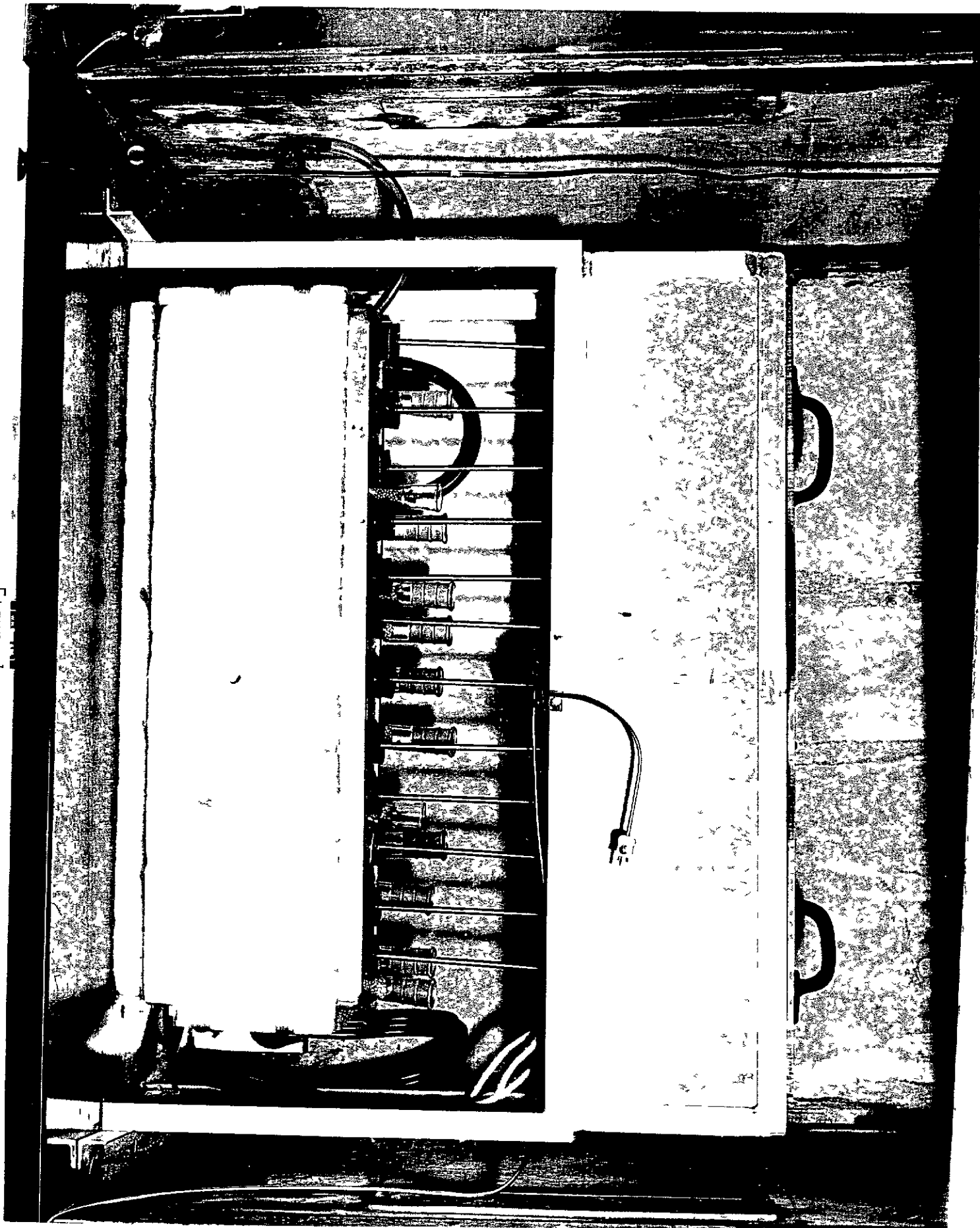
The research led to the following conclusions regarding the assaying of Canadian oil shales

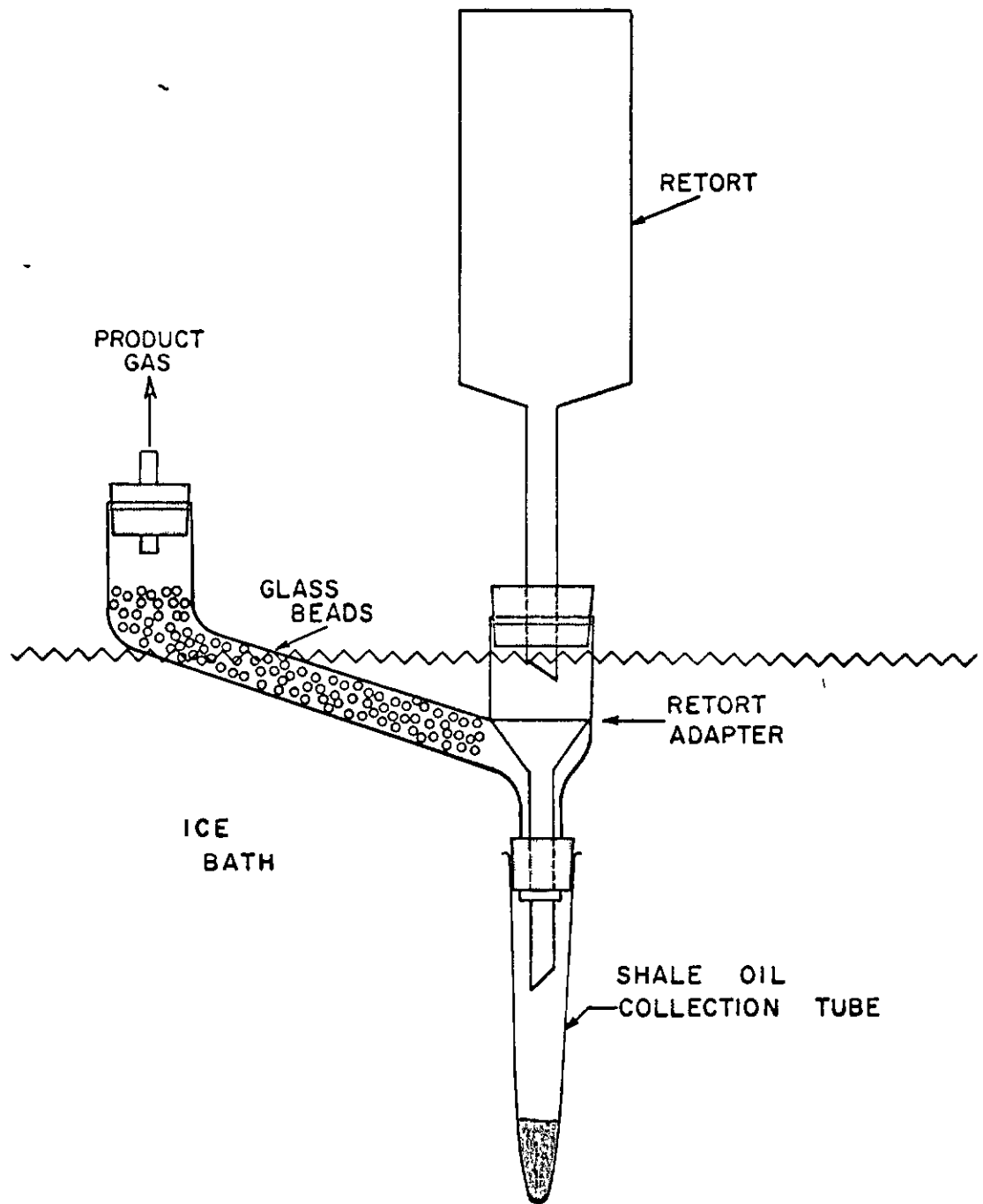
- 1 Pre-heating the furnace to 500°F does not affect the assay
- 2 Using $\frac{1}{4}$ inch shale particles yields results reproducible to ± 10 gal /ton
- 3 The assay is affected by the cooling bath temperature Higher oil yields may be obtained with extremely cold baths.
- 4 The samples are hygroscopic and should not be exposed to the atmosphere for long periods after the drying stage
5. Extended periods of low temperature heating (110°C) will lower the oil yield
- 6 The "coning and quartering" technique of obtaining representative samples may be used with confidence
- 7 The downdraft retort equipment will produce results comparable to the Fischer assay. The results are accurate to ± 1 gallon/ton

TABLE I
SUMMARY OF ASSAY RESEARCH RESULTS

	<u>Test Conditions</u>	Average	Deviation		Average
		<u>Oil Assay (Gal/Ton)</u>	<u>Low</u>	<u>High</u>	<u>Water Assay (Gal/Ton)</u>
1	100 gram sample 32°F cooling bath Furnace started at Room temperature	14.6	13.8	15.2	4.4
2.	As above except furnace preheated to 500°F	14.5	14.2	14.8	4.0
3	100 gram sample, no preheat, ice-salt bath at about 60°F These samples stayed in a dessicator for 3 days prior to testing (Note water assay)	14.3	14.0	15.1	6.5
4	As above, except run immediately after drying	14.8	14.6	15.1	4.2
5	100 gram sample, no pre- heat, dry ice and acetone bath at -40°F	15.5	14.7	16.6	4.5
6	Fischer Assay	14.3	13.9	14.8	4.6
7	100 gram samples, oven dried for 16 days at 110°C, 32°F ice bath	12.0	9.5	13.6	4.6

Figure 1





SUN OIL SHALE ASSAY EQUIPMENT

ANALYSIS OF ASSAY OIL

The shale oil which was accumulated from the assay experiments was combined and sent to Sun Oil Company's Research and Engineering Laboratory in Marcus Hook, Pennsylvania. Extensive analytical work was performed on the sample of shale oil submitted. Since the total quantity of oil available at this time was only a few hundred milliliters, much of the work had to be done on a micro-scale, and a few tests had to be omitted.

The results of these analytical studies are summarized in Tables 2 through 7 and in Figure 3. Table 2 is the inspection data on the whole sample and on individual fractions. These data include volume percent of each fraction, elemental analyses, Conradson carbon content, pour point, viscosity, API gravity, and valuable minerals content. Tables 3 through 6 show the hydrocarbon results on the naphtha, kerosene, gas oil, and residue fractions. These data include weight percents of resins, aromatics, olefins, and saturates, also, refractive index, density, and average molecular weight for each fraction. Table 7 is the distillation data for the Manitoba and Saskatchewan shale oil. Figure 3 depicts the true boiling point distillation curve of the oil. The discontinuities in the curve are probably due to the combined samples of assay oil which had been obtained under many various retorting conditions, as described in the section on assay research.

The data which were obtained from the initial analytical work performed on the Manitoba and Saskatchewan shale oil sample showed that the oil was a low gravity, highly aromatic, and hydrogen deficient hydrocarbon mixture. The nitrogen and sulfur contents of the shale oil were quite high, thus the oil as retorted is

not suitable for charging to any existing refinery as a crude oil. However, with catalytic hydrogenation this shale oil may be converted into a synthetic crude which might be an excellent refinery feedstock. The hydrogenation would remove the undesirable nitrogen and sulfur, increase the hydrogen-carbon atomic ratio, increase the API gravity, and hopefully produce a high quality gasoline and fuel oil crude stock. The high aromaticity of the oil might even be significant for petrochemical feedstock purposes.

TABLE 2

INSPECTION DATA ON WHOLE SAMPLE AND FRACTIONS
OF CANADIAN SHALE OIL

Boiling Range, °F	Whole Oil	IBP - 375	375 - 535	535 - 834	834+
Vol %	100 0	30 5	7 7	39 1	22 7
Wt %	100.0	28 5	7 2	40 6	23 7
Wt % Carbon	79 77	78 03	79 67	81 35	84 02
Hydrogen	9 64	10 57	9 97	9 70	8 42
Oxygen	2 74	2 58	2 23	2 35	1 62
Nitrogen	1 18	0 73	0 86	1.15	1 63
Sulfur	6 87	7 1	6 9	5 5	3 8
TOTAL	100 20	99 01	99 63	98 90	99 49
Conradson Carbon	4	ND	ND	0 3	32 5
Pour Pt, °F	+15	ND	-15	+35	+124
Viscosity 100°F, SUS	78 3	ND	ND	183 9	ND
210°F, SUS	35 65	ND	ND	38 54	73109
Gravity, API	11 5	26 5	26 4	10 7	<10
Nickel, ppm					33
Vanadium, ppm					14

ND - not determined

TABLE 3
 NAPHTHA FROM CANADIAN SHALE OIL

init -375°F

FIA ANALYSIS		
Aromatics	68 Vol	%
Saturates	11 Vol	%
Olefins	21 Vol	%

TABLE 4
 KEROSENE FROM CANADIAN SHALE OIL

375-535°F

Aromatics	89 Wt	%
Saturates	3	
Olefins	6	

Saturates + Olefins

n_D^{20}	1.4453
d_4^{20}	0.7989
MW	228

Aromatics

n_D^{20}	1.5429
d_4^{20}	0.9934
MW	190

n_D^{20} is refractive index at 20°C
 d_4^{20} is density corrected to 20°C
 MW is the average molecular weight

TABLE 5

GAS OIL FROM CANADIAN SHALE OIL

535-834°F

Resins	30 Wt %
Aromatics	61
Olefins	6
Saturates	3

Aromatics 61 Wt %

n_D^{20}	1 5865
------------	--------

d_4^{20}	1 0102
------------	--------

MW	271
----	-----

Saturates 3 Wt %

n_D^{20}	1 4604
------------	--------

d_4^{20}	0 8364
------------	--------

MW	328
----	-----

Resins 30 Wt %

Wt %	Carbon	79 29
	Hydrogen	8 95
	Oxygen	5.41
	Nitrogen	2 50
	Sulfur	3 00

TOTAL	99 15
MW	290

TABLE 6

RESIDUE FROM CANADIAN SHALE OIL

834°F+

Asphaltenes	43	Wt %
Resins	28	
Aromatics	26	
Saturates	3	

Aromatics 26 Wt %

n_D^{20}	1.5694
d_4^{20}	1.1351
MW	508

Saturates (+ Olefins) 3 Wt. %

n_D^{20}	1.4653
MW	395

Asphaltenes 43 Wt %

Wt % Carbon	83.28
Hydrogen	6.50
Oxygen	3.60
Nitrogen	2.50
Sulfur	4.14
TOTAL	100.02
MW	2,125

Resins 28 Wt %

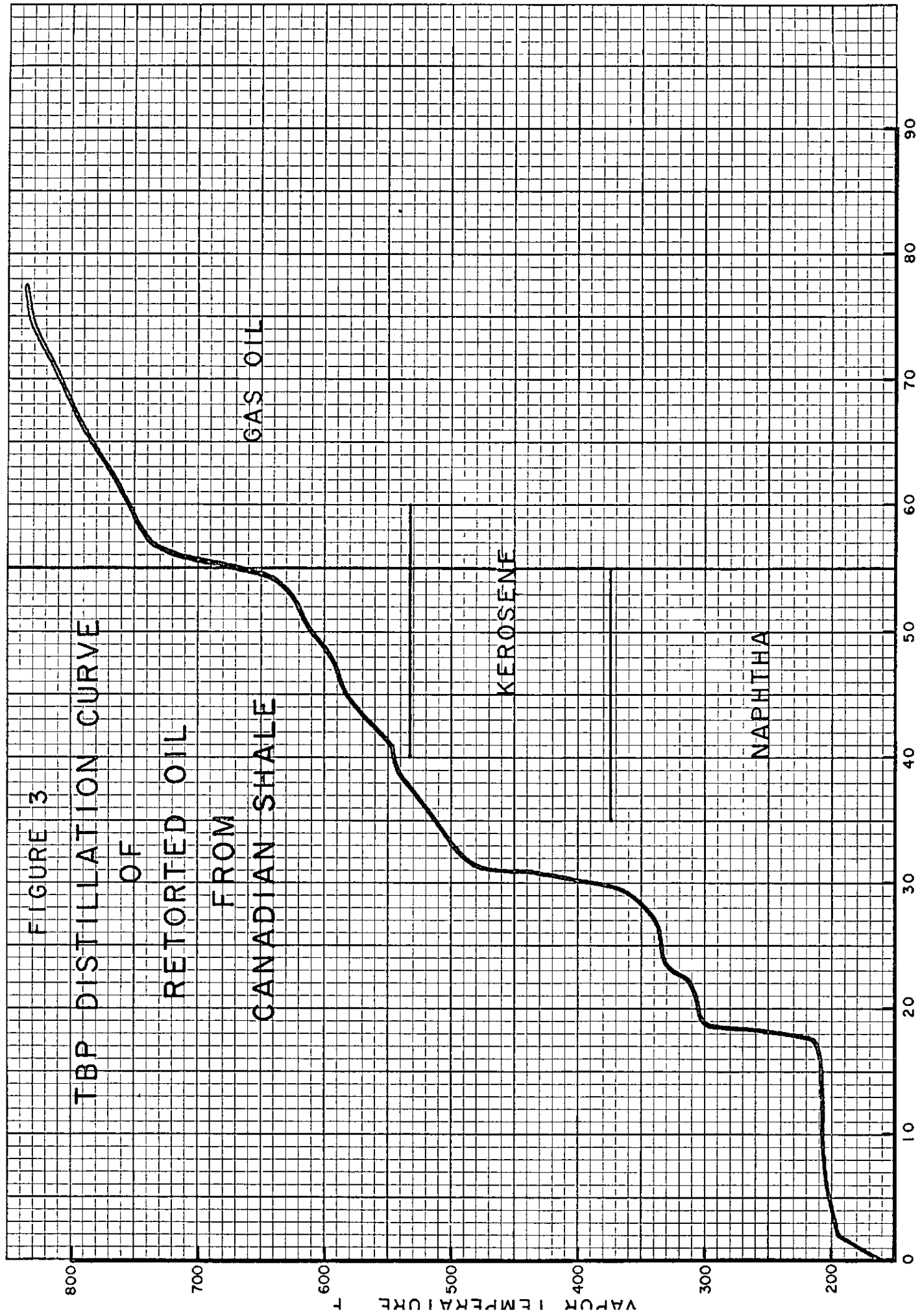
Wt % Carbon	83.50
Hydrogen	9.02
Oxygen	2.48
Nitrogen	1.92
Sulfur	5.48
TOTAL	102.40
MW	502

TABLE 7
DISTILLATION OF CANADIAN SHALE OIL

V T °F	Vol %	Cut No	Boiling Range, °F	Vol %	Wt %	Specific Gravity 60/60°F
155	1 BP	1	155-375	30.5	28.5	8957
194	1.7					
198	2.8	2	375-535	7.7	7.2	8960
199	3.9					
201	5.0	3	535-834	39.1	40.6	9952
203	6.1					
205	7.2	Res	834+	22.7	23.7	1.0+
207	8.3					
207	9.4					
208	10.5					
208	11.6					
208	12.7					
210	13.8					
210	14.9					
210	16.6					
210	17.7					
300	18.8					
302	19.9					
306	21.0					
309	22.1					
329	23.3					
333	24.9					
333	27.1					
352	29.3					
375	30.5					
483	31.5					
492	32.5					
501	33.5					
510	34.6					
518	35.6					
526	36.6					
535	38.2					
547	39.3					
547	40.9					
566	42.5					
581	44.7					
590	46.3					
597	48.0					
602	49.0					
613	50.7					
623	52.3					
649	54.5					
737	56.1					
746	57.7					

V T °F	Vol %
756	59.9
761	61.5
773	63.2
786	64.8
803	68.6
817	70.8
831	74.0
834	77.3

FIGURE 3
TBP DISTILLATION CURVE
OF
RETORTED OIL
FROM
CANADIAN SHALE

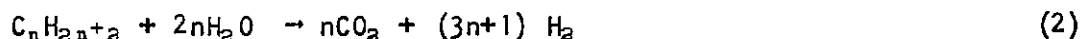
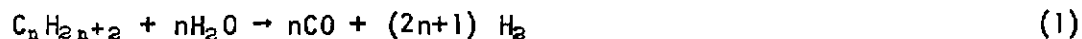


VOLUME % DISTILLED

GAS ANALYSIS WORK

As previously mentioned, the Manitoba and Saskatchewan shale oil is hydrogen deficient and high in sulfur and nitrogen content. Hydrogenation will be required to convert the material to a high grade feedstock. Since the pure hydrogen required for hydrogenation is expensive, it would be desirable to have a supply of hydrogen readily available for the processing of the shale oil.

One of the most economical processes for producing hydrogen is the steam-hydrocarbon process. This requires water and hydrocarbon gas as raw materials. The basis for the steam-hydrocarbon manufacturing process is the fact that hydrocarbons react catalytically with steam as follows:



Both of these reactions are endothermic. Reaction (2) above is considered to be reaction (1) followed by



Similar reactions occur between unsaturated hydrocarbons and steam.

One of the highest costs in the production of hydrogen by the steam-hydrocarbon process is the cost of the required hydrocarbon gas. If this gas were readily available, the costs of manufacturing hydrogen would be greatly reduced. One source of the hydrocarbon gas might be the gas evolved from retorting the shale itself. An extensive research effort is being made to determine the quantity and quality of gas evolved during the retorting process.

Equipment for collecting gas samples which are produced from retorting the oil shale was designed and built at the Production Research Laboratory of Sun Oil Company near Dallas, Texas. Figure 4 is a simplified drawing of the basic equipment used in the experimental work. Figure 5 is an actual photograph of the equipment used. The gas collection equipment is used in conjunction with a downdraft assay retort previously described. A glass cylinder with graduated markings is filled with an acidified sodium sulfate solution and is attached to the gas exit portion of the retort adapter. The lower end of the graduated gas collector is affixed to a drain valve and a levelling tube to keep the evolved gas at atmospheric pressure at all times. As gas is produced in the retort, it displaces the liquid in the collecting cylinder into the levelling tube. The drain valve below the cylinder is manually adjusted to keep the liquid levels in the tube and cylinder equal. The acidified sodium sulfate solution is used to prevent any gases which are evolved from dissolving in the displaced liquid. As the gas accumulates in the cylinder, the volume produced is read directly from the graduated markings.

A plot of cumulative gas evolved as a function of retorting time and temperature is shown in Figure 6. Fifty-gram oil shale samples assaying 18.2 gal./ton were used for this study. The average total quantity of gas evolved at the end of the retorting cycle was 1860 cc of gas. This can be converted to 1192 cubic feet evolved per ton of oil shale retorted, or 2750 cubic feet evolved per barrel of shale oil produced.

The gases which were evolved in these experiments were analyzed by mass spectrometer. The average analysis for the samples evaluated are given in Table 8.

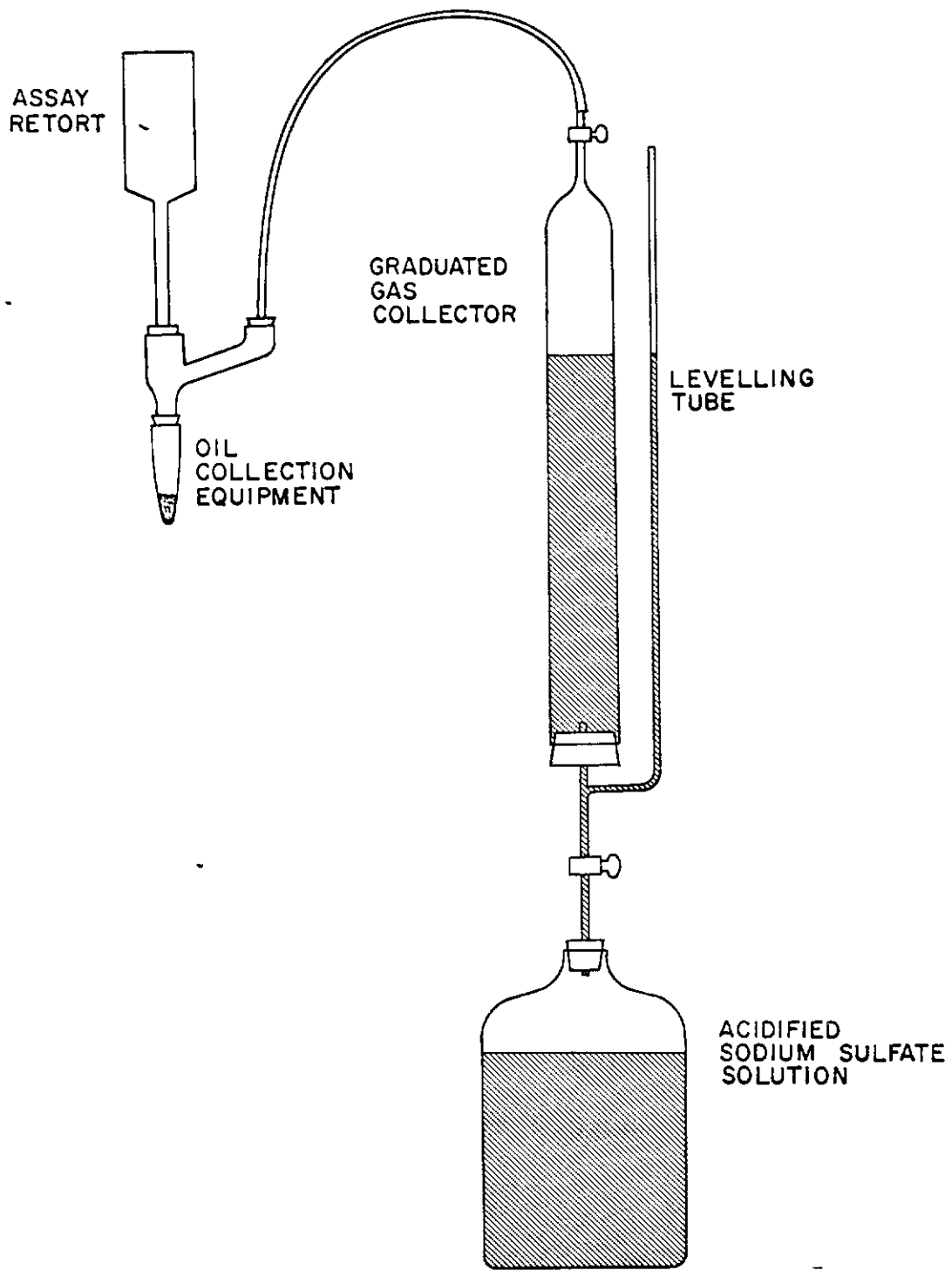
As can be seen in the analysis, the component present in the largest amount is hydrogen, the most desirable gas. In fact, about 1100 cubic feet of hydrogen

are present per barrel of shale oil produced. The total volume of hydrogen required to completely convert one barrel of Canadian shale oil to gasoline is estimated to be about 2400 cubic feet. Thus, more than half of the required hydrogen may be obtained from the gases produced while retorting.

TABLE 8

MASS SPECTROMETRIC ANALYSIS
OF GASES EVOLVED FROM RETORTING
CANADIAN OIL SHALES

<u>COMPONENT</u>	<u>VOLUME %</u>
Hydrogen	40.3
Methane	15.0
Ethylene	1.0
Ethane	2.6
Propylene	1.3
Propane	0.7
Butadiene	0.0
Butylenes	0.7
Isobutane	0.1
n-Butane	0.3
Pentenes	0.2
Isopentane	0.0
n-Pentane	0.0
Hexenes	Trace
Hexanes	0.0
Benzene	Trace
Toluene	0.0
N ₂ and CO	2.7
CO ₂	23.3
H ₂ S	10.2
Air	1.6
C ₆ Diolefins	<u>Trace</u>
TOTAL	100.0



GAS COLLECTION EQUIPMENT

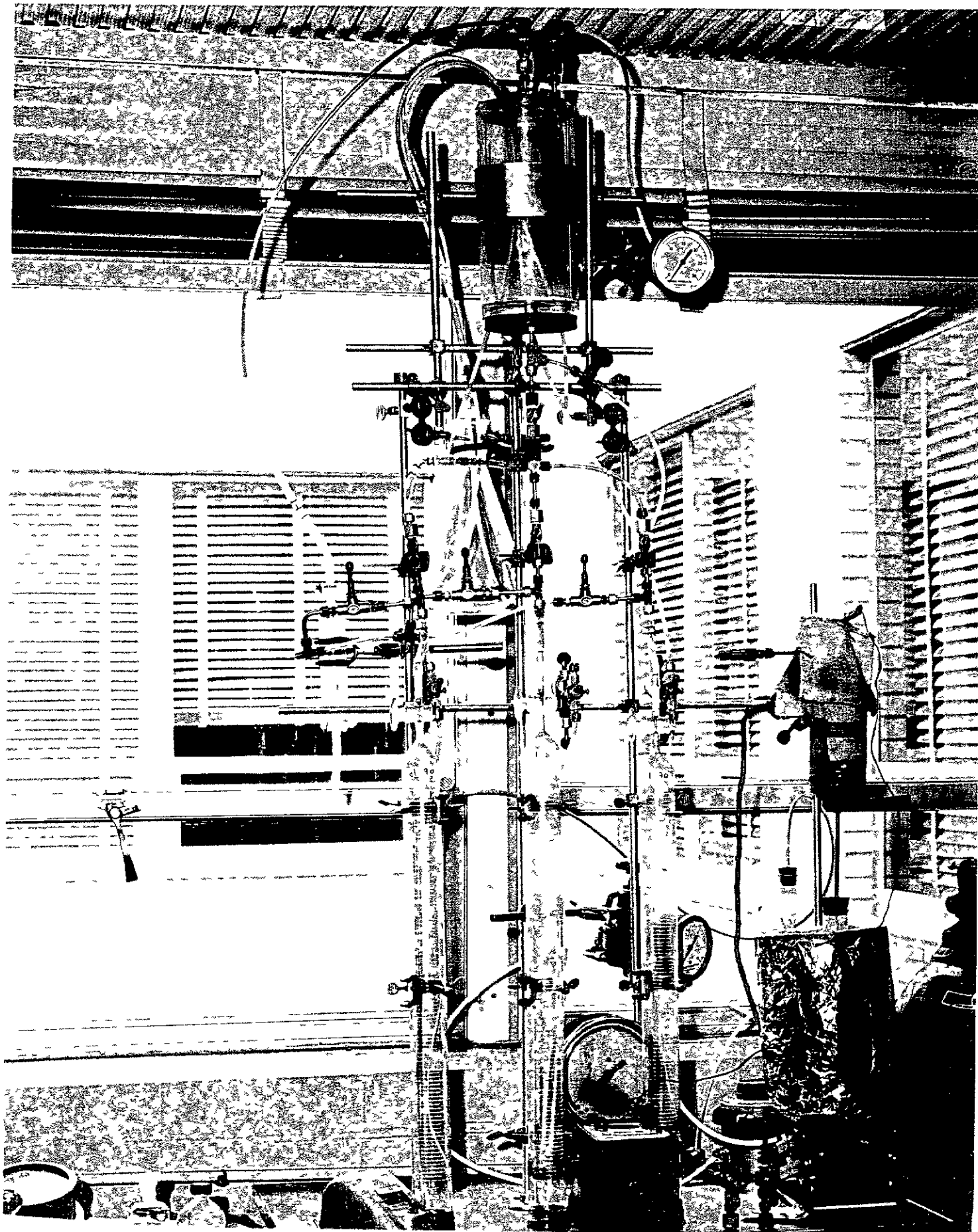


Figure 5

RETORTING TEMPERATURE REQUIREMENTS

It was noticed early in the assay work of Manitoba and Saskatchewan oil shales that the temperatures required for decomposing the kerogen into shale oil were somewhat lower than those temperatures required for the Colorado oil shales. Kerogen decomposition in Colorado oil shales occurs predominately in the range of 700 - 950°F.

A research project was initiated to determine the temperatures required for retorting Canadian oil shales. The downdraft assay retorts and oil collection equipment were used for this research. Identical samples of oil shale were charged to the retorts, and maximum retorting temperatures at 50° intervals between 500° and 900°F were attained and held for 30 minutes. The total oil produced at each temperature was compared to the downdraft retort assay and the results are shown in Figure 7. Saskatchewan and Manitoba oil shales begin retorting at approximately 500 °F and are essentially completely retorted at 800°F. The significance of this information is that a commercial retorting process for Canadian oil shales may have less heat requirements than does a process for other oil shales, such as Colorado shale. This may possibly reduce the retorting cost for Canadian oil shales, which is a substantial cost in the overall economics.

CUMULATIVE GAS EVOLVED
AND TEMPERATURE
VS
RETORTING TIME
50 GRAM SAMPLE
SASKATCHEWAN AND MANITOBA
OIL SHALES

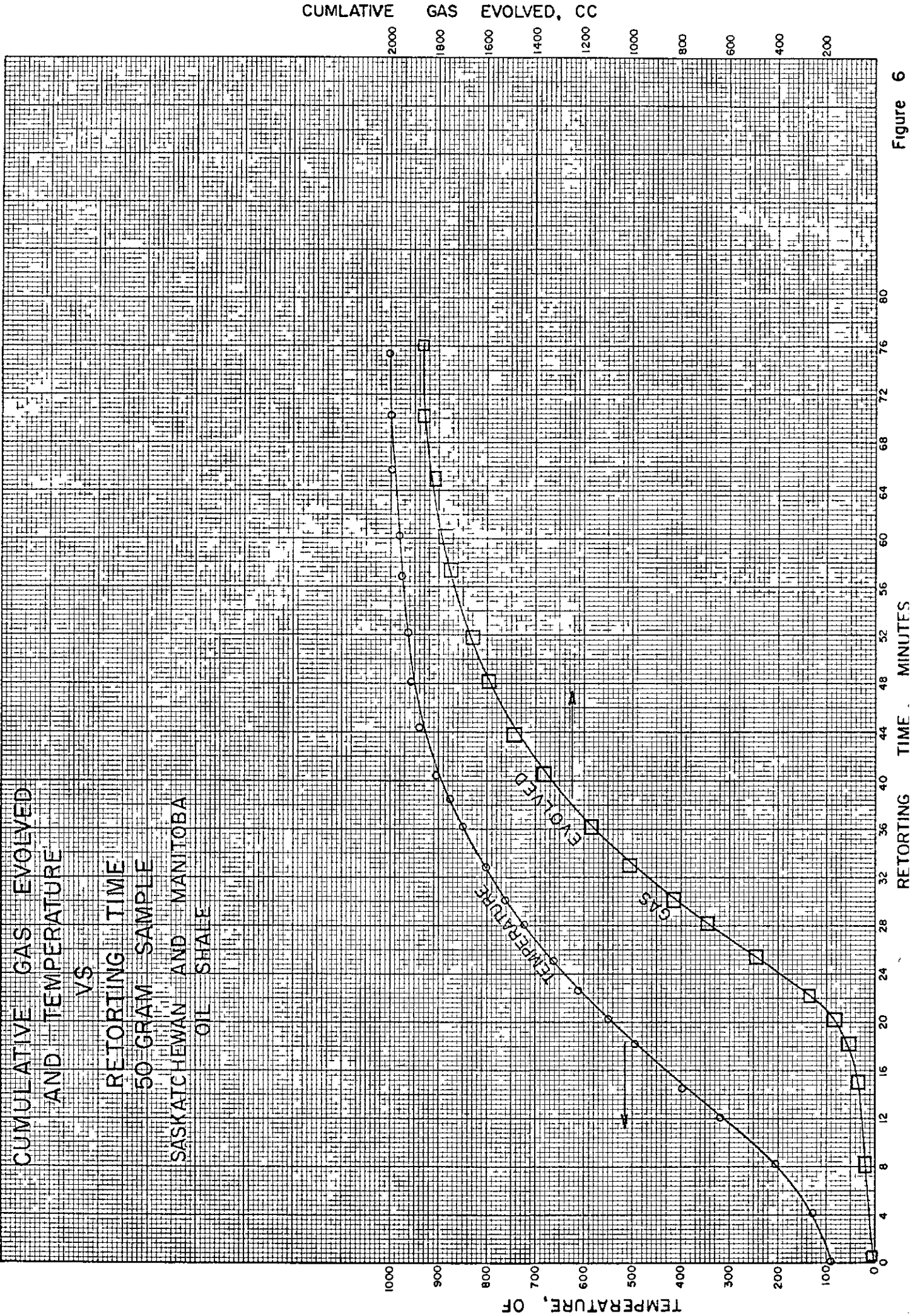


Figure 6

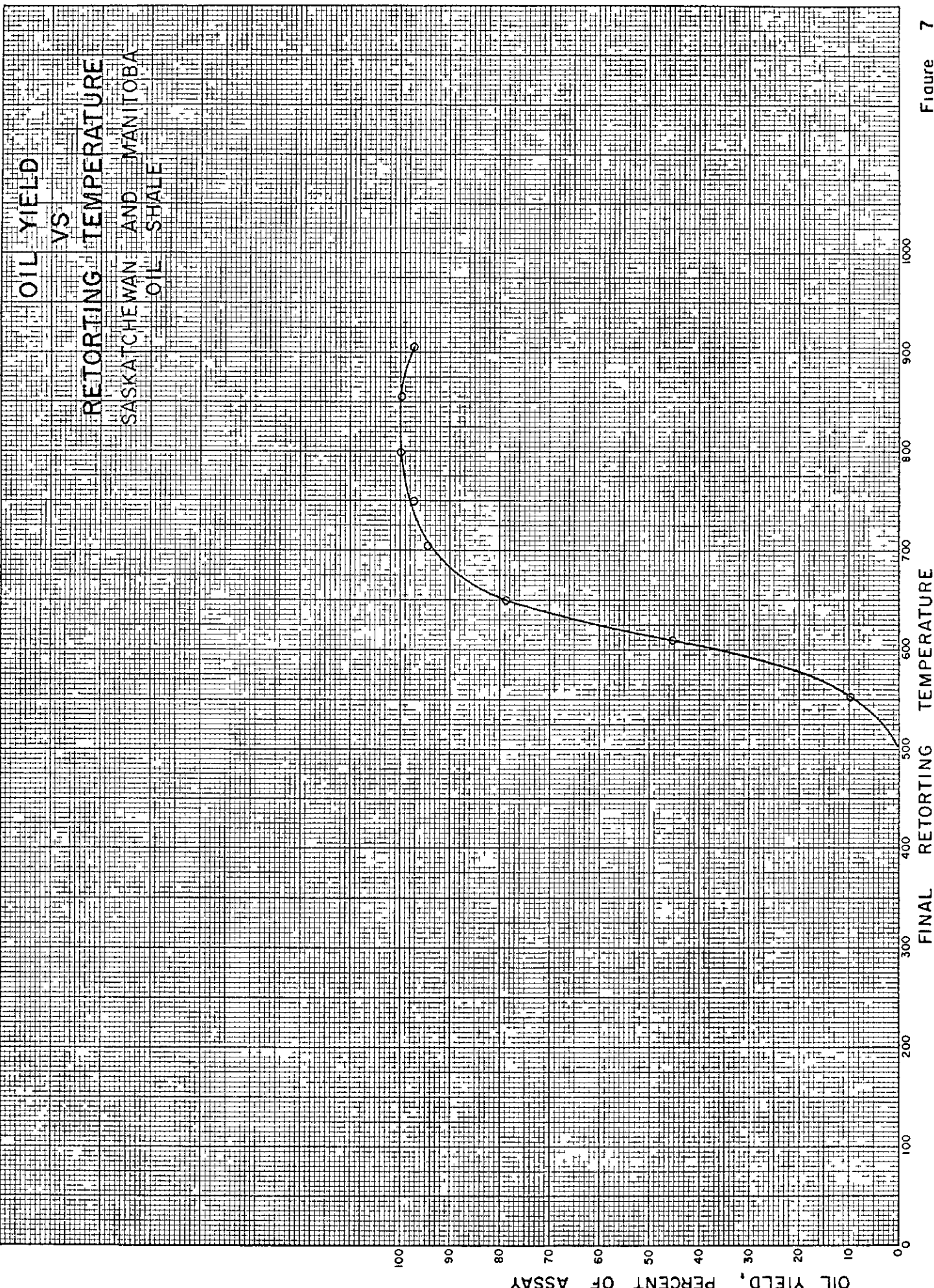


Figure 7

ELECTRICALLY HEATED BATCH RETORT

A batch retort was designed and built to correct the problems encountered with the gas combustion retort previously described. The new retort is heated with electrical Calrod units closely spaced for uniform, quick heating. A diagram of the retort and collection equipment is shown in Figure 9. Photographs of the retort and peripheral equipment are shown in Figures 10 through 13.

The rate of heating in this retort can be controlled closely with an automatic controlling system connected in series with the electrical supply which powers the Calrod heaters. (See Figure 11.) Any rate of heating may be applied to the retort material, so that the effects of retorting rates may be studied. The entire retort and oil shale may be brought up to 900°F within 30 minutes.

The retort capacity is about 50 pounds of Canadian oil shale which has been crushed to 1/4 inch material. This amount of shale produces from 0.2 to 0.5 gallons of shale oil per run, depending on the oil content of the shale. The retort is shown in Figure 12.

The collection equipment is shown in Figure 13. The method of collecting the shale oil mist and vapors is by condensation and settling rather than by mechanical separation, such as the cyclone separator previously mentioned. The oil collection is accomplished by passing the oil mist and vapors through a long water-cooled heat exchanger at low velocities, so that as the particles cool and more vapors condense on each individual mist droplet, the particles will fall out onto the surfaces of the condenser wall. The condensers are placed

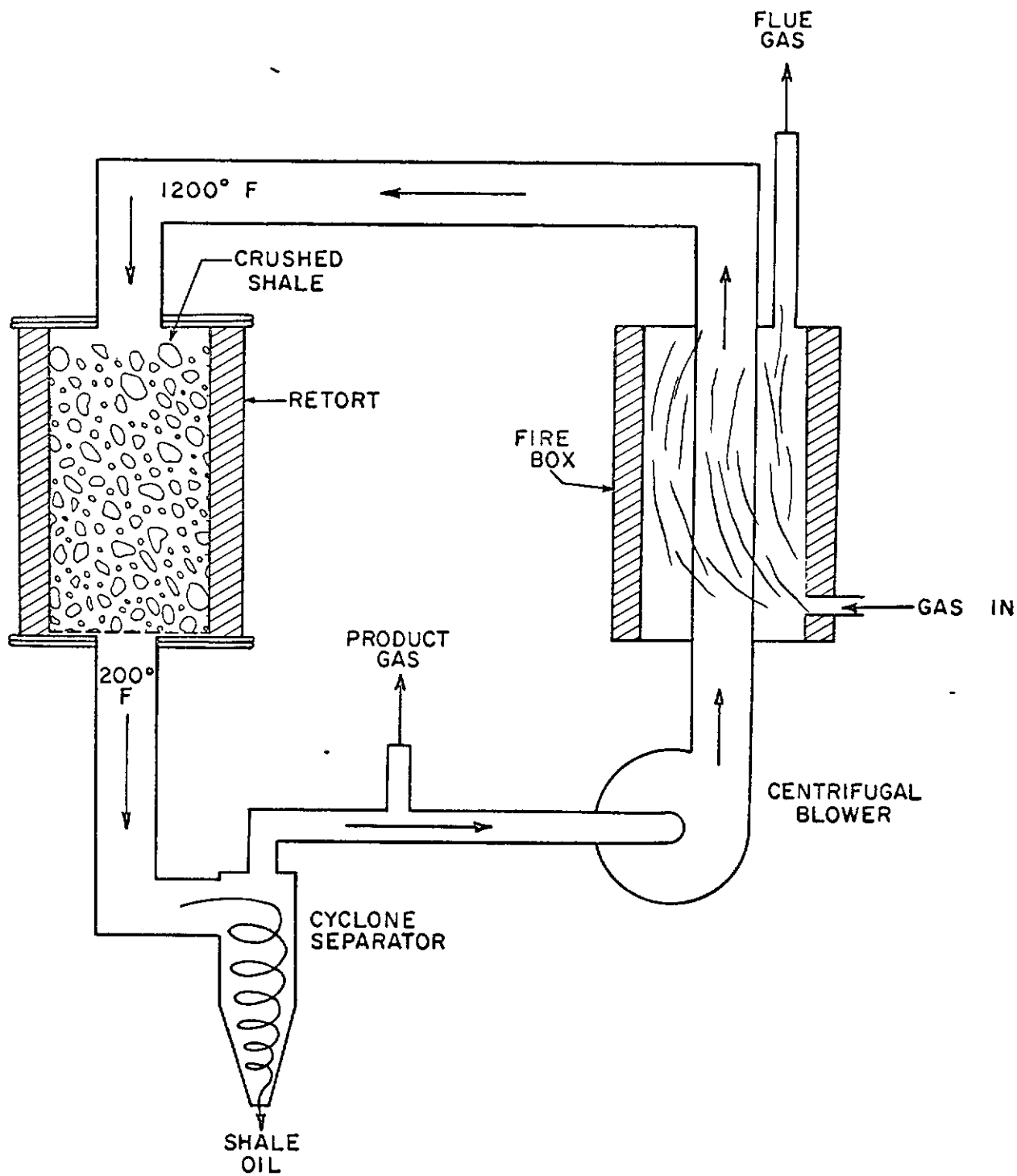
on a slope so that the condensed oil will drain off. Past the water-cooled condensers is a glycol-dry ice-cooled condenser for collecting the light ends. The non-condensables are passed through a gas meter to measure the quantity of gas evolved during retorting. Samples of gas can be taken at various times during each run for analysis.

The shale oil which was produced from the electric retort has been inspected for pour point, viscosity, API gravity, and an Engler distillation has been performed. The results of this inspection are found in Table 9 and Figure 14. A complete analysis is underway at the Marcus Hook Laboratory, but no results are yet available.

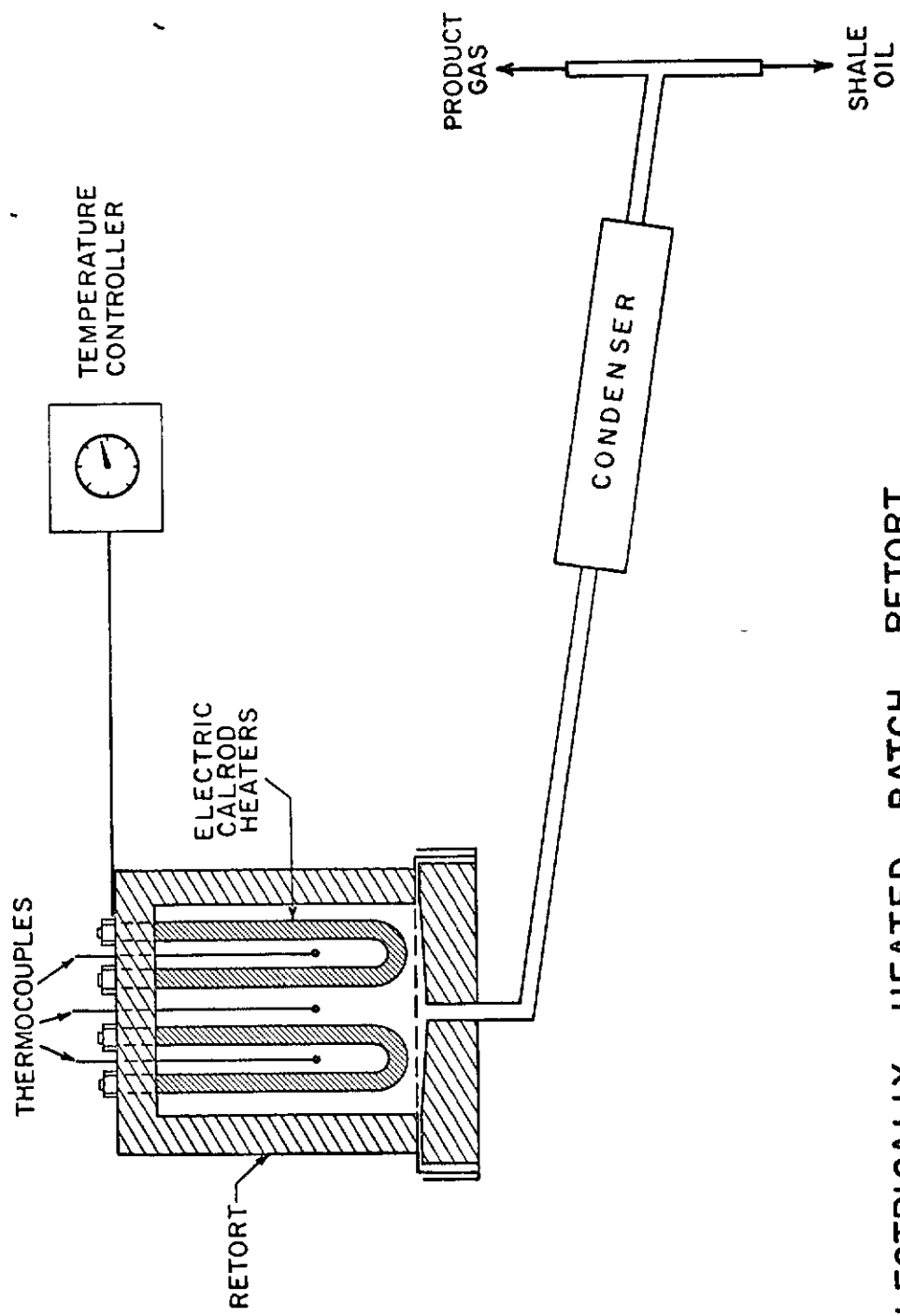
BATCH GAS COMBUSTION RETORT

A batch retort which would produce larger samples of shale oil for analysis was designed and built at Sun's Production Research Laboratory. The retort was similar to the batch gas combustion retorts which the U. S. Bureau of Mines used in the research on Colorado oil shales, except that the Sun retort used external heat as opposed to internal heat supplied by burning the product gases. The retort utilized nitrogen and recycled product gases for the heat exchange media. A diagram of the retort is shown in Figure 8.

This retort proved unsatisfactory for several reasons. Reproducible samples were difficult to achieve because of the oil collection equipment used, and the gas temperatures which entered the retort were difficult to control. Only 50-75% of the oil was collected with the cyclone separator, and the lighter fractions of the oil escaped with the product gas. Analytical work performed on the collected oil showed that the oil composition and characteristics were inconsistent and varied with the different experimental runs, so the retort was abandoned.



BATCH GAS COMBUSTION RETORT



ELECTRICALLY HEATED BATCH RETORT

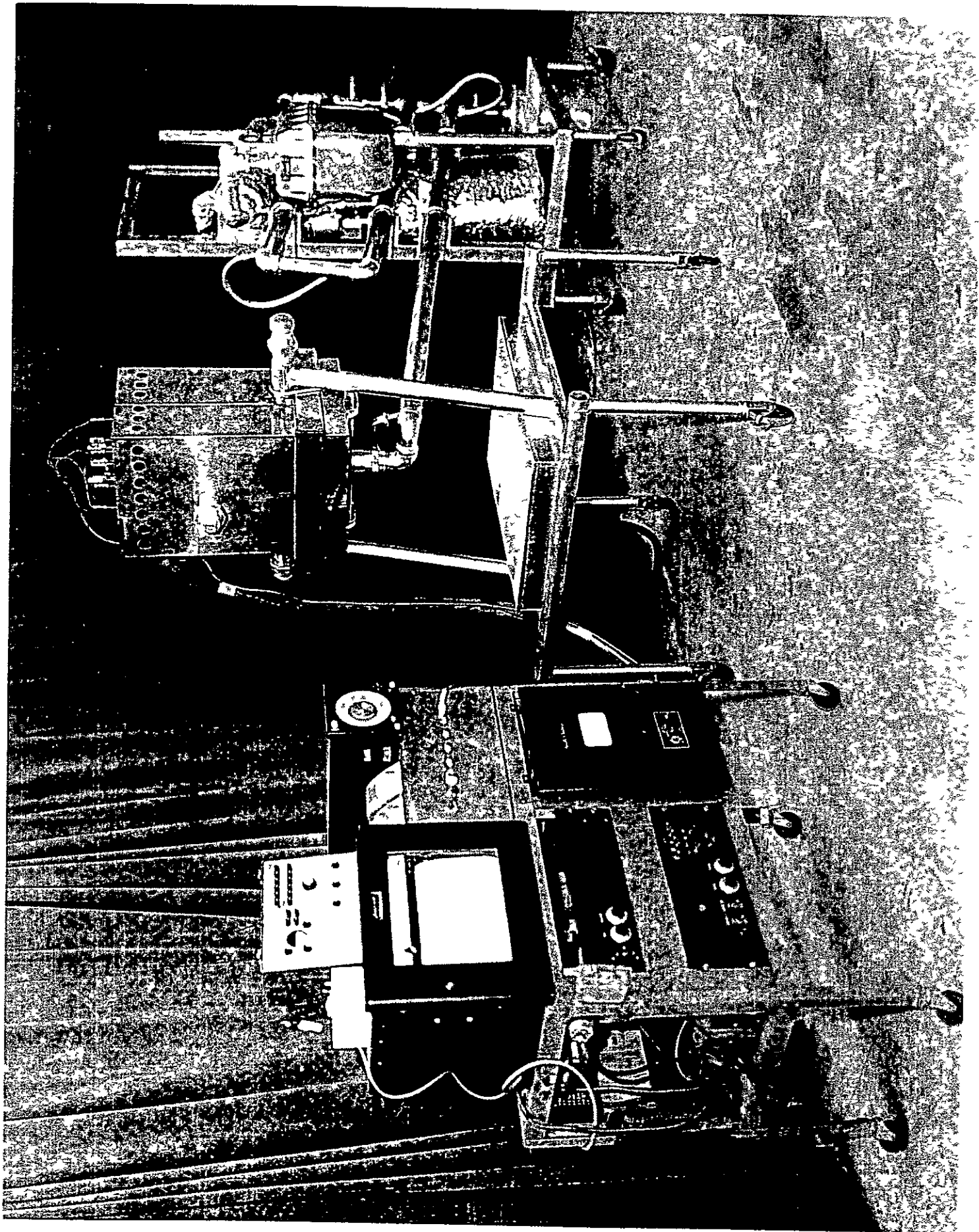


Figure 10

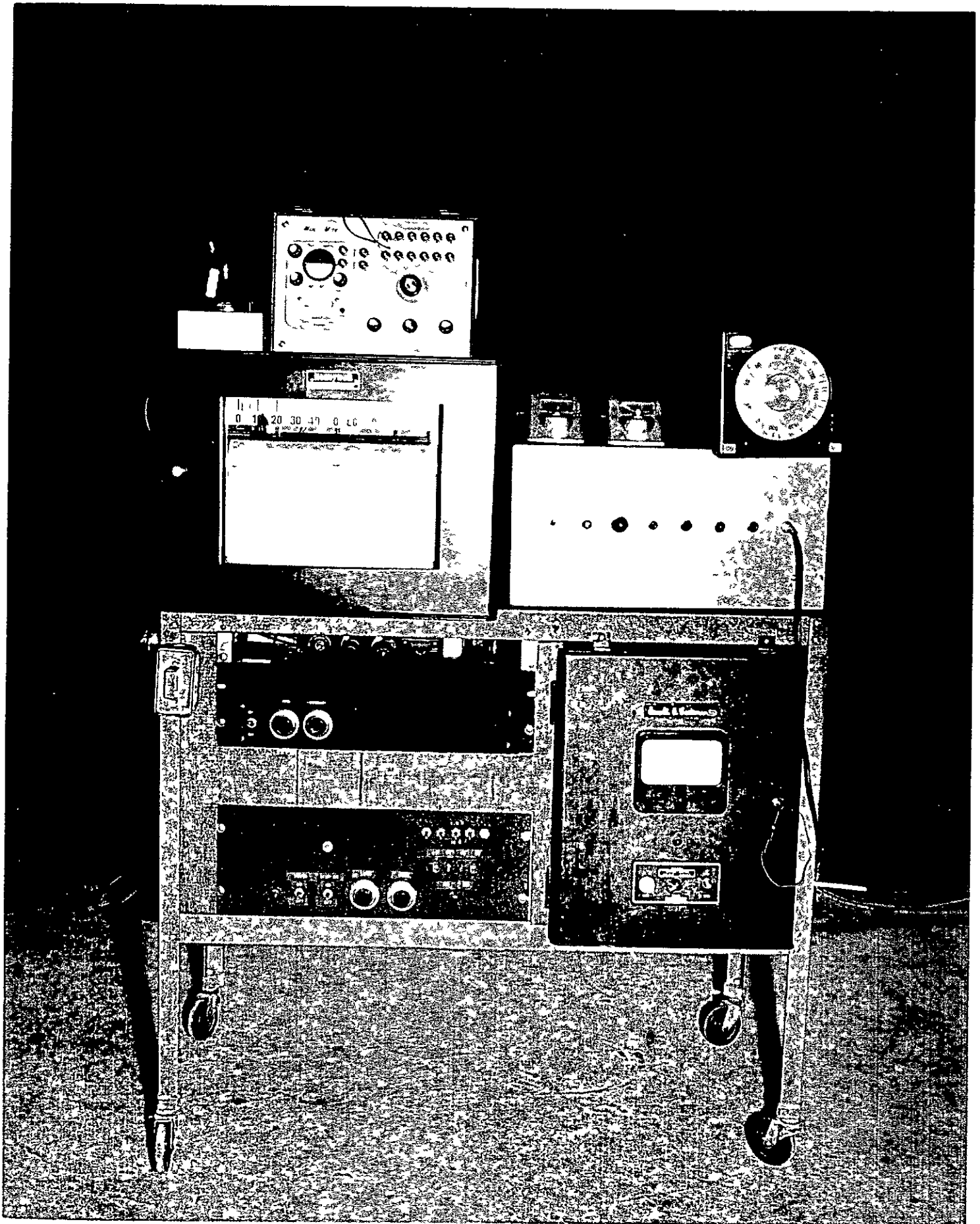


Figure 11

Figure 12

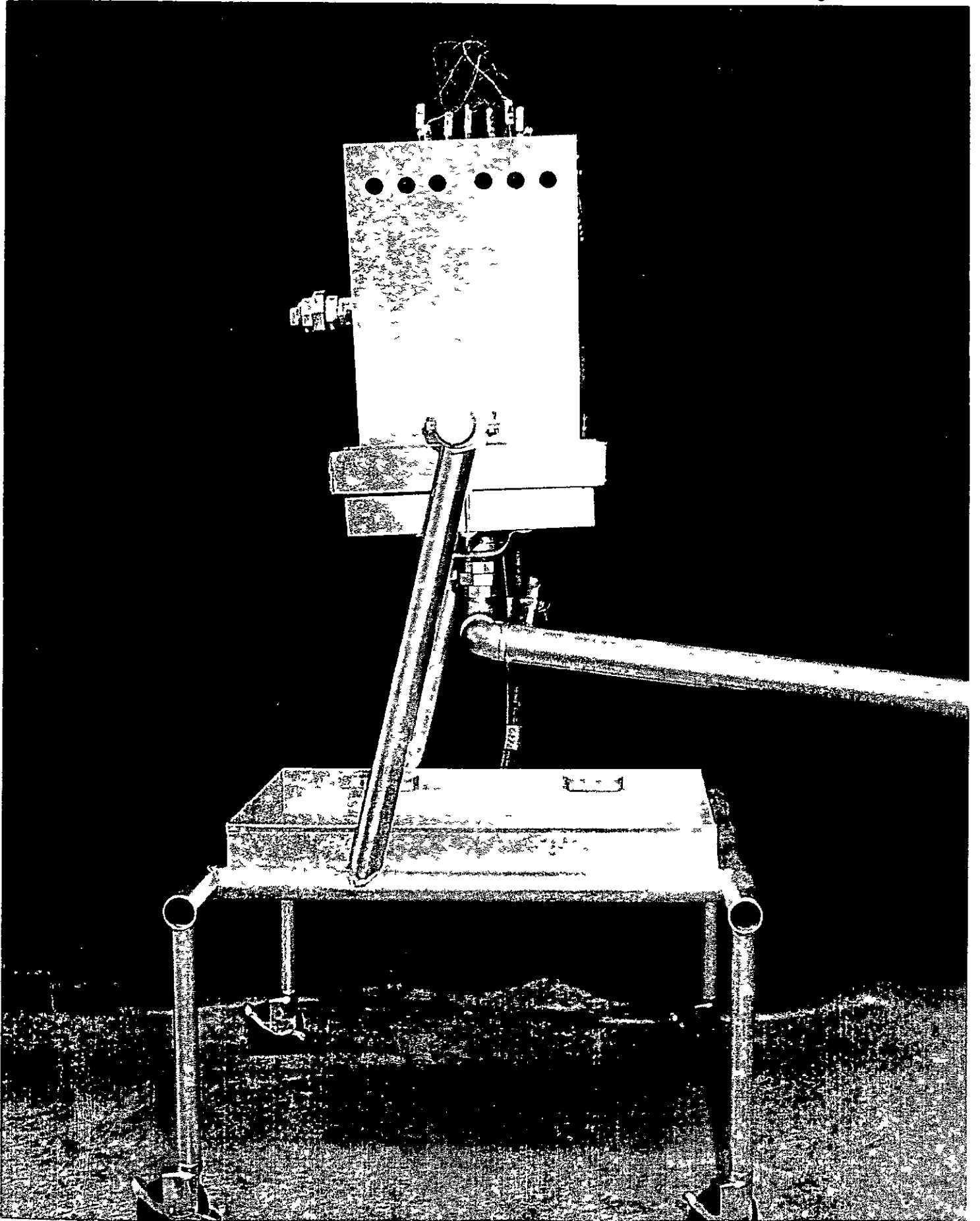


Figure 13

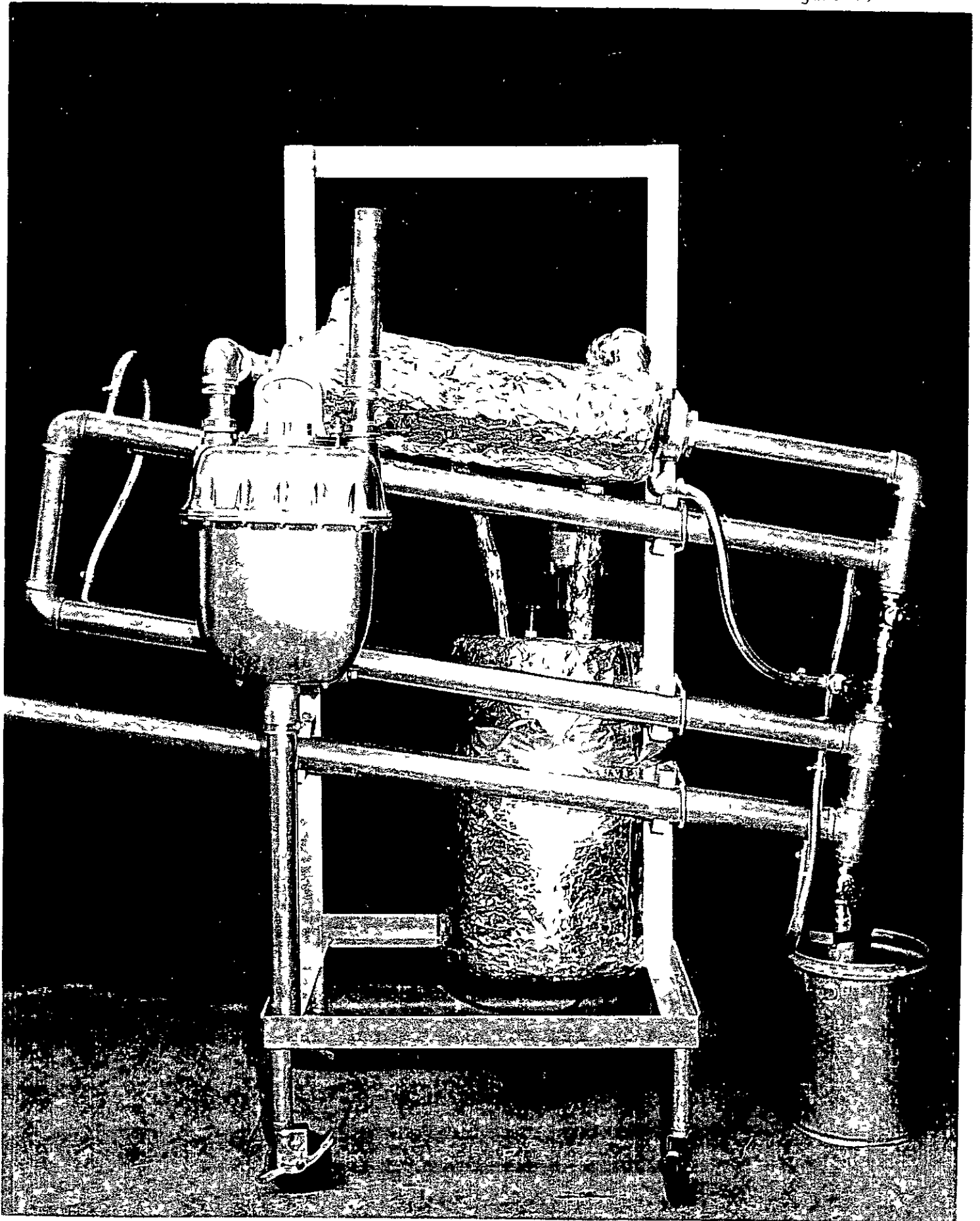


TABLE 9

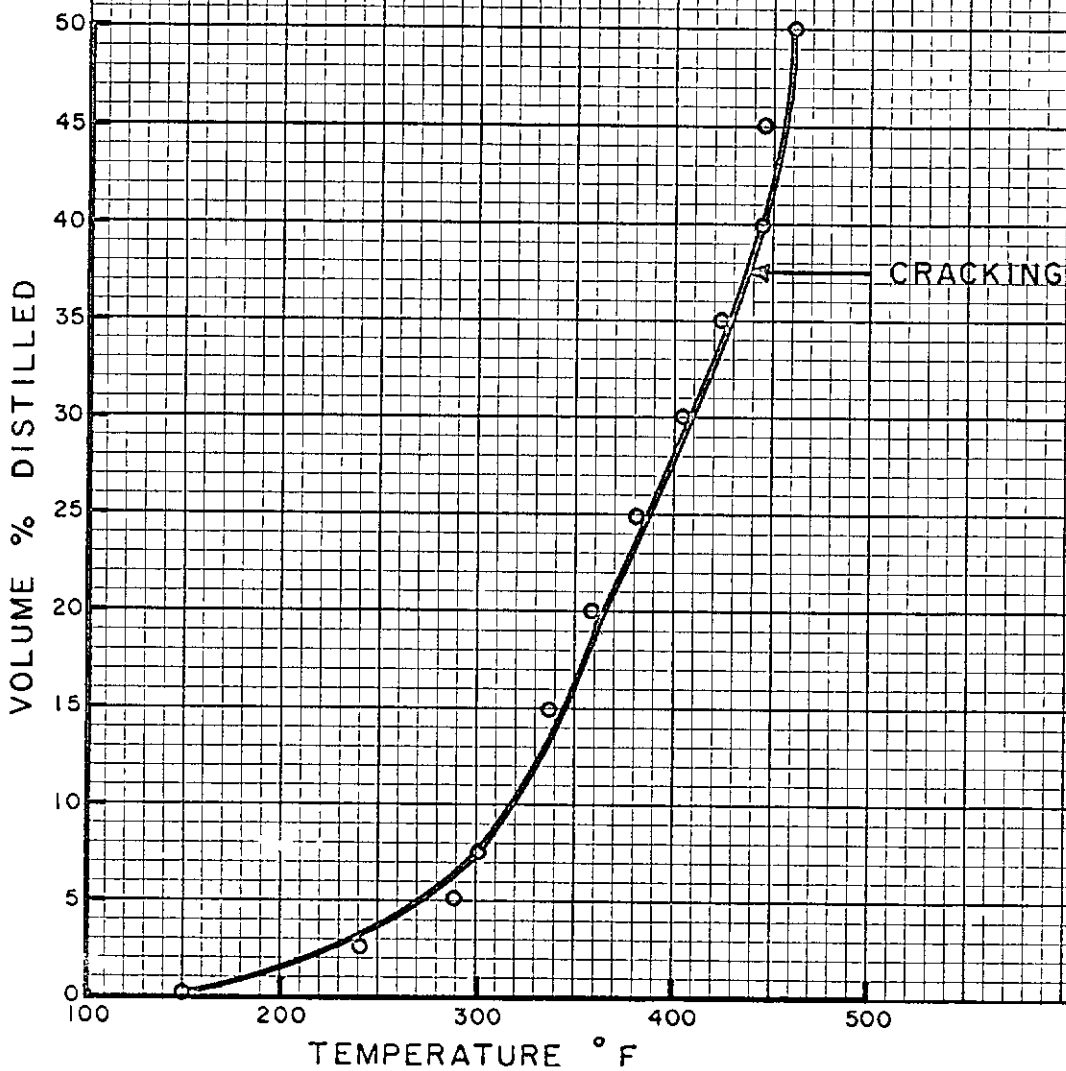
INSPECTION OF CANADIAN SHALE OIL
FROM ELECTRIC BATCH RETORT

Pour Point	10°F
Viscosity at 60°F	14.4 Cp.
Viscosity at 204°F	1.6 Cp
Specific Gravity at 60°/60°	0.9786
API Gravity at 60°/60°	13.1
% Sulfur	7.3
% Basic Nitrogen	0.40
% Total Nitrogen	0.52
% Conradson Carbon	1.81

Engler Distillation Curve

<u>Temperature - °F</u>	<u>Volume %</u>
150	IBP
241	2.5
290	5.0
302	7.5
318	10
338	15
358	20
380	25
402	30
424	35
444	40
446	45
460	50
Cut Off (Cracking)	
Residue	50

FIGURE 14
ENGLER DISTILLATION
OF
CANADIAN SHALE OIL
FROM
ELECTRIC BATCH RETORT



HYDROGEN-CARBON ANALYSES

In any commercial retorting operation high temperature is required. Total heat requirements are also large. One source of the heat for the process is from burning the fixed carbon which remains on the spent shale after retorting. The reaction



produces 14,100 BTU's when one pound of carbon is burned in air. Therefore, a research project was initiated to determine the amount of carbon which remains on the spent Canadian shale after retorting. Numerous samples were run with a Coleman H-C Analyzer on various grades of shales, ranging from 10 to 20 gallons of oil per ton. The average carbon content of the spent Canadian shales was found to be 12.0 weight per cent. The range of carbon contents was from 7.2% to 16.9% by weight.

It has been calculated that about 500,000 BTU's are required to raise one ton of Canadian oil shale from room temperature to retorting temperatures and produce shale oil. Approximately 36 pounds of carbon, or about 2.5% by weight in the spent shale, would be required to produce this heat. Based on the average 12% carbon found in the spent shale, it appears that an excess of carbon would be available to produce the heat required for the retorting process.

CONFIDENTIAL
RESEARCH ACTIVITIES

The research activities presented in this report consider only those which Sun Oil Company feels are not confidential in nature. Obviously, there are certain other areas of research being pursued on the oil shales of Manitoba and Saskatchewan which are confidential to Sun Oil Company.

One of the efforts made in 1965 which Sun considers confidential is a detailed economic study of commercially producing synthetic fuels from the Canadian oil shales. Many case studies were performed, assuming various average grades of the shales, various ore bed and overburden thicknesses, and various sizes of operation. Some of the assumptions used in the study involve processes which are still in the research stage at Sun and must necessarily remain secret at this time.

Much work has been done on developing a retort which might be used in a commercial process. Hopefully, this retort will prove to be more economically attractive than the other existing retorts which are known to the public. Since patents and other legal protections are presently being applied for, the details of this developmental work are not publicly available for this report.