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EFFECTS OF TEMPERATURE DISTRIBUTION ON INTERNAL-COMBUSTION OIL SHALE RETORTING

by

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ABSTRACT

This thesis represents a study made of the effects of retorting zone location on oil quality for a $\frac{1}{2}$-ton-per-day internal-combustion oil-shale retort. Operating conditions are not established; only the effects of temperature distribution on the product are considered.

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A word of appreciation goes to the Oil Shale Corporation for their help in performing gas and shale analysis and to the Colorado School of Mines Research Foundation, Inc. for their supply of necessary equipment and materials.

INTRODUCTION

The gas combustion retorting process has been developed by the Bureau of Mines because of its simplicity, ruggedness, and ability to be self-sustaining. During its study, the Bureau established that under particular circumstances oil begins to reflux in the retort. The refluxing increases the lighter hydrocarbon character of the oil and decreases the yield (Matzick and others, 1966, p. 38).

This study was made to establish some correlatives and correlation for the oil quality as a basis for further studies that would involve oil quality. The methods used to establish the correlation are experimental. The work was conducted on an internal-combustion oil-shale retort located at the Colorado School of Mines and described by Mr. C. B. Farris (Farris, Gary, and Dickson, 1966, pp. 115-134). The retort has been modified slightly.

Previous work on this retort dealt with establishing operation conditions and optimizing the operation (Farris, Gary, and Dickson, 1966, p. 129).

This thesis has established the presence of one empirical correlation between naphtha fraction and retorting zone location, along with confirming oil-quality variation with changes in refluxing. The results also produced conclusions concerning multiple steady states and instability.

This thesis is divided into the following parts: theory, equipment and procedure, results, analysis of results, conclusions and recommendations.

THEORY

The classical methods for the conversion of kerogen in oil shale to a liquid involves the pyrolysis of the kerogen. Since the reaction is carried out at a high temperature and is endothermic, any method used to carry out the process must do two things: produce sufficient heat for the reaction and transfer the heat to the solid.

All the classical retorting methods may be classified into two groups. The first group produces the heat required for the reaction externally while the second group produces the necessary heat within the retort.

External heat generation retorts may be classified into three groups according to their methods of heat transfer:

1. Shell and tube heat exchanges where the shale is in the tube,
2. Solid-solid mixtures where preheated solids are mixed with the shale,
3. Fluid-solid mixtures where a preheated fluid is passed through the shale bed.

Internal heat generation retorts are characterized by the combustion of some pyrolysis product within the retort. This type of retort may be represented classically as a tubular flow reactor. This analogy will hold whether the operation is batch or continuous.

COMBUSTION RETORTING

Fundamentally, combustion retorting is characterized by four zones within the retort during operation. These four zones may be demonstrated by following the time history of a particle of shale in the retort or by following the time history of an element of gas flowing through the retort.

Following the time history of a shale particle, we find it is first raised from ambient temperature to that temperature necessary for retorting. This constitutes the first zone in the retort or the preheat zone. After the shale particle has reached the necessary temperature, it will undergo a decomposition reaction where the kerogen is converted to oil, gas, coke, and water by a series of reactions. This constitutes the second zone or retorting zone. When the kerogen is cracked, coke is left on and in the shale particle. After retorting, the coke undergoes combustion to supply the heat for the process. This is the third zone or combustion zone. After combustion, the shale ash is cooled, and the sensible heat is retained in the processing zone. This is the fourth zone or ash-cooling zone.

An element of gas has the opposite time history, passing through zones 4 to 3 to 2 to 1 and out. The gas in the system has the duties of recovering the sensible heat from the shale, supporting combustion, transferring heat for retorting and preheating, and carrying the oil from the retorting zone.

The combustion retorting process is shown schematically in figure 1. If we give a characteristic velocity to each of the three major elements in the process (shale, gas, and zones), the classical process may be generalized. Let V_s be the velocity of the shale, V_g be the velocity of the gas, and V_z be the velocity of the zone. All of these are with respect to fixed coordinates.

Using this system of velocities, one may say that, when V_s is zero, the operation is batch, and when V_z is zero, the operation is continuous.

These examples of classical combustion retorting are the N.T.U. Retort, the Union Oil Company Retort, and the Bureau of Mines Gas Combustion Retort.

The N.T.U. (Nevada, Texas, Utah) Retort is a $V_s = 0$ or batch process where V_z and V_g are downwardly directed.

Like any batch process it involves the basic steps of charging, reacting, and dumping. The retort operates by starting a fire on top of the shale and then passing diluted air down through the retort. The flow of gas developes the four characteristic zones (see figure 2). The oil leaves with the gas through the bottom of the retort. This process could have probably been operated in any other direction with V_z and V_g upwardly or horizonally directed.

The N.T.U. Retort has the following advantages:

1. Downward flow of gas and oil,
2. Heat recovery due to cocurrent gas and

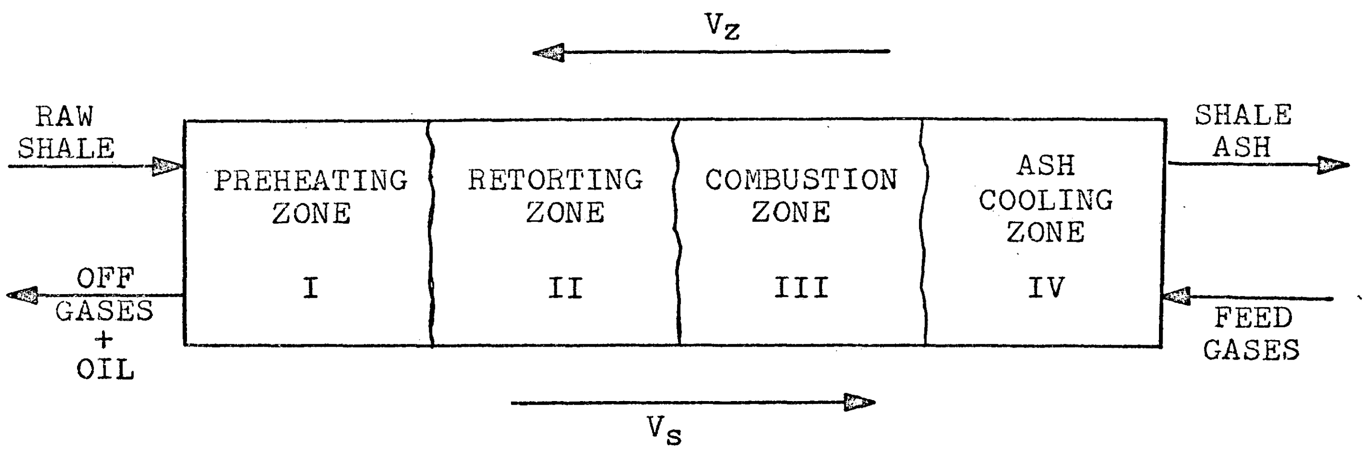


Fig. 1 Schematic of Classical Combustion Retort

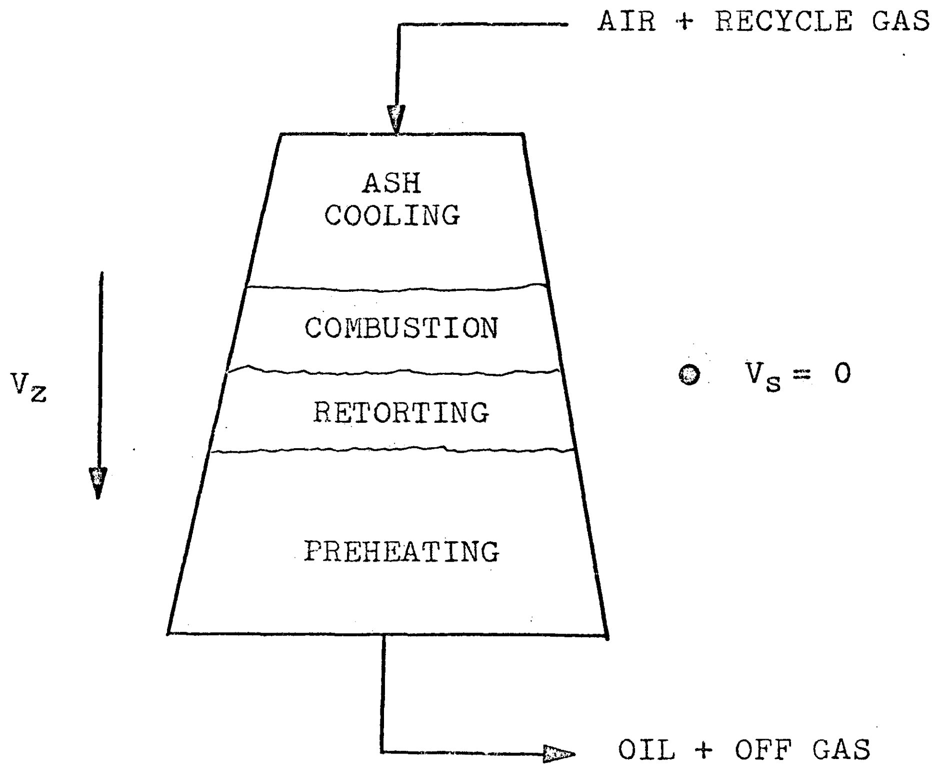


Fig. 2 Schematic of N.T.U. Retort

oil flow below the combustion zone,

3. Heat conduction enhanced by condensation of oil in shale.

The N.T.U. Retort has the disadvantage of being a batch process.

The Union Oil Co. Retort is a $V_z = 0$ or continuous process where V_g is downwardly directed and V_s is upwardly directed.

In this process raw shale is fed into the bottom of the retort by a hydraulically operated piston completely submerged in a crankcase of oil (see figure 3). Air enters through the top of the retort and is forced down through the bed of shale where the characteristic zones are formed. The spent shale and clinkers are pushed off the top and out of the retort by a revolving plow mechanism. Most of the oil mist is coalesced in the bottom of the retort. The liquid overflows the crankcase in the bottom of the retort in the same line as the gas stream.

The Union Oil Co. Retort has the following advantages:

1. Downward flow of gas and oil,
2. Heat recovery due to cocurrent gas and oil flow below the combustion zone,
3. Heat conduction enhanced by condensation of oil on shale,
4. Completely self-sustaining operation,
5. Internal oil collection to allow a lesser degree of external oil recovery,
6. Ability to handle a large range of particle sizes.

The Bureau of Mines Gas Combustion process is a $V_z = 0$ process where V_g is upwardly directed and V_s is downwardly directed.

In this process shale is fed by gravity to the retort; recycle gas passes in through the bottom of the retort while air diluted with recycle gas passes into the combustion zone (see figure 4).

The gas combustion retort has the following advantages:

1. Heat recovery due to cocurrent gas and cil flow above the combustion zone,
2. Completely self-sustaining operation,
3. Stable location of combustion zone,
4. Simplicity and ruggedness of operation.

REFLUXING

When kerogen is decomposed in the series kerogen to bitumen to oil, gas, coke, and water, the oil forms a mist within the shale bed. The momentum of the gas is supposed to carry the mist from the retort. If the residence time for the mist is sufficient in the retort, the mist particles will tend to coalesce and form larger mist particles. As the particles increase in size, the control that the gas momentum has on the mist particle becomes less. The decreasing gas control allows the mist particles to coalesce on the shale. When the oil coalesces on the shale, it will either be carried with the shale or flow downward over the shale.

There are two systems in which the results from reflux-

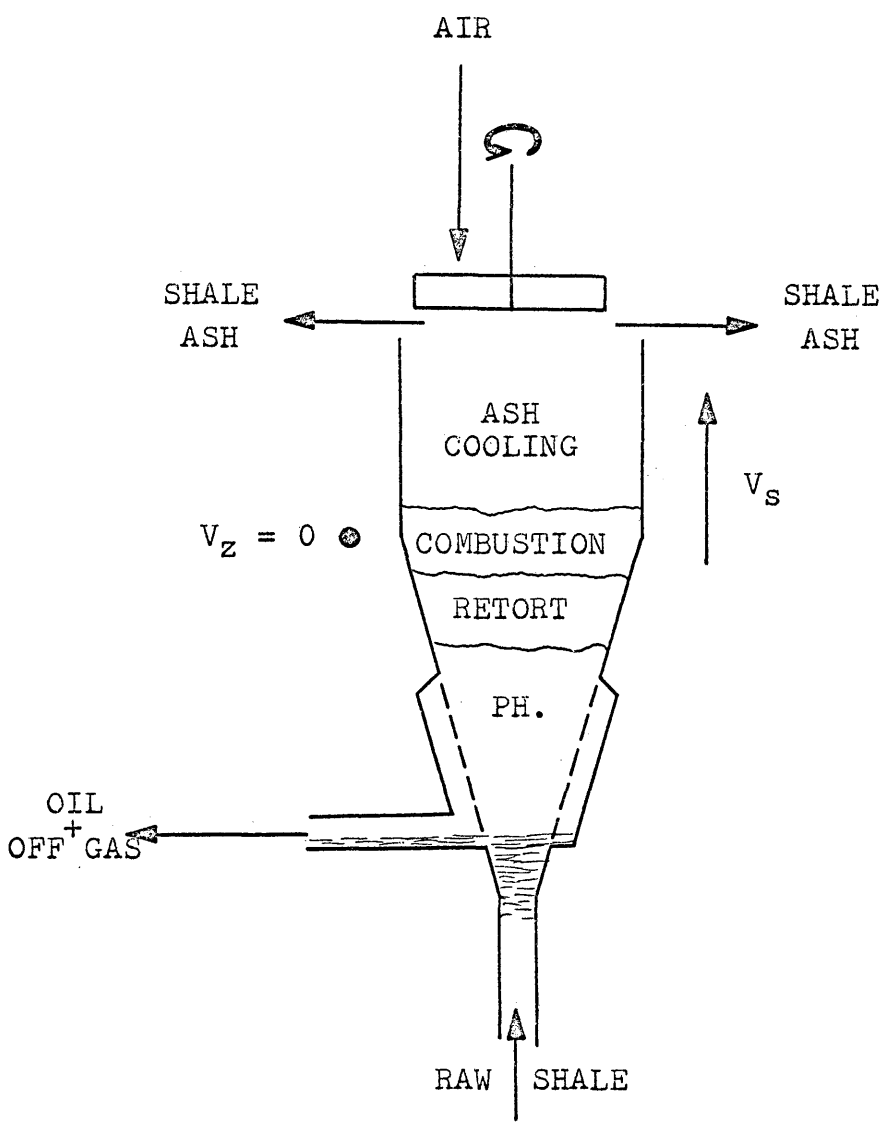


Fig. 3 Schematic of Union Oil Company Retort

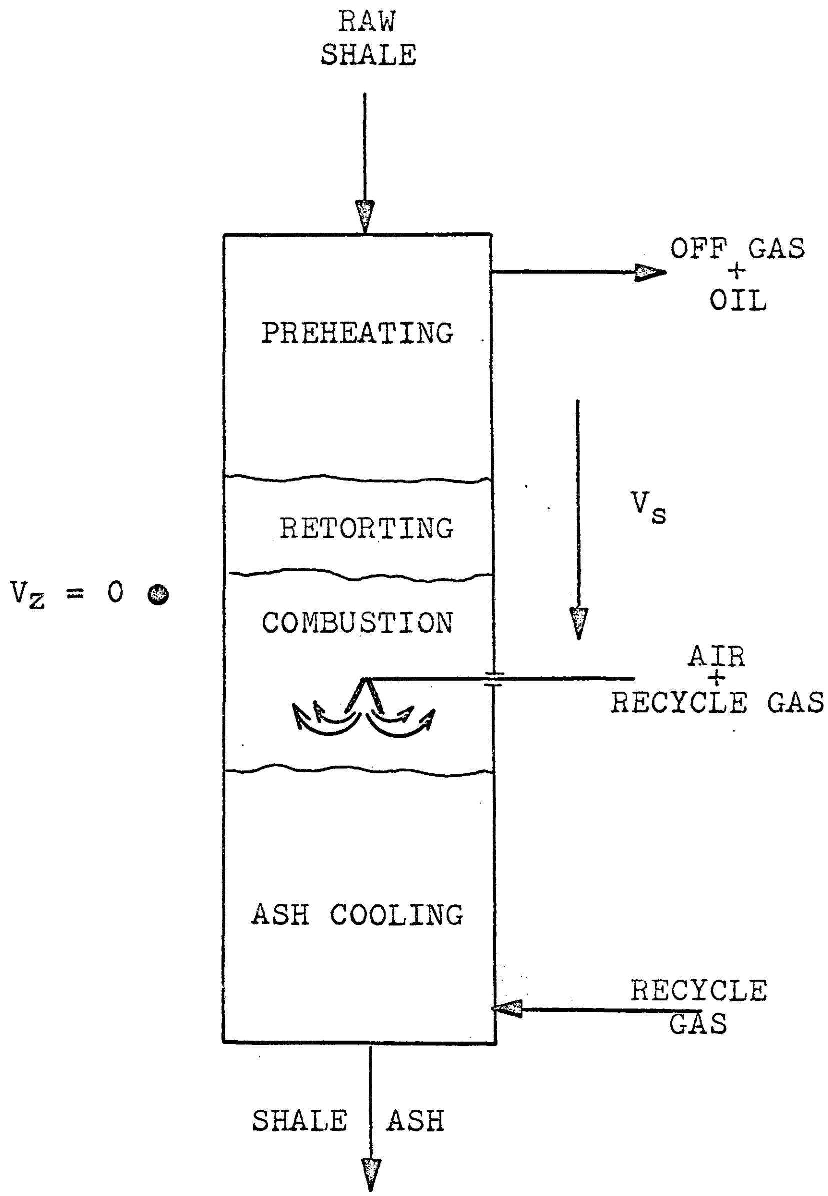


Fig. 4 Schematic of Bureau of Mines Gas Combustion Retort

ing will be very different. The first type of system has the retorting zone below the combustion zone as in the N.T.U. and Union Oil Retorts; the second has the retorting zone above the combustion zone as in the Bureau of Mines Gas Combustion process.

In the first type, with the combustion zone above the retorting zone, the shale will move upward with respect to the zones. The coalesced oil will have two opposing forces acting on it, gravity tending to make the oil flow downward and the shale tending to carry it up with respect to the zones.

In the second type, the two forces will act together to cause the oil to move into the retorting and combustion zones.

When the oil in the second type of system moves into the retorting zone, three things will happen: light ends of the oil will be boiled off, heavier parts will be thermally cracked, and the remainder will be burned in the combustion zone. The quality and quantity of the oil recoverd will depend on to what extent boil-off and thermal cracking proceed. If the boil-off and thermal cracking proceed completely with no burning, the yield of lighter distillates will increase. If no cracking takes place and only boil-off goes to completion, the yield of lighter distillates will remain constant with the total yield decreasing. Finally, if little boil-off and cracking take place, there will be a decrease in yield of lighter distillates and total product.

In the first type of system with the retorting zone below the combustion, the extent of refluxing will depend on how much oil is carried by the shale particles into the retorting and combustion zones.

EQUIPMENT AND PROCEDURE

The experimental part of this study will be described under three topics: pilot plant, oil analysis, and procedure.

PILOT PLANT

The retorting pilot plant is basically the same as that used by Farris (1966, p. 115) but with modification in the retort and changes in the recovery system.

The retort (see figure 5) is a $9\frac{1}{2}$-ft-long, 6-in-dia steel pipe with a 1/3-ton-capacity hopper resting on the top. The shale is withdrawn from the bottom of the retort by a star valve connected by a chain drive to a variable-speed transmission. The transmission allows a continuous range of shale thru-put from 0 to 150 lb per hr.

Off gas and oil mist are withdrawn through two 4-in-dia pipes intersecting the retort 45 deg below vertical and 9 ft above the shale discharge.

A portable propane burner is placed in the side of the retort 6 ft above the shale discharge for start-up. The burner opening is sealed during operation.

There is an inlet for air and recycle gas through the side of the retort immediately above the shale discharge.

A $\frac{1}{2}$-in-dia stainless-steel tube runs down the center of

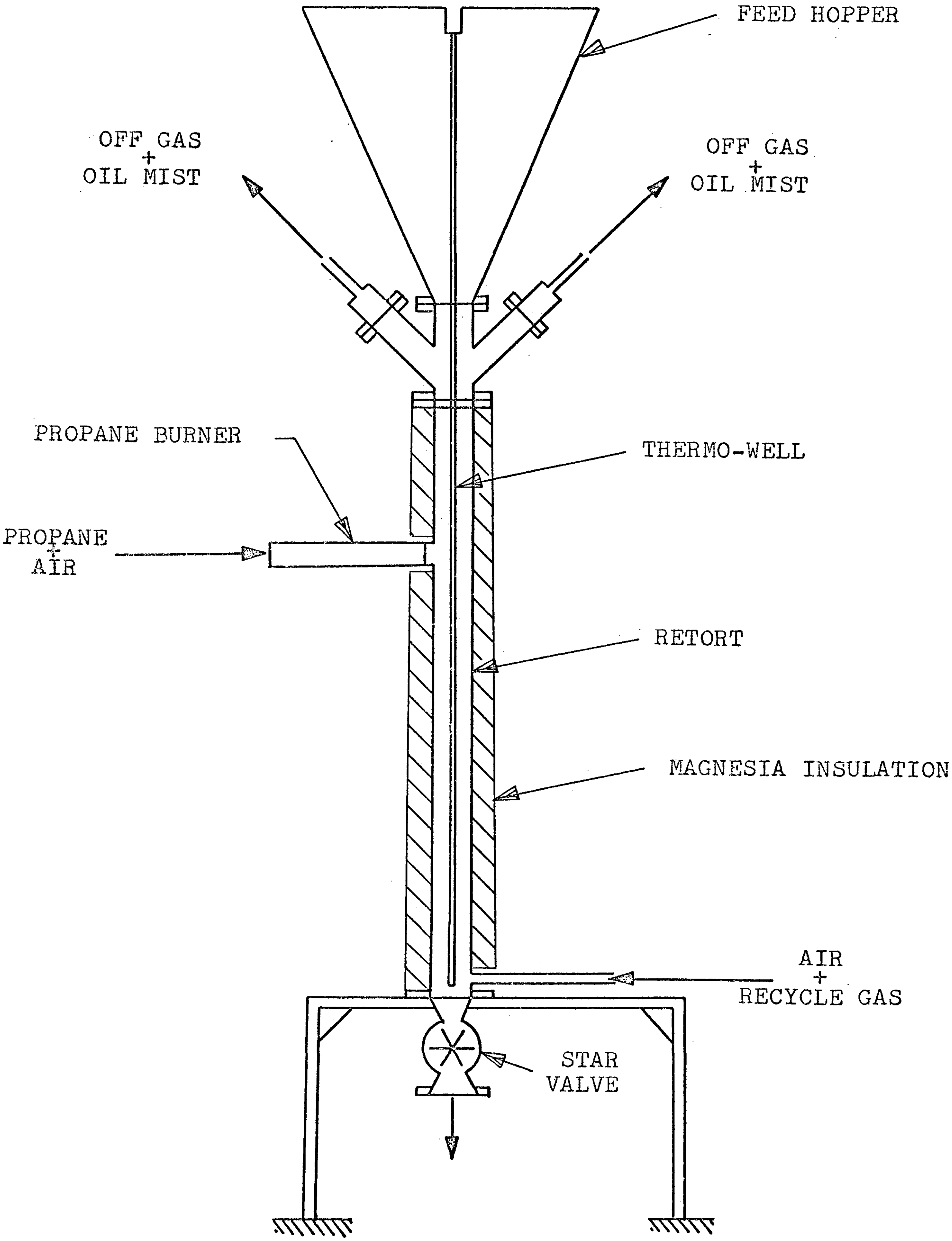


Fig. 5 Schematic of Retort

the retort. The tube contains 8 thermocouples 12 in apart. The thermocouples may be moved in the tube to measure temperatures at any location.

The retort is covered with 3 in of magnesia insulation.

The oil mist recovery system (see figure 6) consists of a cyclonic mist eliminator, a finned-tube condensor, two cyclones, a surge tank, and a positive displacement blower.

When the off gas and mist leave the retort, they first enter the cyclonic mist eliminator. This is a central shaft fitted with eight automotive generator fans in a 6-in-dia pipe. The fans have plates mounted on them so that most of the gas and mist must pass through them. The fans are run at 3000 rpm, thus imparting a high momentum on the mist particles and causing them to coalesce on the wall. The gas leaves through the side of the mist eliminator while the oil drains into a jar attached to the bottom.

The remaining gas and mist pass to the finned-tube condensor where more mist and water are condensed due to the large surface area.

The oil and gas now pass to the first cyclone where the condensed oil and water are separated from the gas.

After the first cyclone, the gas stream passes through a blower used to drive the system, a second cyclone, and a 30-gal surge tank. After the surge tank, the gas stream is split, and part is recycled to the retort, and the remaining gas is vented to the atmosphere.

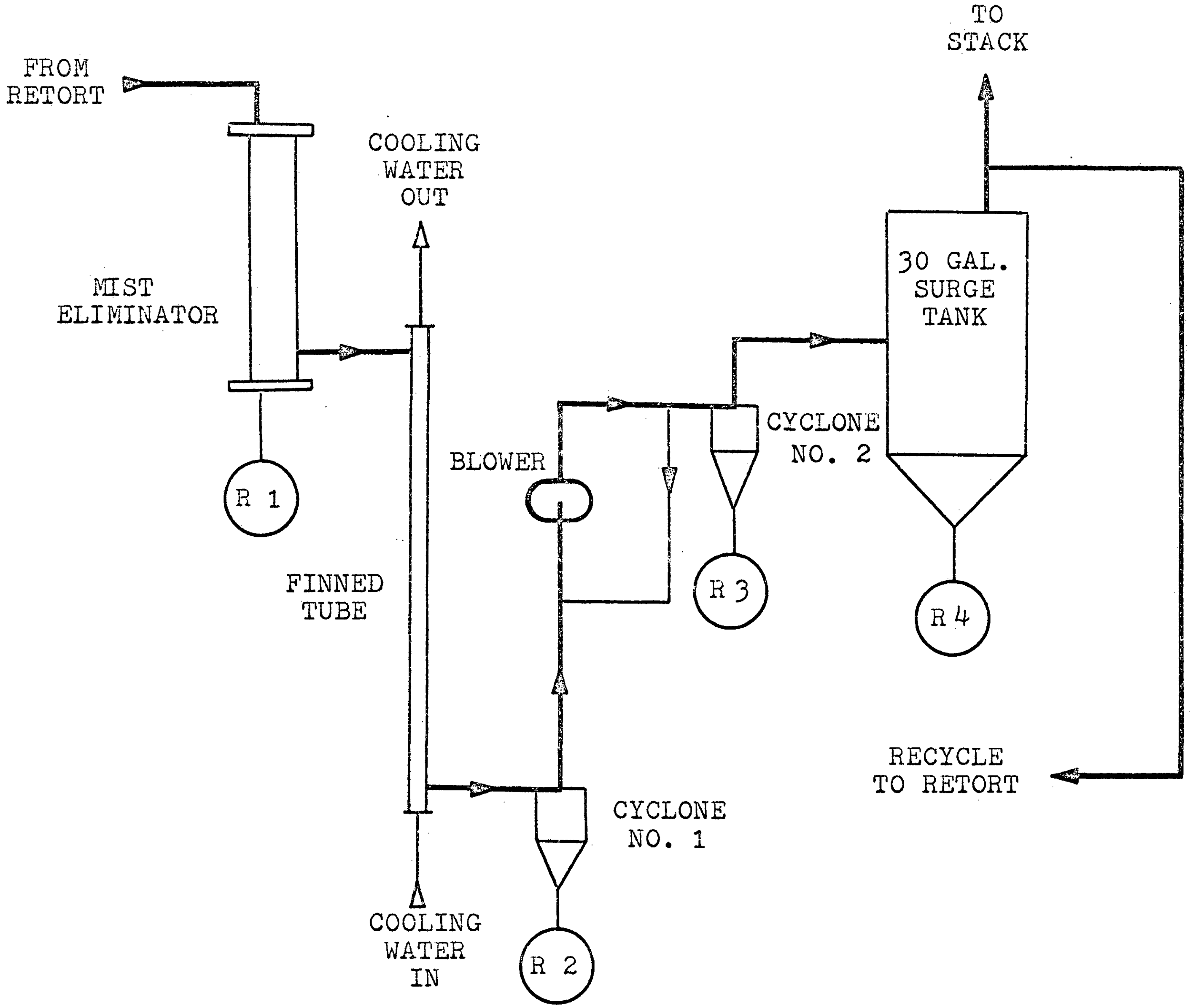


Fig. 6 Schematic of Oil Recovery System

The retort pilot plant is operated by first charging the retort and feed hopper with the necessary quantity of shale. The ignited propane burner is then placed in the side of the retort, and the blower is started. The burner is allowed to burn for ten minutes so that the shale will start burning in the retort (this is sufficient time to raise the temperature at that location to 1100°F). The burner is removed, and the shale clinker formed at the burner level is broken up with a steel rod. The burner opening is sealed; the air, recycle gas, and shale discharge are turned on and adjusted to the desired rate; and the mist eliminator is turned on.

The retort is shut down by turning off the shale discharge, air, and recycle gas; removing the star valve to dump everything in the retort and hopper; and then turning off the blower and mist eliminator.

Minus 1/4-in shale was supplied by the Colorado School of Mines Research Foundation. This shale was screened to plus-six mesh by hand on a vibratory riddle.

OIL ANALYSIS

Analytical procedures are run on the crude oil for two reasons: first to get material balances and oil recoveries for the retort operation and second to obtain corresponding oil qualities.

Tests run on the crude oil are water content, viscosity, gravity, pour point, and analytical distillation. The neutral naphtha fraction is analyzed to determine the relative percentages of the three hydrocarbon groups: saturates, olefins, and aromatics.

For each oil sample, the wet-oil emulsion is analyzed for water by use of the standard A.S.T.M. method.

For the remaining tests, dry-oil samples are used. The oil emulsion is broken by allowing the oil to set in a sealed container for 24 hr at 110°F. Twenty-four hours is sufficient time to reduce the water content from 25 percent to 0.1 percent in the continuous oil phase. Oil samples for further analysis are taken from the continuous oil phase.

Standard A.S.T.M. methods are used to determine pour point and Saybolt viscosity at 100°F.

The API gravity is determined at 110°F with an hydrometer and then corrected to 60°F.

The analytical distillation of the crude oil is made by using a modification of the Bureau of Mines method (Dinneen, Ball, and Thorne, 1952, p. 2632). The apparatus for the distillation is shown in figure 7.

A 300-ml oil sample is initially distilled at atmospheric pressure to an end point of 377°F (corrected for the local atmospheric pressure for a temperature of 392°F at a pressure of 760 mm Hg). The cumulative volume is recorded every 25F° starting at 125°F through 350°F and at 377°F. The atmospheric pressure distillation yields the naphtha fraction and cumulative volume points 1 through 11 on the

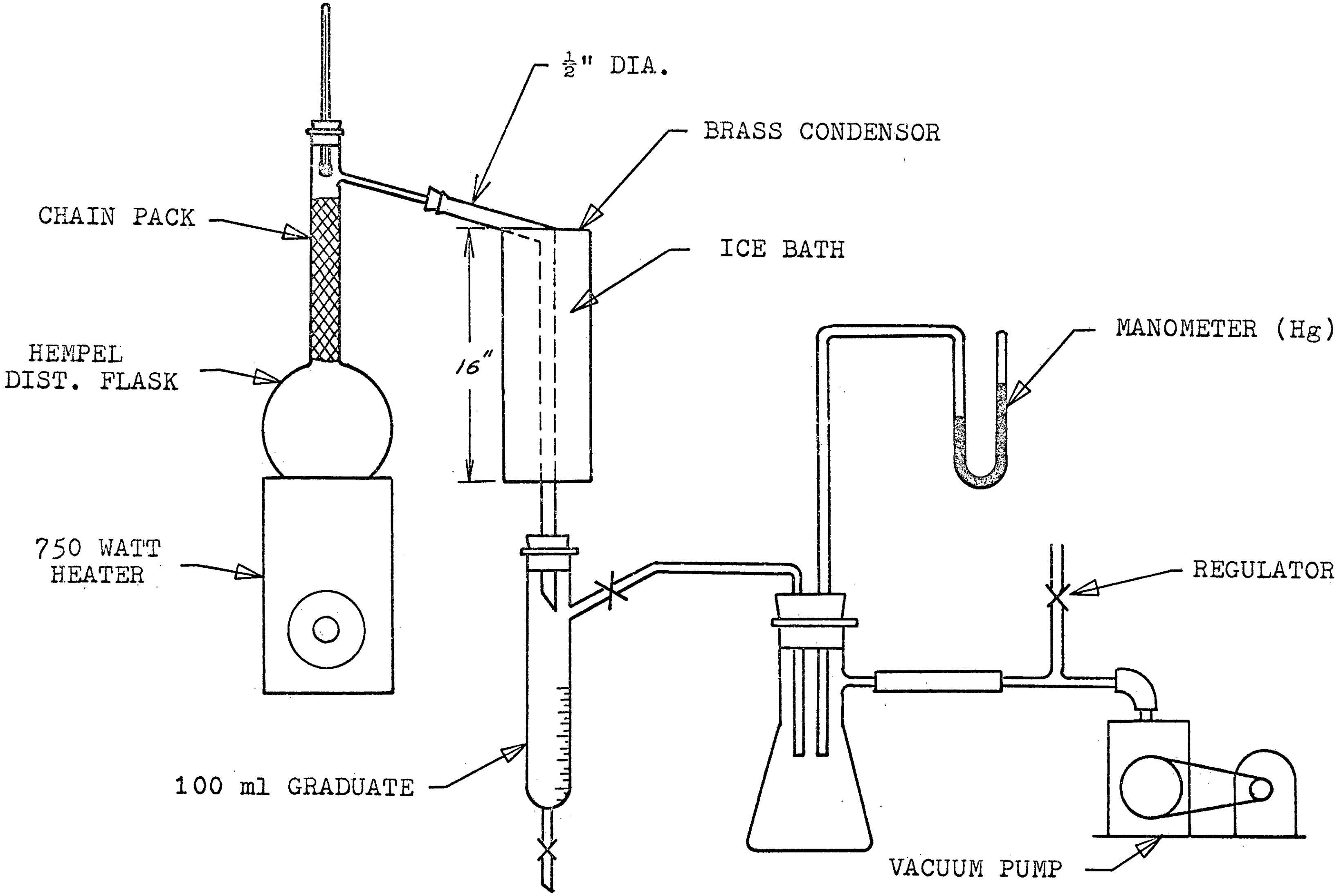


Fig. 7 Crude Oil Distillation Apparatus

distillation curve.

The remaining oil is distilled at 40 mm Hg. The cumulative volume is recorded every 25F° starting at 250°F and going through 375°F and finally at 392°F. The vacuum distillation yields the light-distillate fraction and samples 12 through 18 on the distillation curve.

The hydrocarbon analysis of the naphtha fraction is made using a silica-gel adsorption technique developed by the Bureau of Mines (Dinneen, Bailey, Smith, and Ball, 1947, p. 992). Only neutral naphtha samples are analyzed.

There are two variations in the hydrocarbon analysis developed by the Bureau of Mines. First the number of drops per sample is not always the same and depends on the amount of naphtha available for analysis. When 10 ml are available, 6-drop samples are taken; but when less that 10 ml are available, 5-drop samples are taken. The second variation is in the determination of the end point of the analysis. In this method, when the refractive index on the down side of the aromatic plateau crosses the value of 1.3, this is the end point.

The off gas from the retort is analyzed by using Orsat analysis for CO_2, illuminates, O_2, and CO. The hydrocarbon analysis of the gas was found to be about 2 percent (by TOSCO).

EXPERIMENTAL PROCEDURE

In the experimental work, an attempt was made to establish different temperature profiles in the retort and then analyze the oil quality and recovery corresponding to each profile.

The retort and pilot plant were started up in the usual manner. For all runs, the optimal air and recycle rates used by Farris were employed (1966, p. 131); only the shale rate was varied. It was hoped that, by changing the location of the maximum temperature in the retort, a significant effect would be observed on the quality and quantity of oil recovered.

The location of the maximum temperature was changed from as near the top of the retort as possible to as near the bottom of the retort as possible.

When one total run was made, the maximum temperature was kept within a 4- to 6-in region to determine overall recovery. Meanwhile several oil samples were taken by varying the location over this 4- to 6-in range to determine oil quality.

When oil samples were taken, oil was collected over a period of $\frac{1}{2}$ to 1 hr. In such cases the temperature profiles monitored over that time were linearly averaged. For recovery data, the temperature profiles for the complete run had to be averaged.

RESULTS

The results from the experimental procedure are presented in this section under temperature distributions, oil qualities, and recovery.

TEMPERATURE DISTRIBUTIONS

Figures 8 through 17 show the development of the temperature profile in the retort from start-up (run No. 3-28). At start-up, the retort was operated at 30 lb per hr. figures 8 through 11 demonstrate the start-up and follow through for this shale rate. If this shale rate would have been allowed to continue, it would have developed the profile shown in figure 20 for run No. 3 to 10. But after 7 hr of operation, the shale rate was cut to 11 lb per hr, and figures 12 through 17 show the development of the new temperature profile.

Figures 18 through 26 show the retort temperature profiles corresponding to their respective oil samples. It is assumed that the retorting zone starts when the shale bed reaches 750°F (Farris, 1966, p. 120). The distance from the 750°F point to the off-gas line (9-ft level) is used for analysis. It is assumed that the residence time and the probability of mist coalescence are proportional to this length. The distance from the initial point of retorting to the off-gas line for each oil sample is shown in table I.

TABLE I

LENGTH FROM RETORTING
ZONE TO OFF-GAS LINE FOR OIL SAMPLES

	2-18	2-28	3-10	I 3-25	II 3-25	I 3-28	II 3-28	III 3-28	IV 3-28
L_{rs}	0.85	0.10	3.89	1.54	1.10	1.53	0.61	0.07	0.16

The distance from the initial point of retorting to the off-gas line for each total run is shown in table II.

TABLE II

LENGTH FROM RETORTING
ZONE TO OFF-GAS LINE FOR TOTAL RUNS

	2-18	2-28	3-10	3-25	3-28
L_{rs}	0.85	0.10	3.89	1.17	0.26

OIL QUALITIES

The oil-analysis data for each of the oil samples is presented in table III. The data for the distillation curves is shown in table IV. A sample distillation curve is shown in Appendix I, and a sample adsorpto-graph from the chromographic analysis of the neutral shale oil naphtha is shown in Appendix II.

Naphtha fraction, light-distillate fraction, viscosity, and hydrocarbon analysis are each plotted against the distance from the retorting zone to the off-gas line in figures 29 through 32, respectively. A table of oil qualities from this retort and several other retorts for U.S. shales is presented in Appendix III.

RECOVERY

The oil recovery for each of the runs is presented in table V. The oil-recovery data is plotted against the distance from the retorting zone to the off-gas line in figure 23.

The material balances for the runs are presented in Appendix IV. A carbon balance for run No. 3-28 is presented in Appendix V.

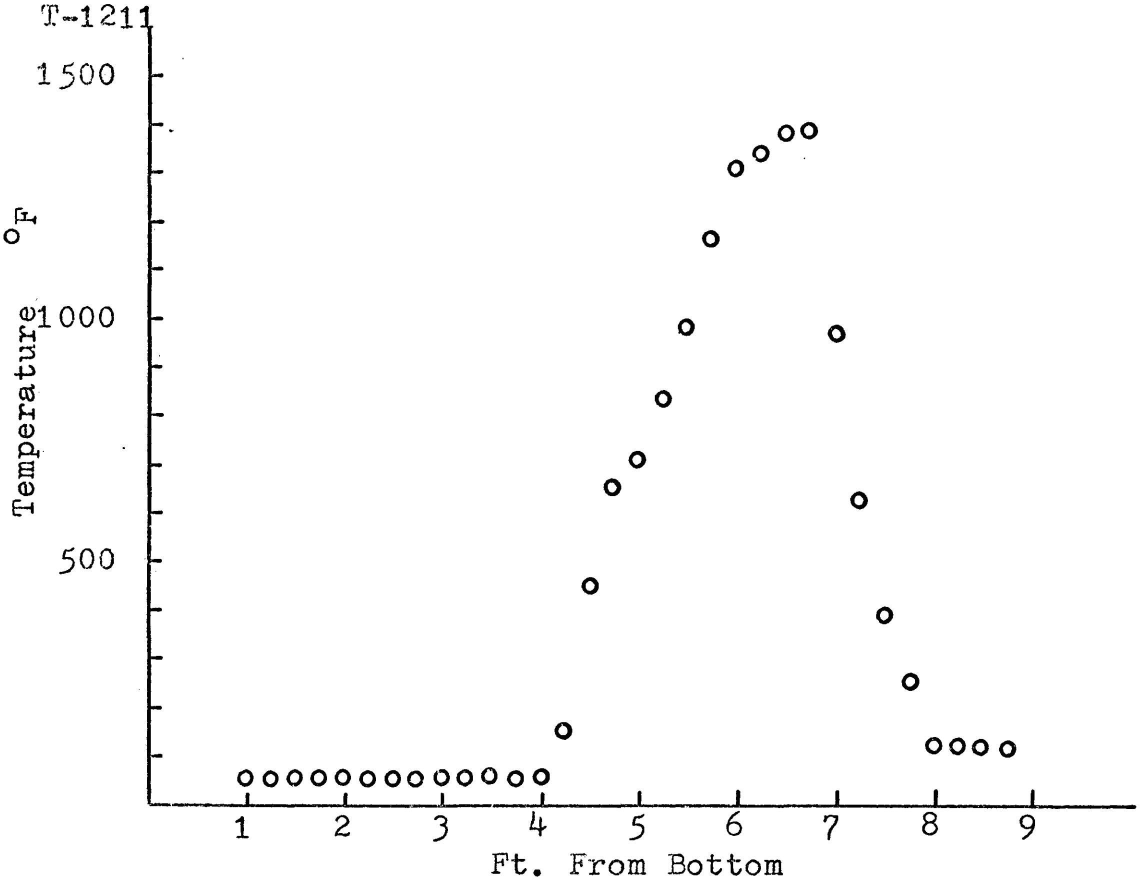


Fig. 8 3/4 Hr Temperature Profile

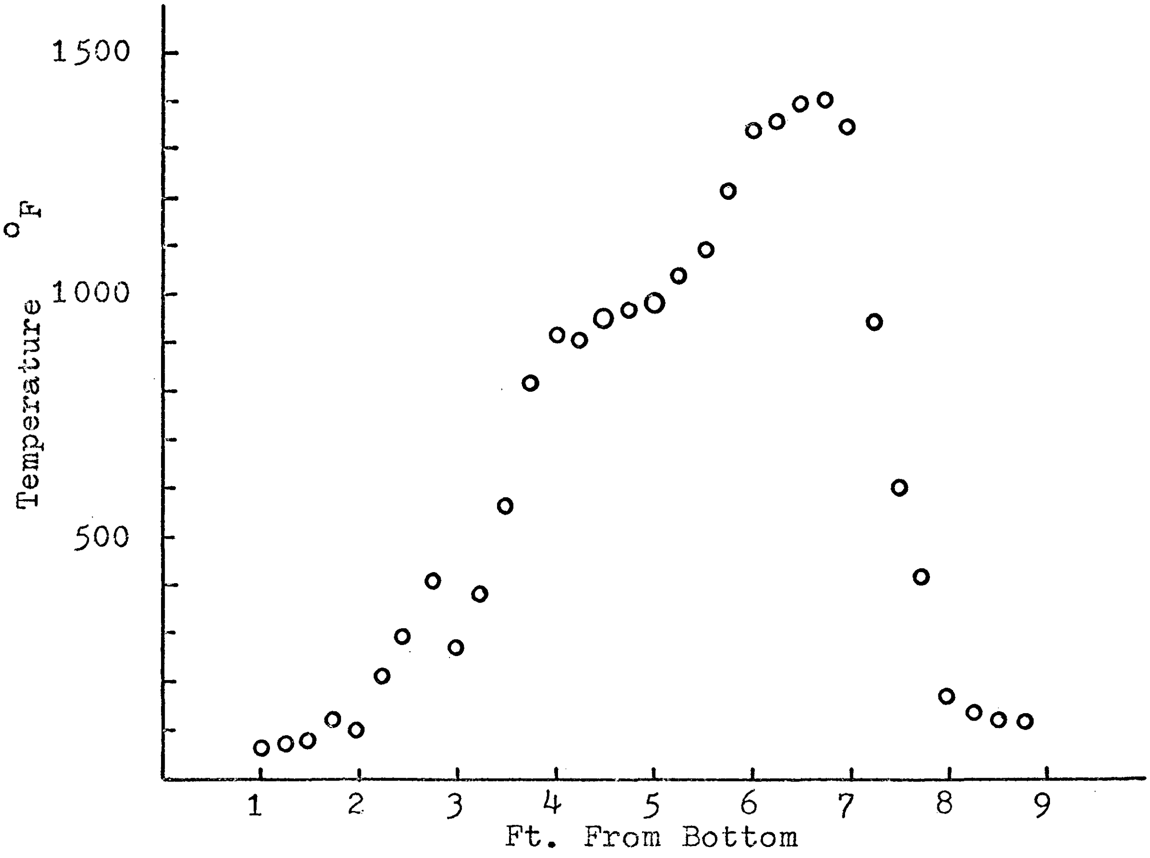


Fig. 9 1 3/4 Hr Temperature Profile

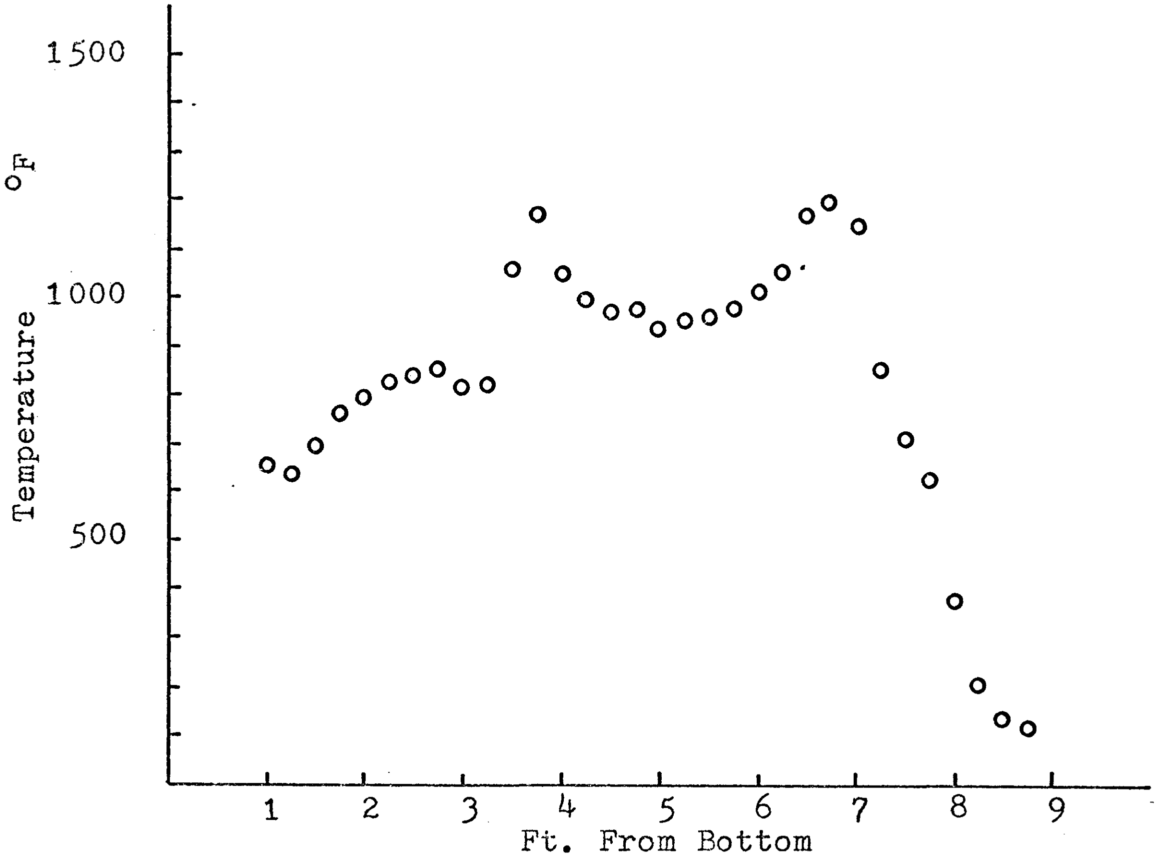


Fig. 10 5 Hr Temperature Profile

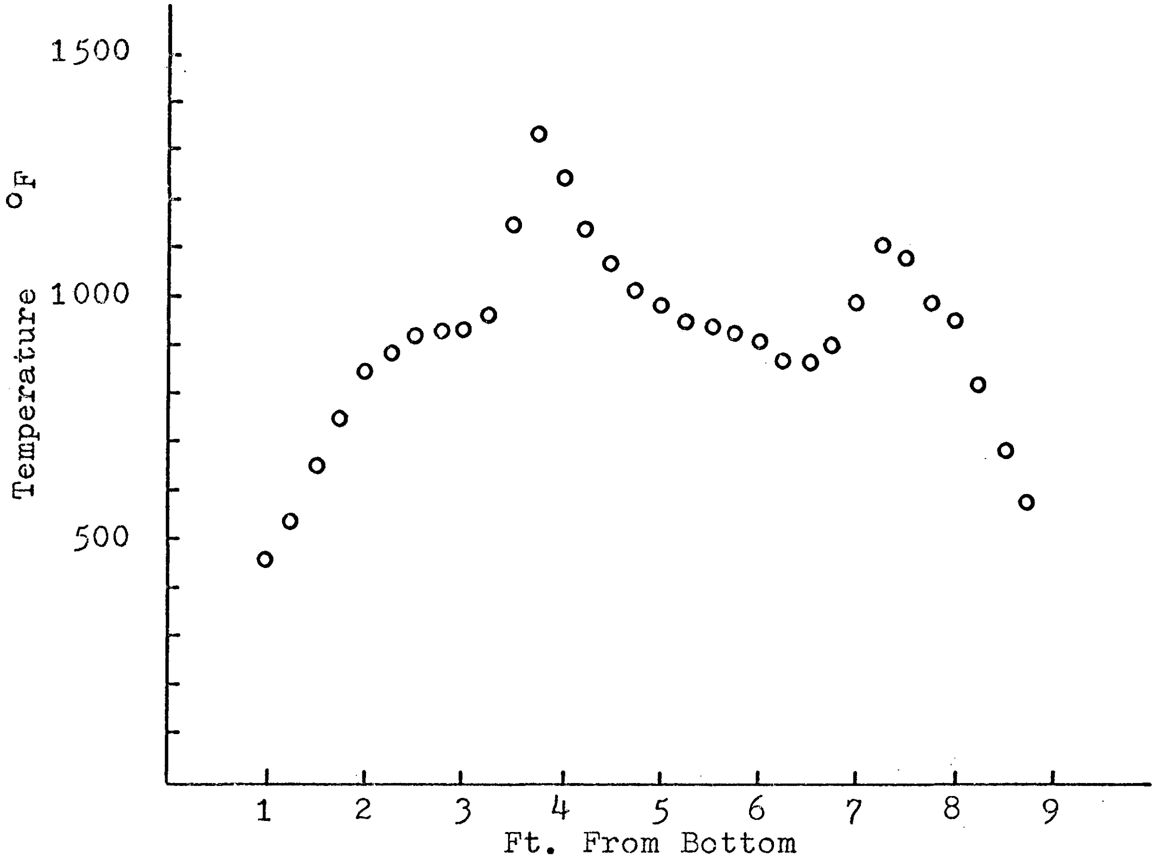


Fig. 11 7 Hr Temperature Profile

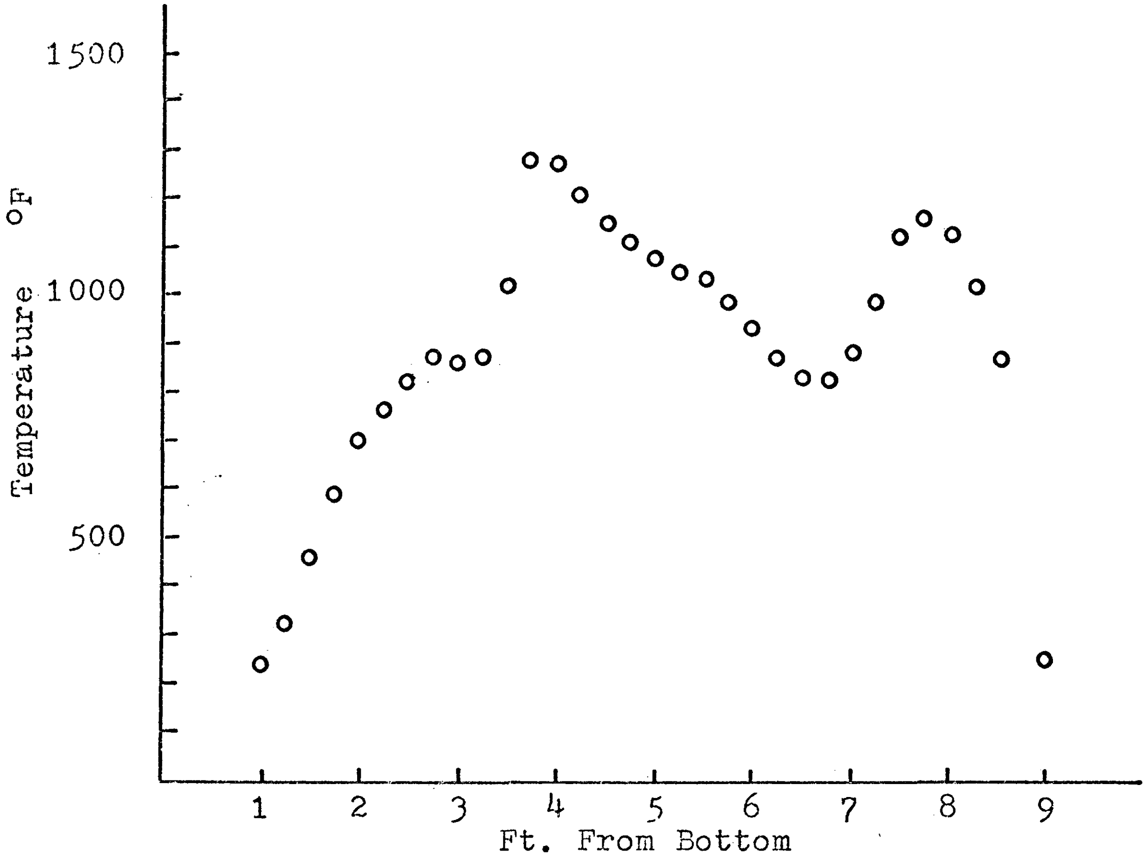


Fig. 12 9 2/3 Hr Temperature Profile

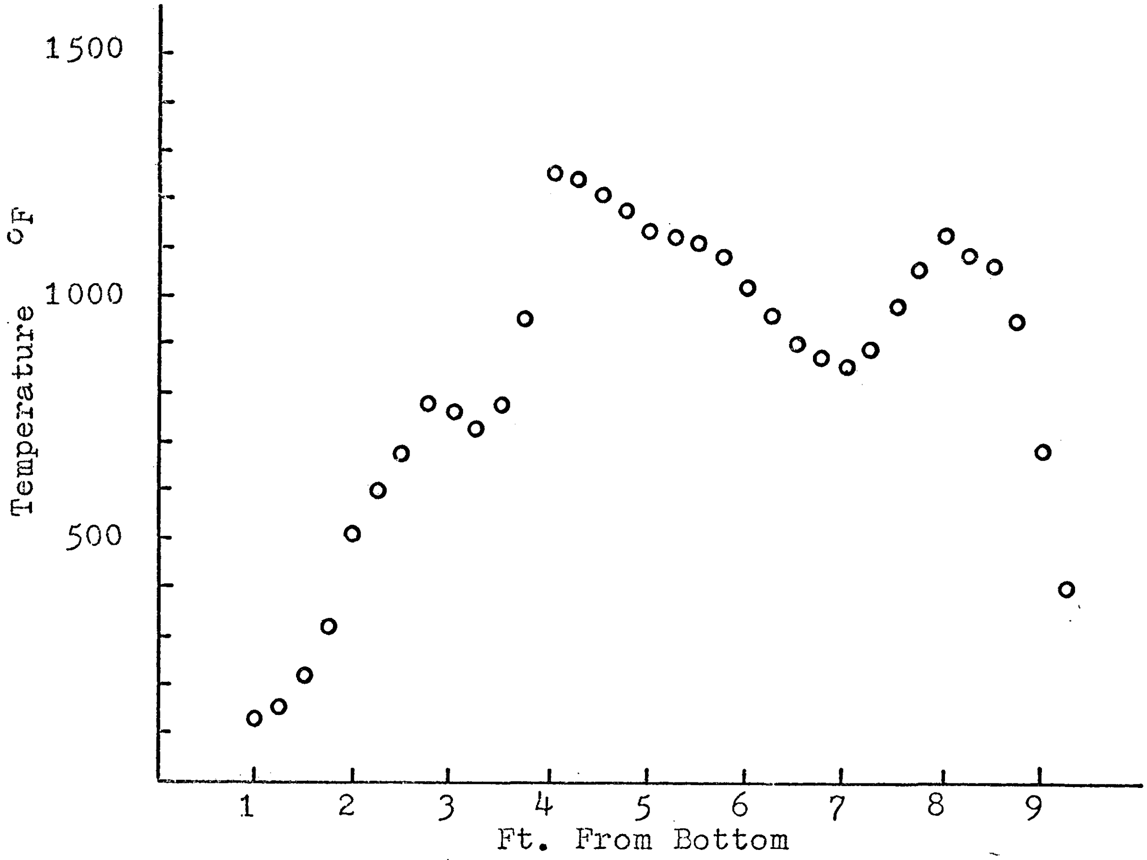


Fig. 13 10 5/6 Hr Temperature Profile

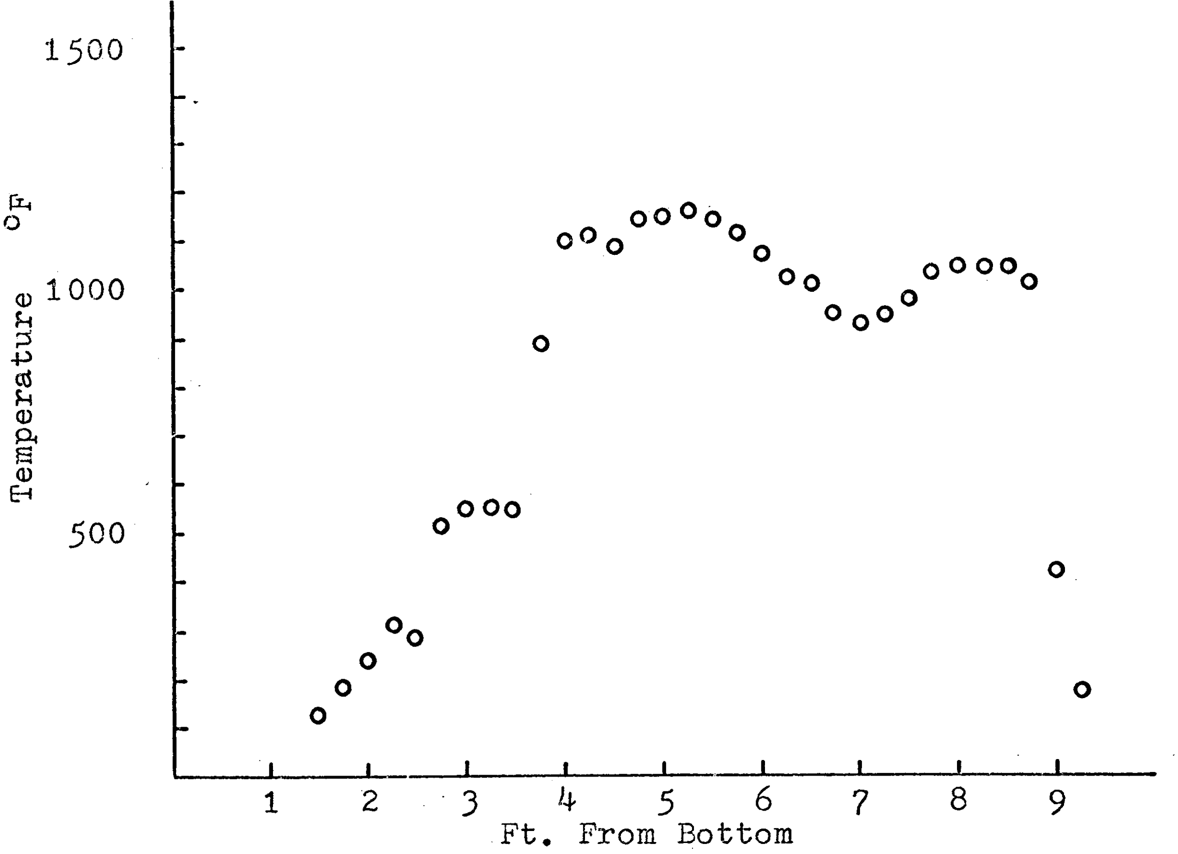


Fig. 14 12 ¼ Hr Temperature Profile

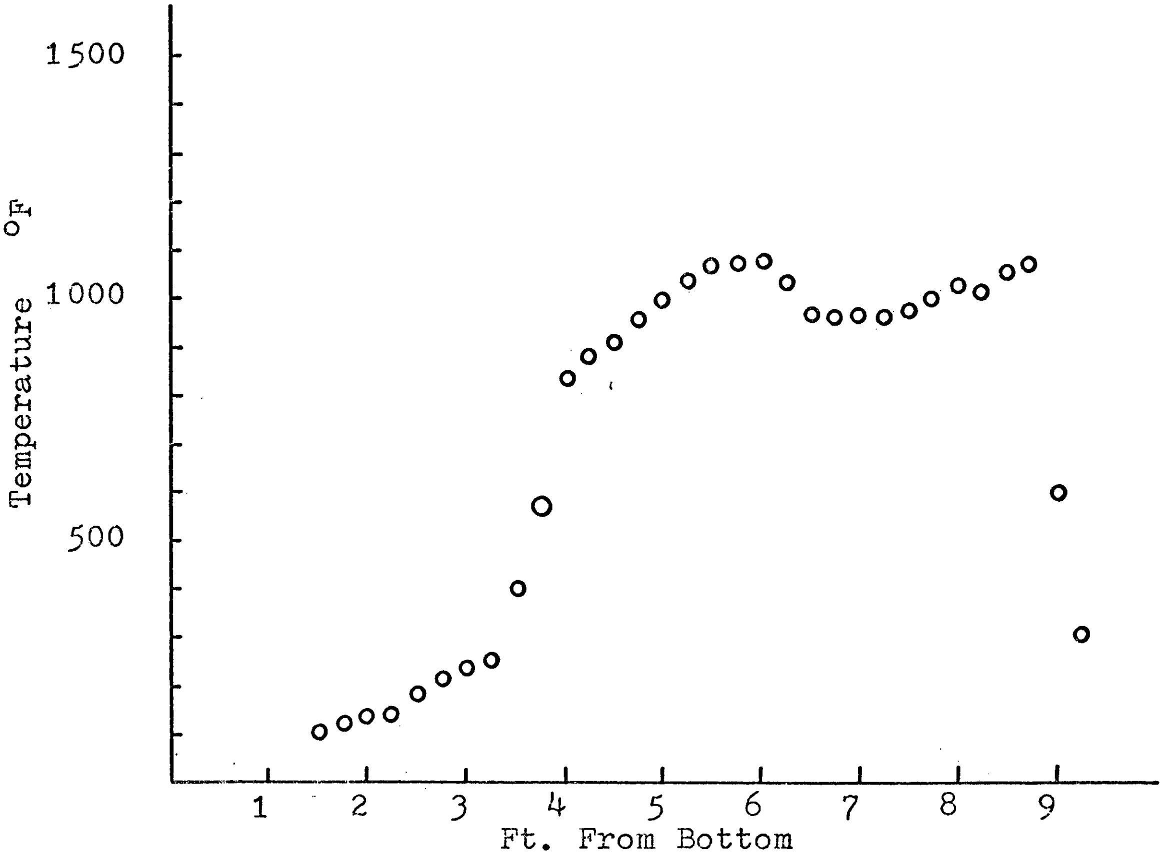


Fig. 15 13 3/4 Hr Temperature Profile

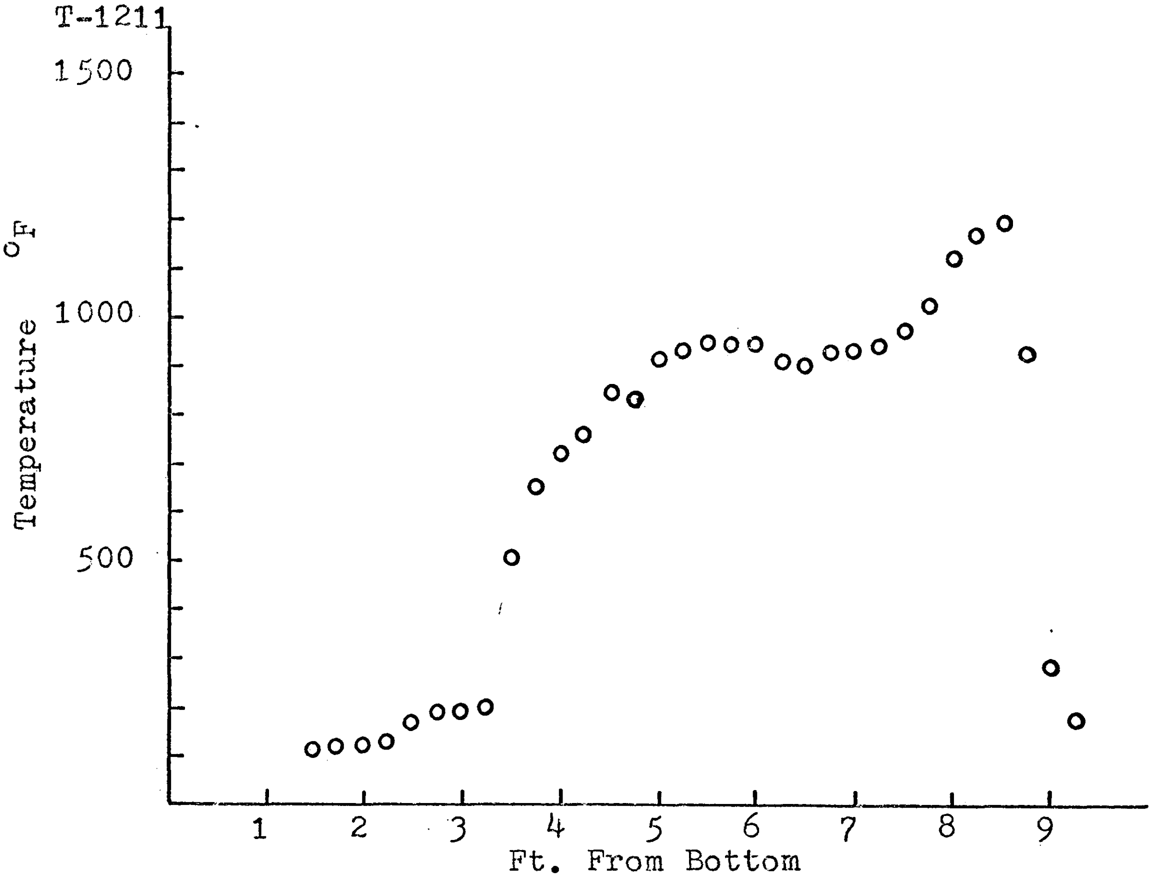


Fig. 16 15 Hr Temperature Profile

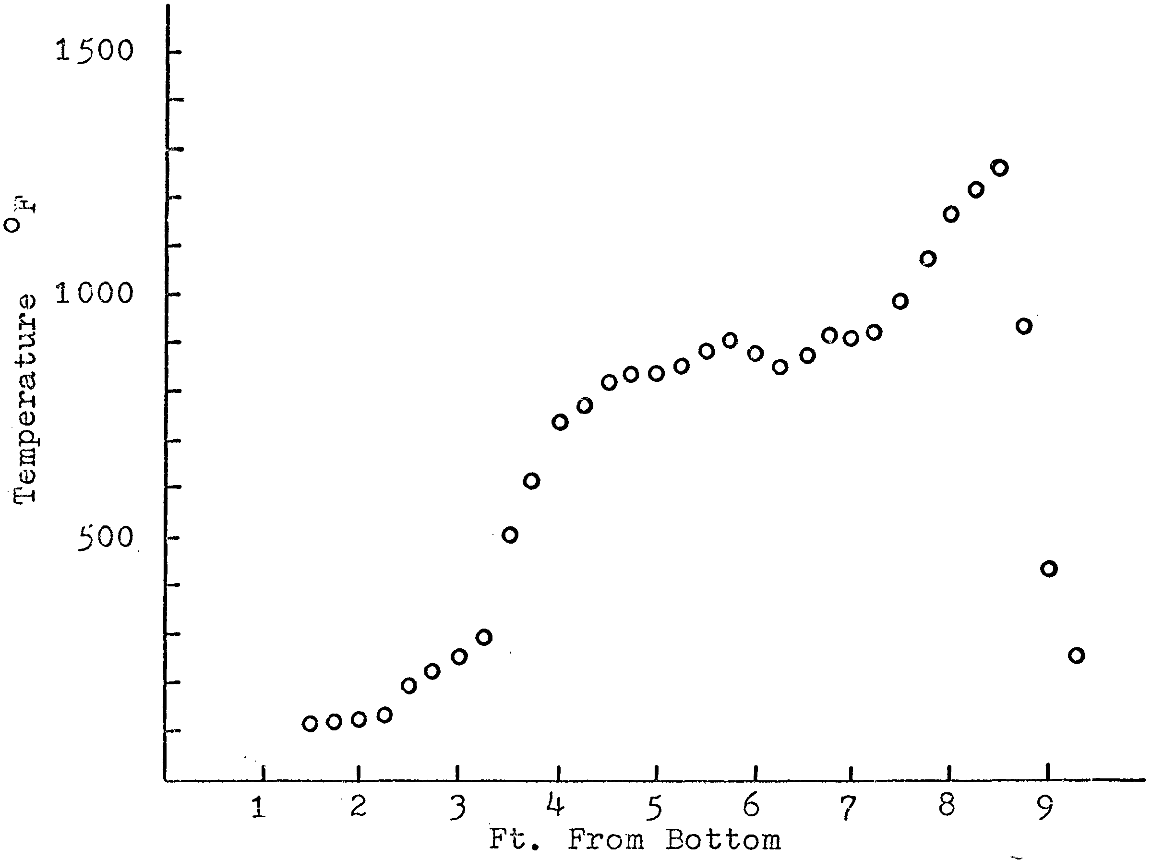


Fig. 17 15 2/3 Hr Temperature Profile

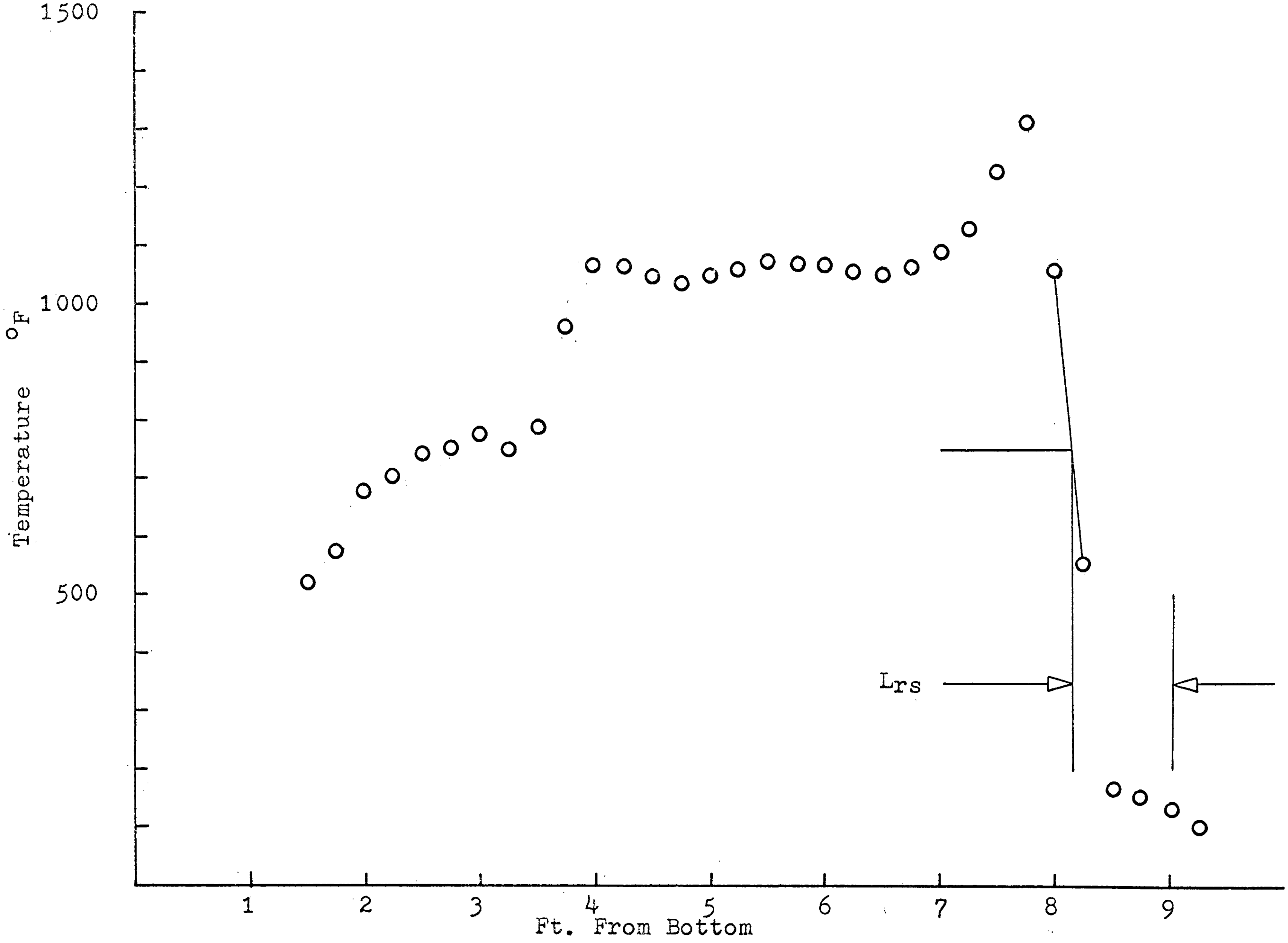


Fig. 18 Sample and Run No. 2-18 Temperature Profile

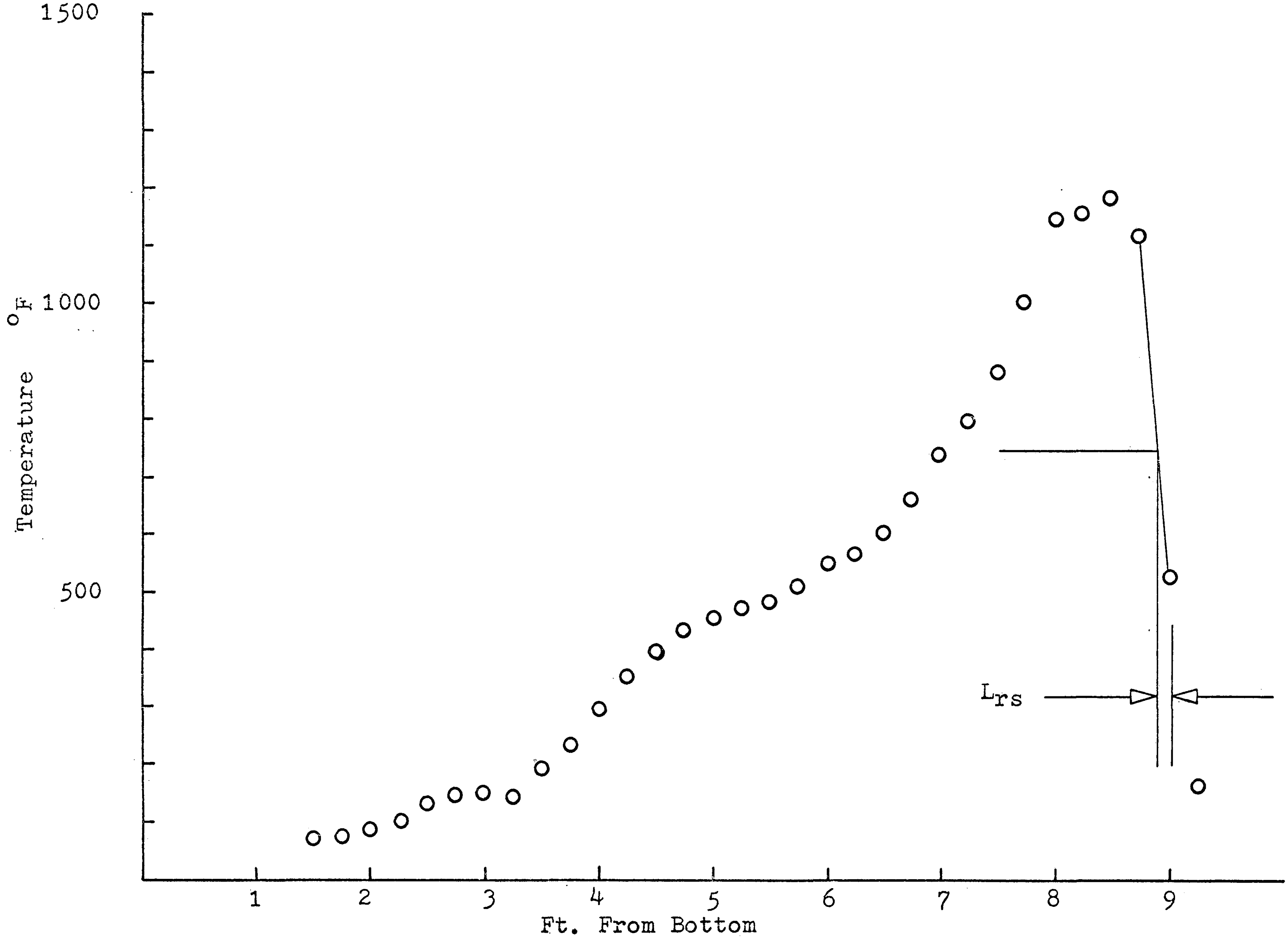


Fig. 19 Sample and Run No. 2-28 Temperature Profile

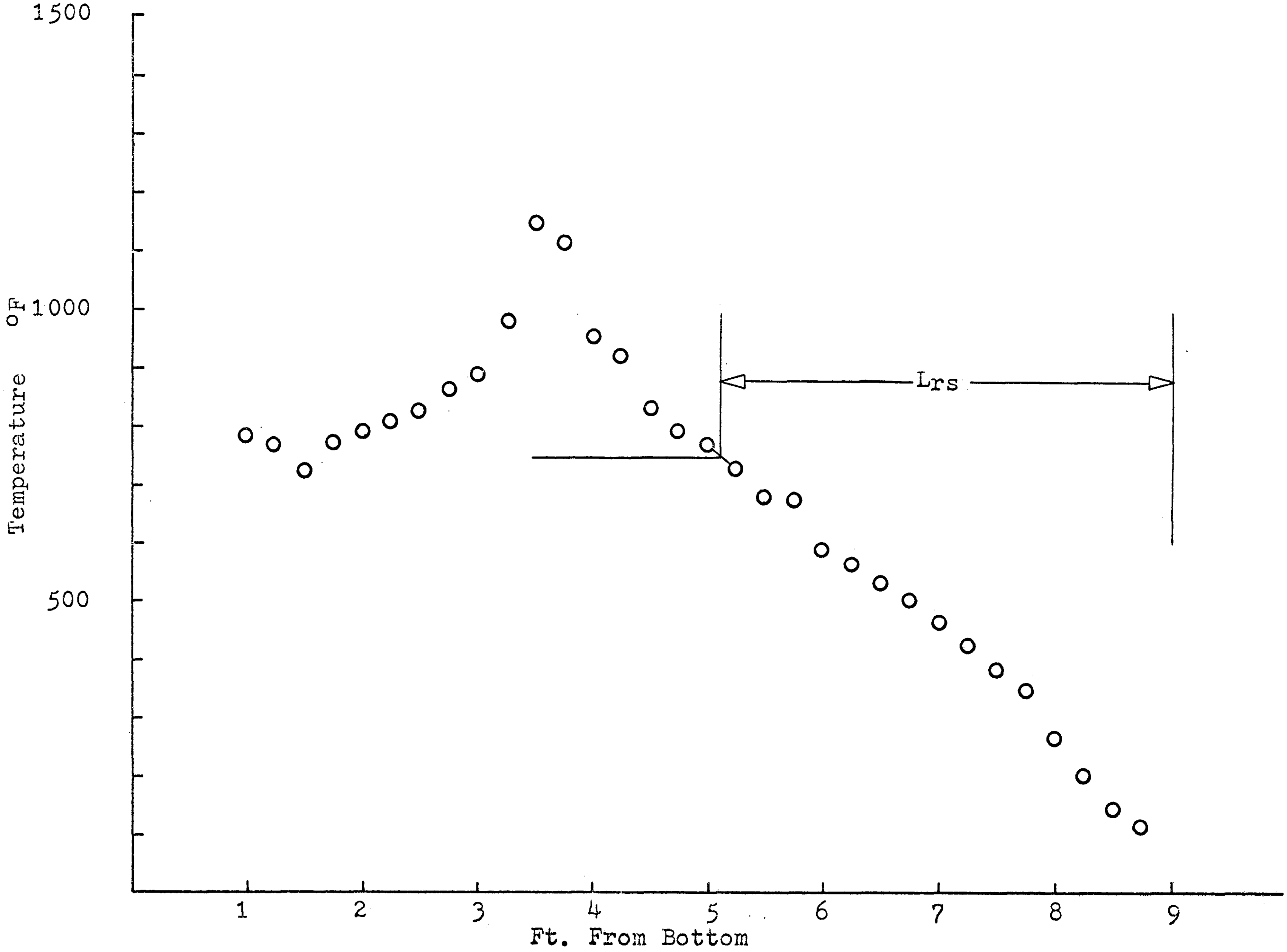


Fig. 20 Sample and Run No. 3-10 Temperature Profile

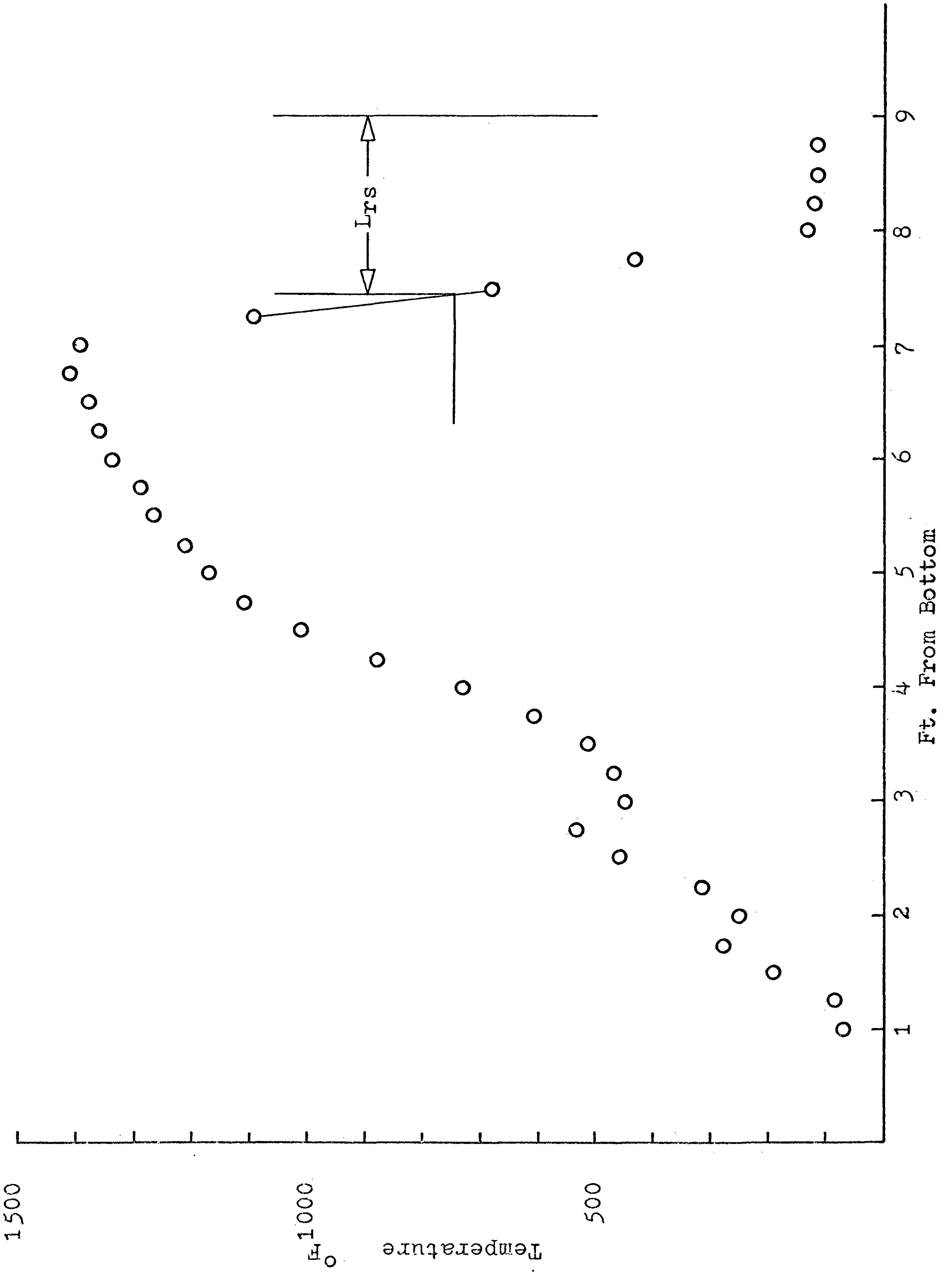


Fig. 21 Sample I-3-25 Temperature Profile

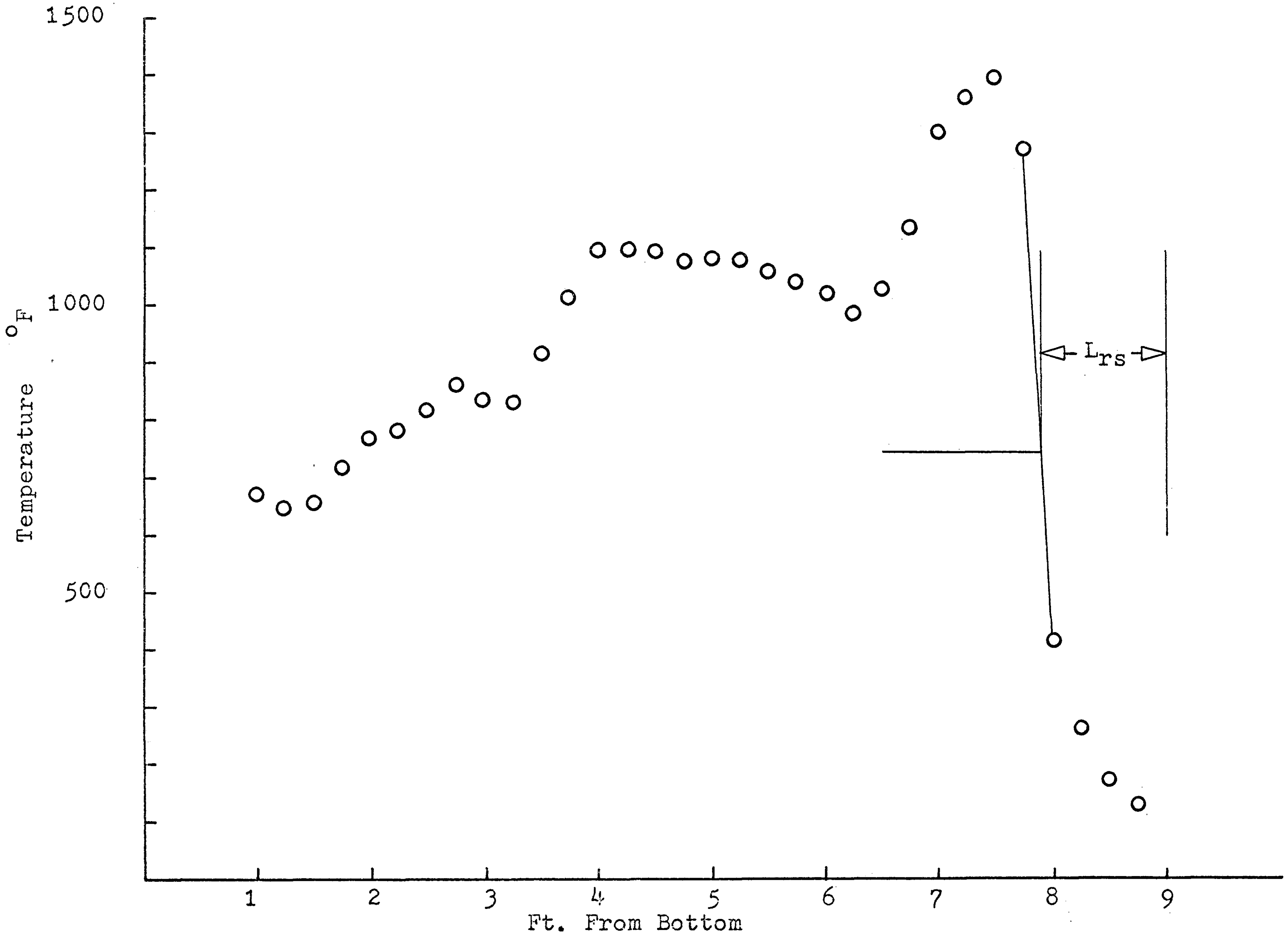


Fig. 22 Sample II-3-25 Temperature Profile

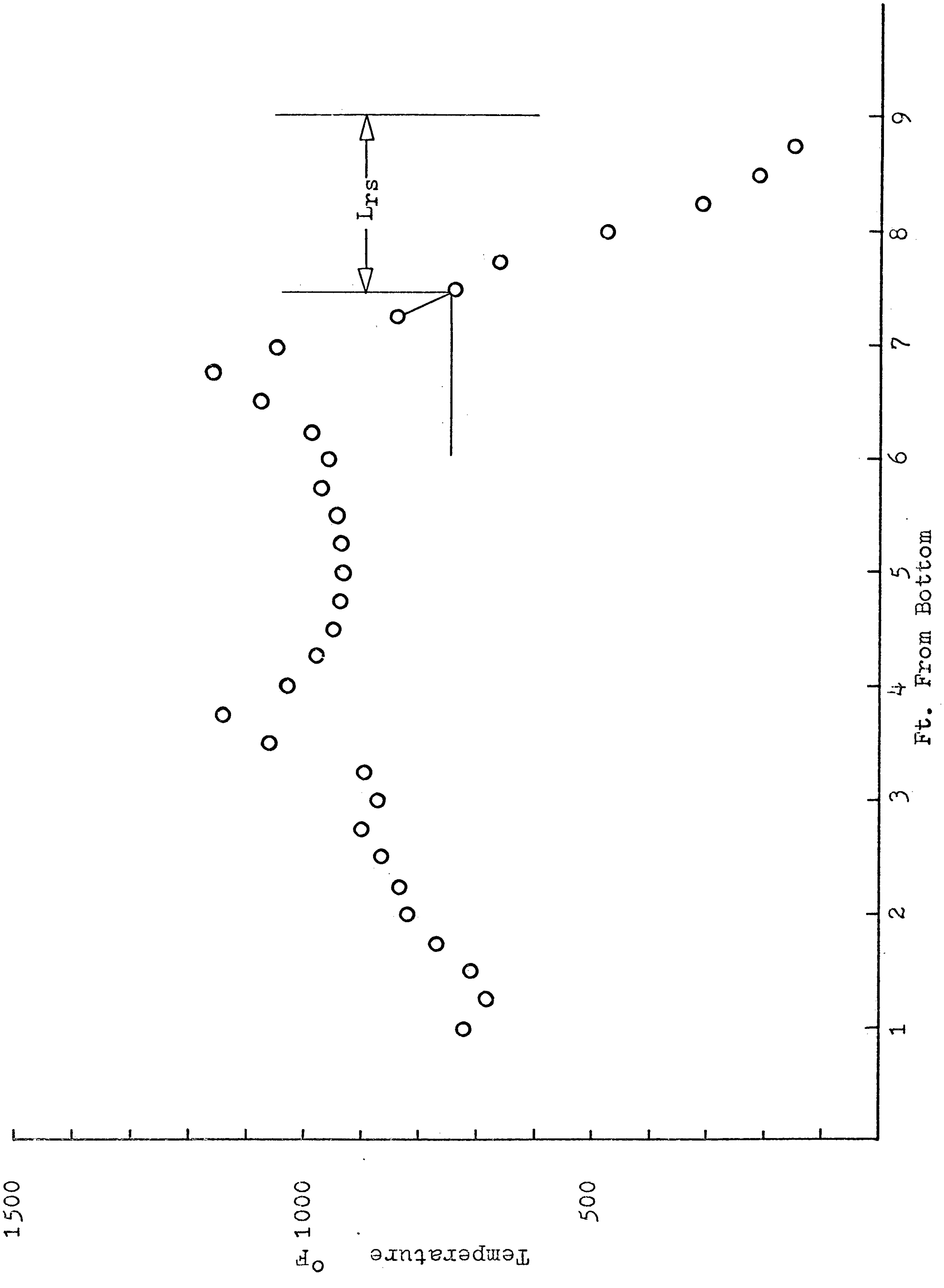


Fig. 23 Sample I-3-28 Temperature Profile

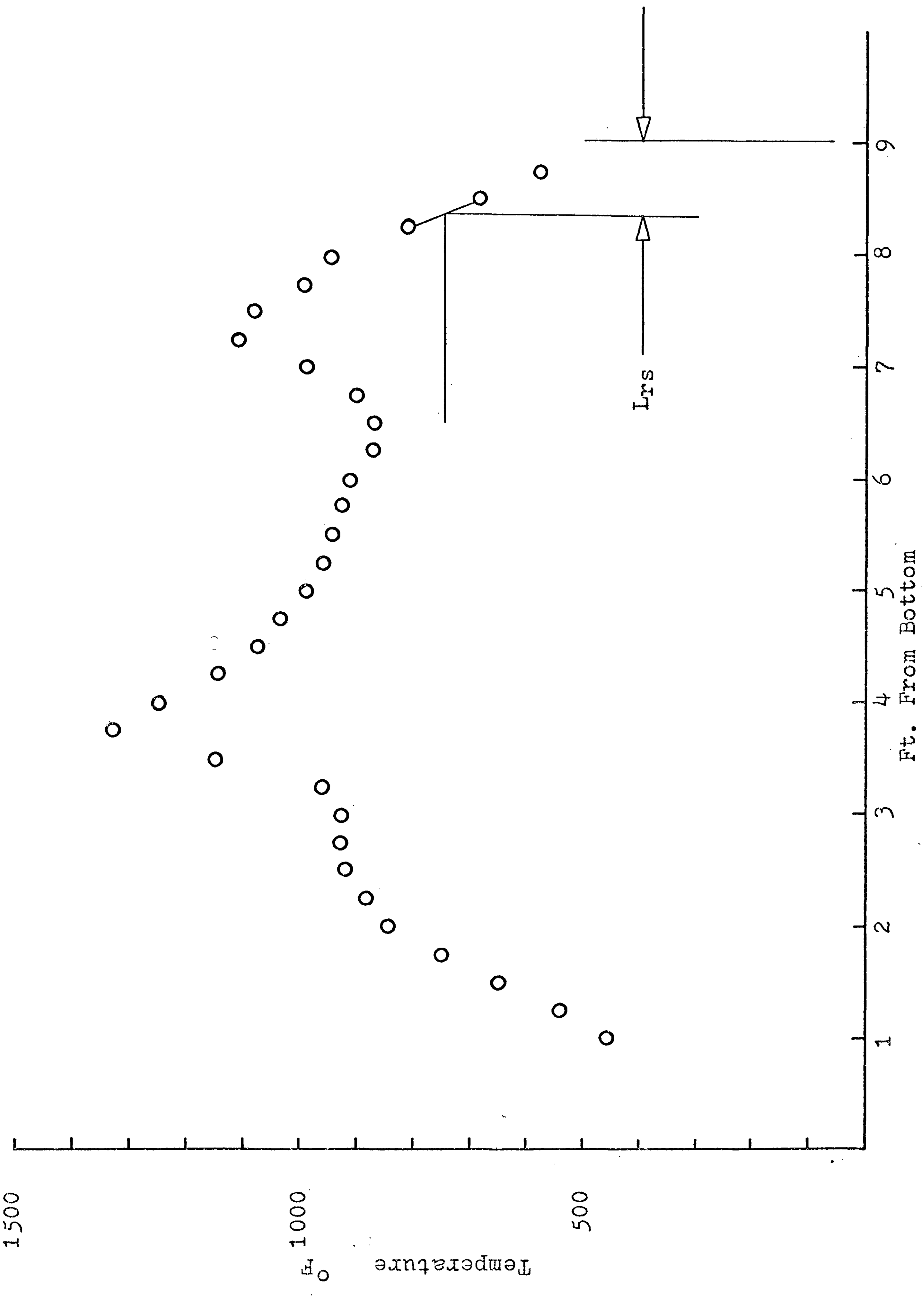


Fig. 24 Sample II-3-28 Temperature Profile

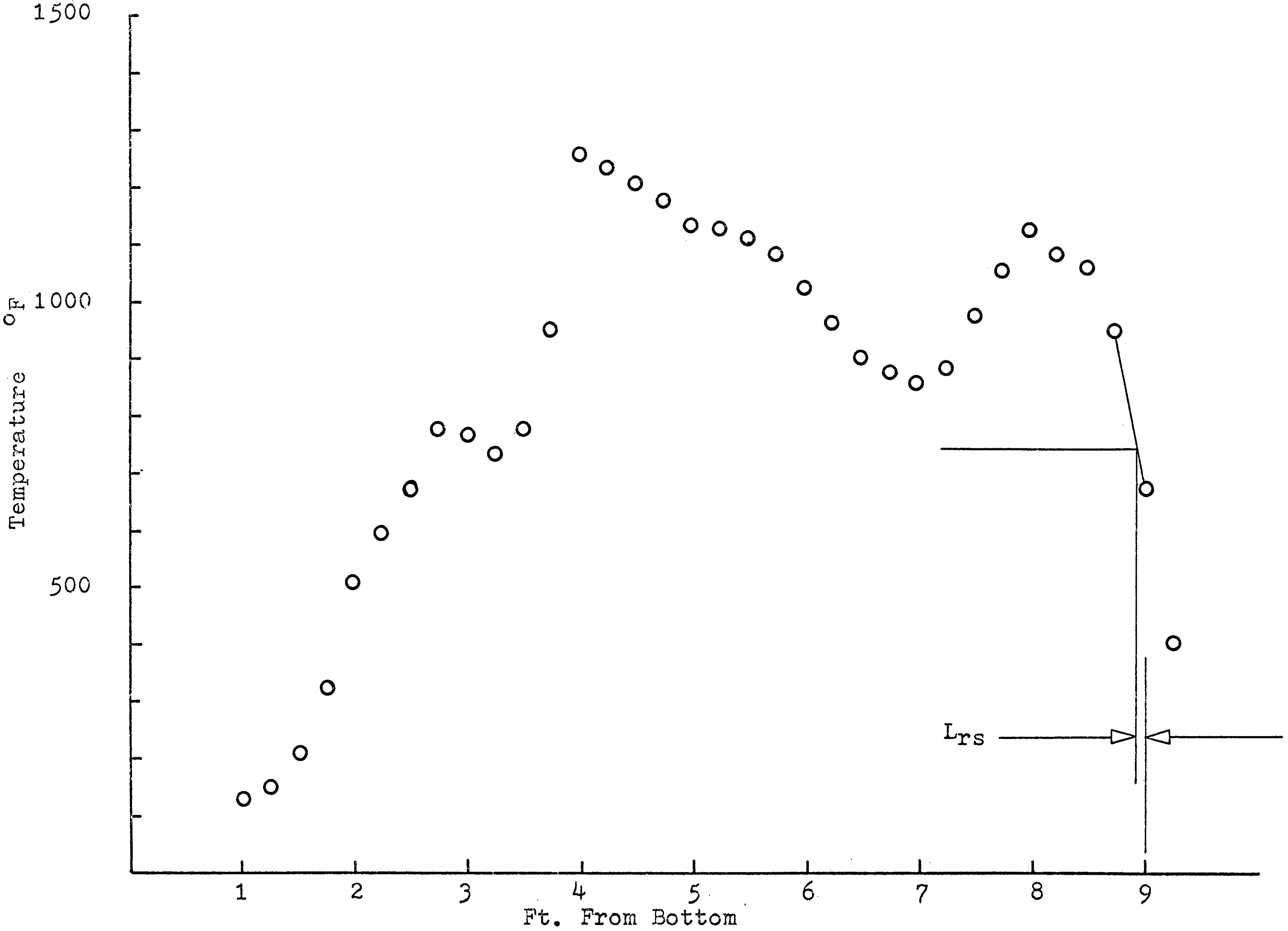


Fig. 25 Sample III-3-28 Temperature Profile

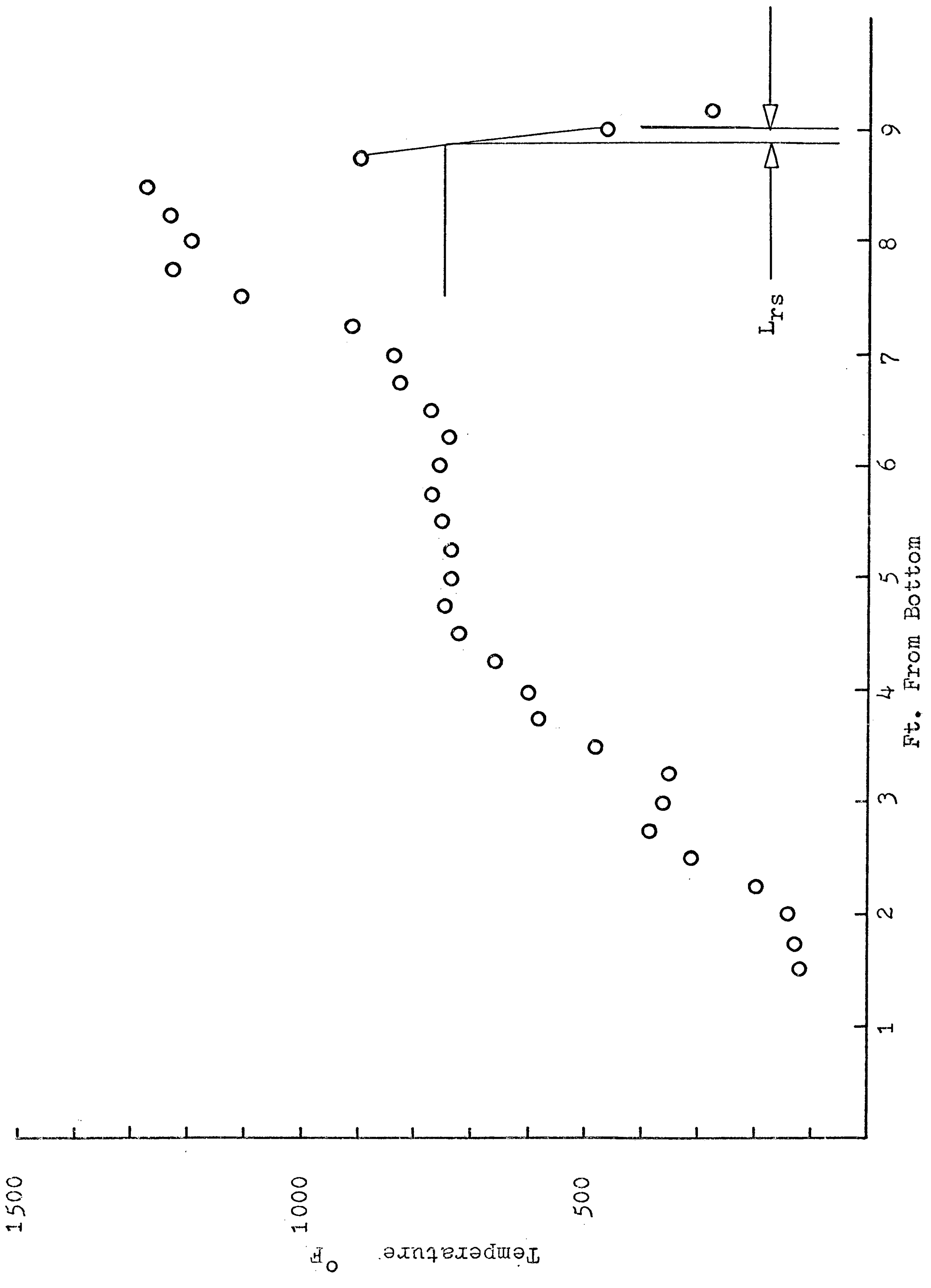


Fig. 26 Sample IV-3-28 Temperature Profile

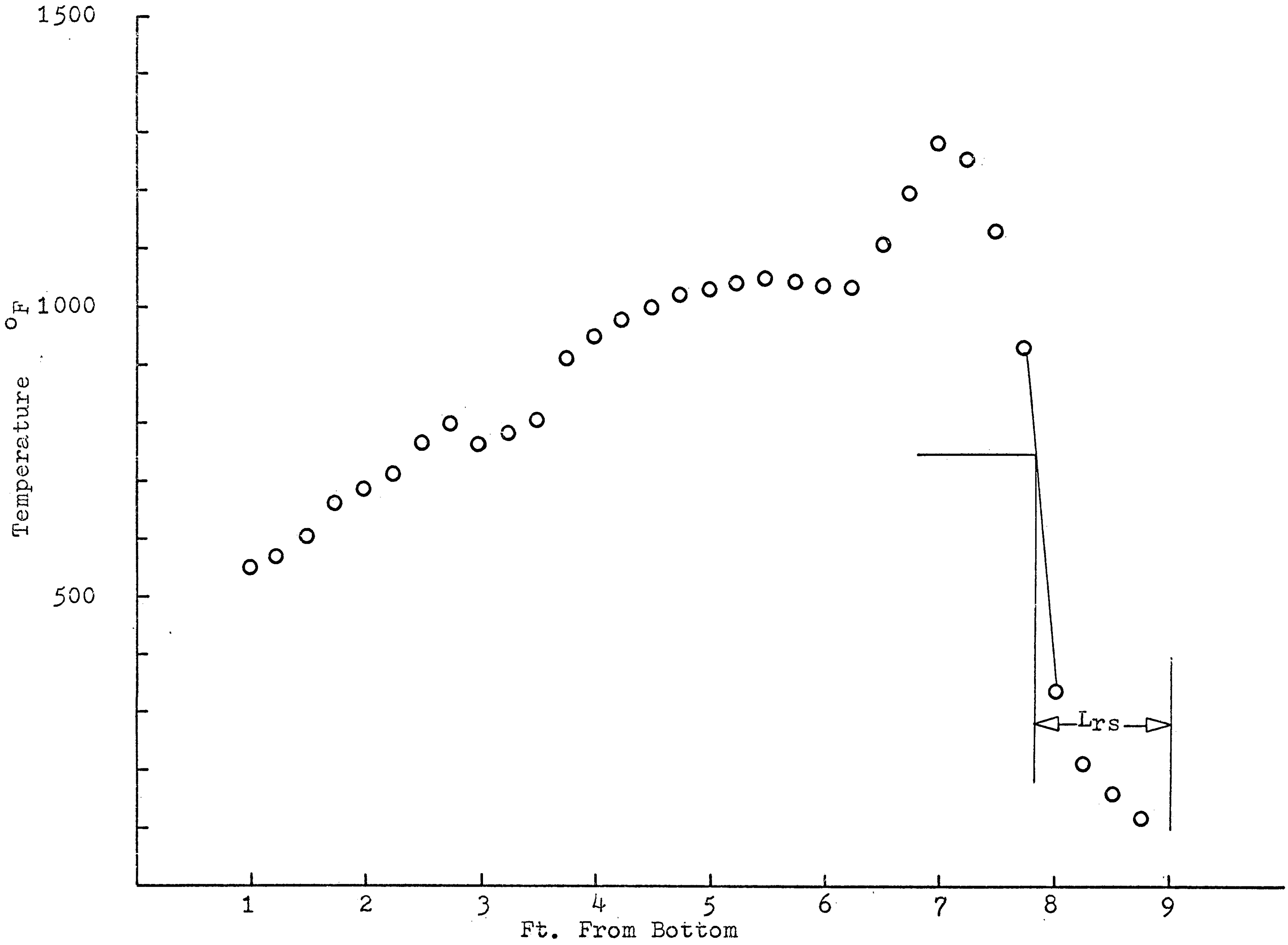


Fig. 27 Run No. 3-25 Temperature Profile

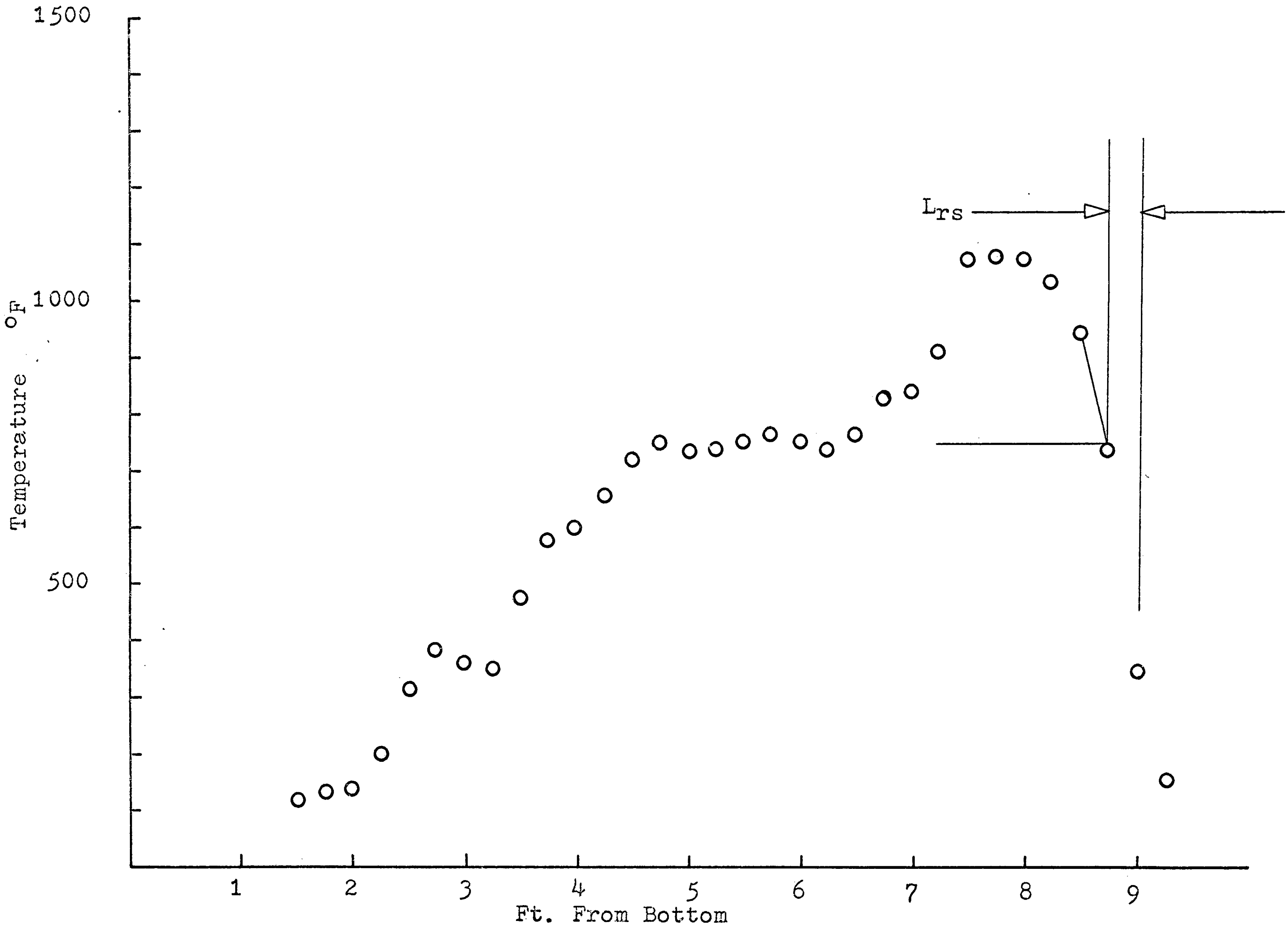


Fig. 28 Run No. 3-28 Temperature Profile

TABLE III

OIL QUALITIES FOR ALL OIL SAMPLES

	2-18	2-18	3-10	I 3-25	II 3-25	I 3-28	II 3-28	III 3-28	IV 3-28
API 60°F				18.6	18.2	19.0	17.8	17.6	17.4
Viscosity SSU 100°F	256	389	183	238	231	187	479	563	
Pour Point	80	80	80	80	80	80	80	80	80
Naphtha Fraction	6.3	4.0	9.2	6.5	5.3	6.0	4.7	4.3	4.3
Light Distillate Fraction	20.4	20.8	22.1	20.8	22.0		17.6	17.0	20.3
Saturates in Naphtha	29.4	25.7	30.0	25.6	31.4	30.8	32.0	31.8	29.2
Olefins in Naphtha	50.6	51.3	50.0	52.5	50.0	48.6	42.6	46.0	47.7
Aromatics in Naphtha	20.0	23.0	20.0	21.9	18.6	20.6	21.8	22.2	23.1

TABLE IV

DISTILLATION DATA FOR CRUDES

				I	II	I	II	III	IV
	2-18	2-28	3-10	3-25	3-25	3-28	3-28	3-28	3-28
2	--	--	--	--	--	--	--	--	--
3	T	T	T	T	T	T	T	T	T
4	0.8	1.0	0.8	0.7	0.8	1.0	0.8	1.0	0.8
5	0.8	1.0	1.0		1.0			1.0	1.0
6	1.0	1.0	1.0		1.3			1.3	1.2
7	1.2	1.0	1.3	1.2	1.3		1.5	1.7	1.2
8	1.5	1.3	2.0	1.7	1.7	1.7	2.0	1.8	1.5
9	2.7	1.7	3.5	2.5	2.3	2.8	2.7	2.0	1.8
10	4.0	2.2	5.8	4.0	3.5	4.7	3.5	3.0	2.7
11	6.3	4.0	9.2	6.5	5.3	6.0	4.7	4.3	4.3
12	8.8	6.5	12.7	9.3	8.8	9.3	7.0	6.7	6.5
13	11.3	9.0	15.5	12.0	11.5	12.5	9.3	8.8	9.3
14	14.0	11.7	18.5	14.8	14.2	15.8	11.7	11.7	12.0
15	17.2	15.0	21.5	17.7	17.2	19.5	14.0	14.3	14.3
16	20.3	18.3	24.8	21.0	20.7	23.0	16.8	16.2	17.7
17	24.2	21.7	28.0	24.7	24.5		20.2	19.2	21.5
18	26.7	24.8	31.3	27.3	27.3		22.3	21.3	24.3

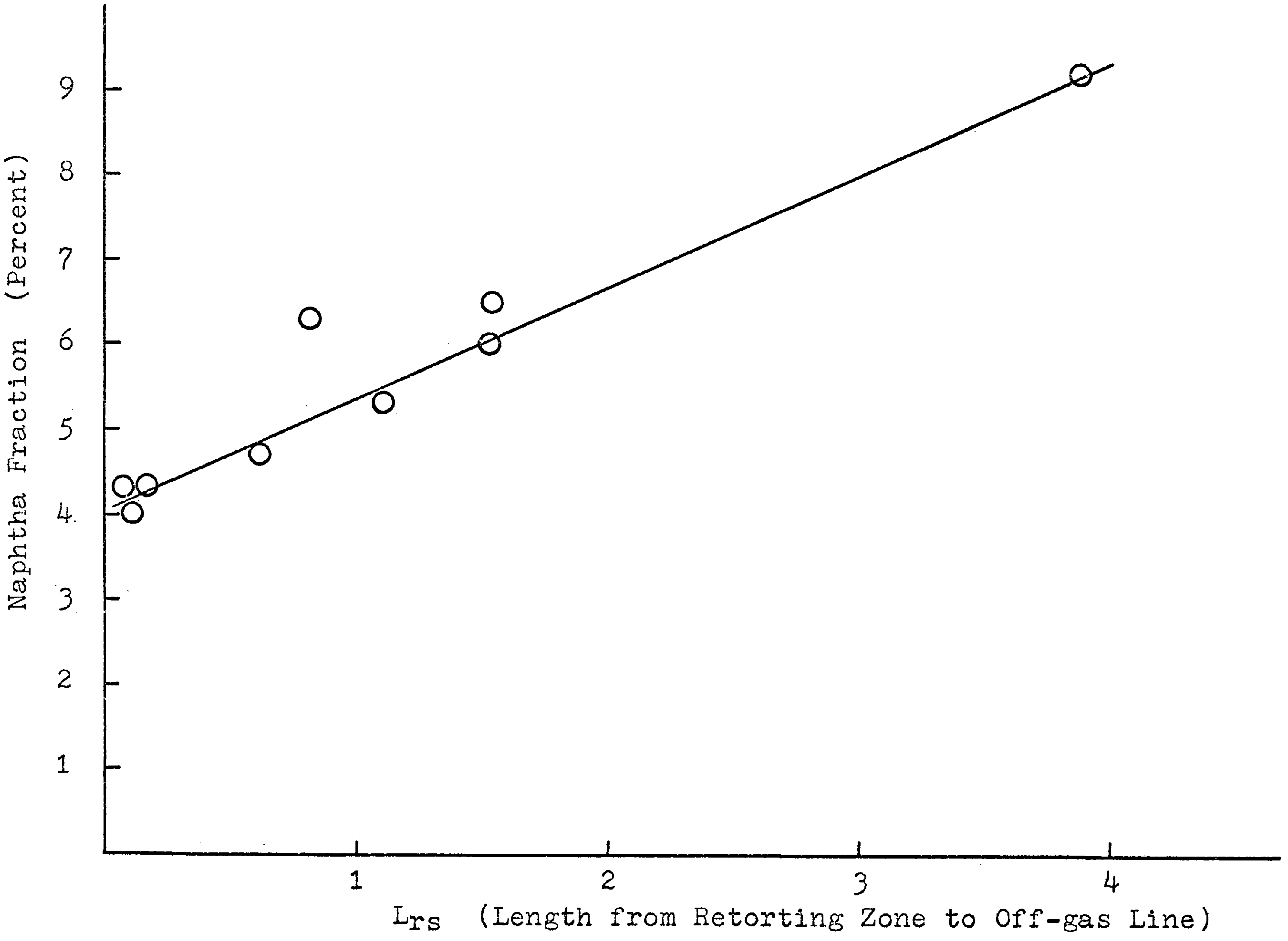


Fig. 29 Naphtha Fraction vs L_{rs}

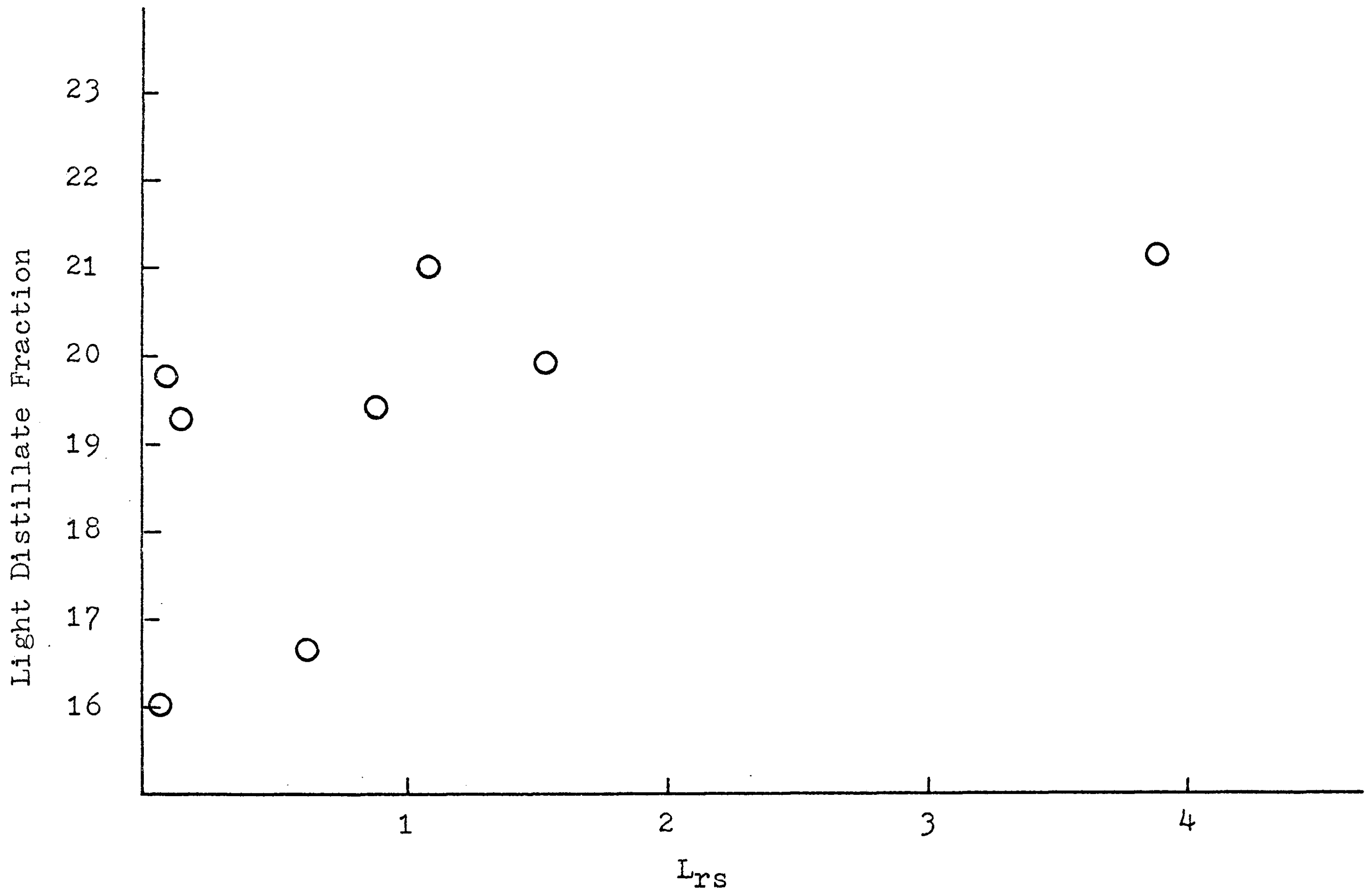


Fig. 30 Light Distillate Fraction vs L_{rs}

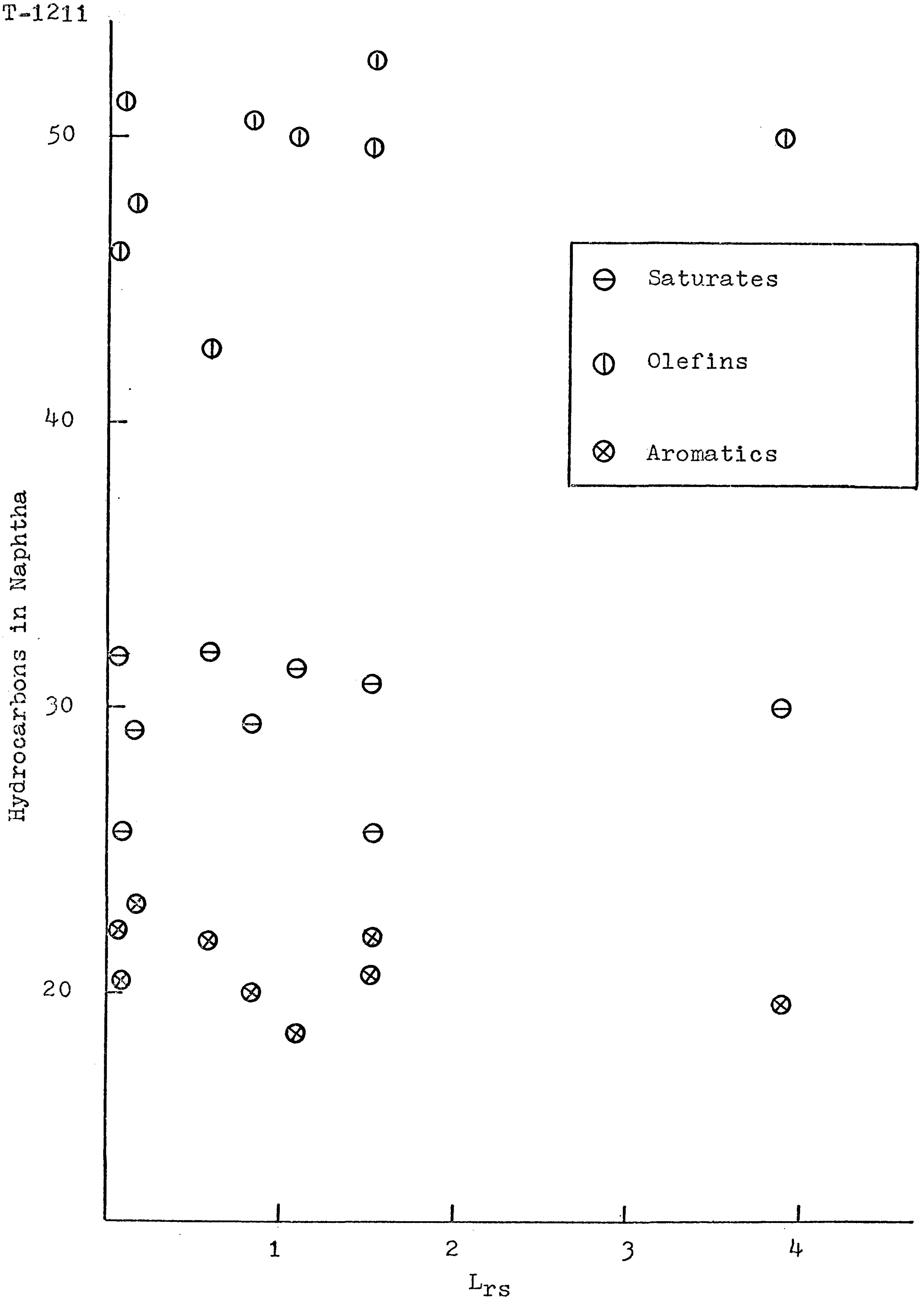


Fig. 31 Hydrocarbons in Naphtha vs L_{rs}

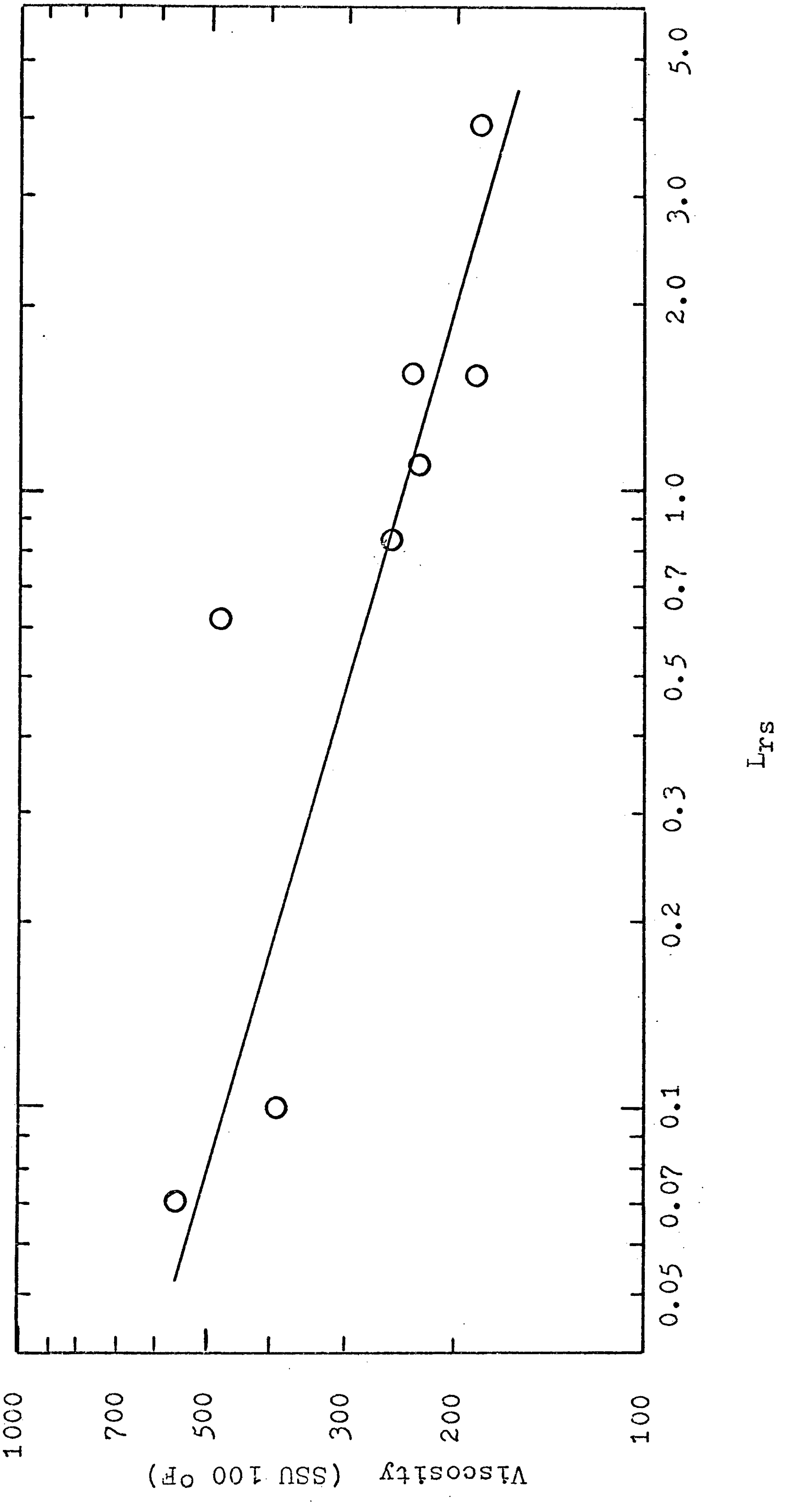


Fig. 32 Saybolt Viscosity vs L_{rs}

TABLE V

TOTAL RUN RECOVERIES

Run No.	2-18	2-28	3-10	3-25	3-28
Recovery	18.3	16.7	6.1	21.0	15.7

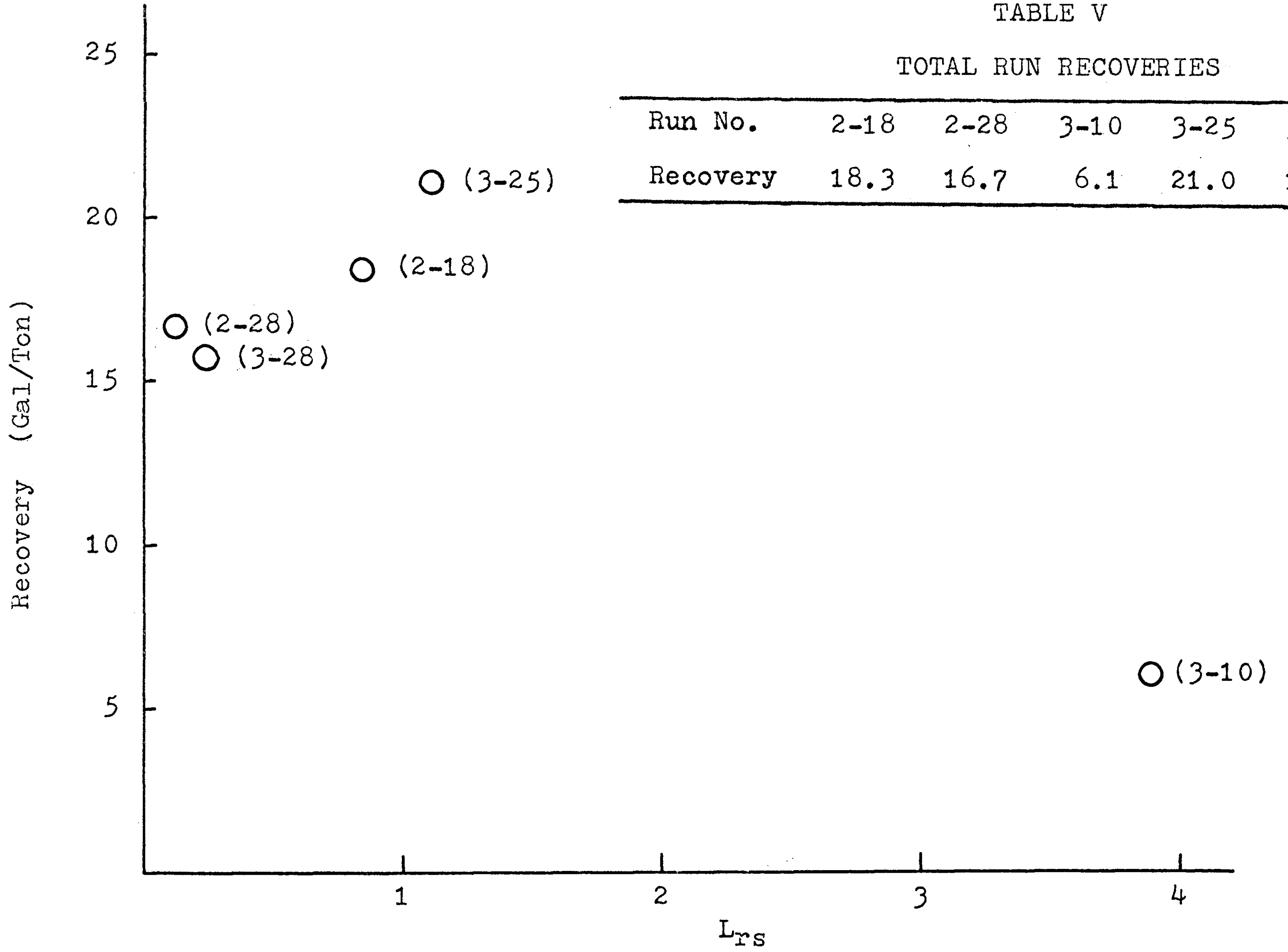


Fig. 33 Recovery vs L_{rs}

ANALYSIS OF RESULTS

In following the development of the temperature profile, starting with figure 8, one notices a pronounced hump at the 4-ft level after 1 3/4 hr. After 5 hr it is seen that this hump develops into a temperature peak approximately equal to the upper peak in the retort.

Why is there a valley between the two peaks? Three possible reasons for these two peaks could be carbonates decomposing in the center region, oil refluxing from above, or both are producing the temperature depression.

Following the temperature-profile development further, one sees that, after 7 hr the lower temperature peak has grown while the upper peak has decreased slightly. The depression of the upper peak and growth of the lower peak could be caused by the refluxing of oil into the combustion zone.

If the system is allowed to operate at the shale rate, producing the 7-hr profile, the temperature profile would continue to that shown for run No. 3-10, figure 20. However, at 7 hr the shale rate was decreased to 11 lb per hr. The decrease in shale rate decreases the fuel rate to the combustion zone, thus allowing the retort to develop the temperature profile shown in figure 17 at 15 2/3 hr. The move to the upper temperature profile indicates that refluxing of oil causes the formation of the valley in the temperature profile. At the upper temperature profile, the fact that the distance from the retorting zone to the combustion zone is very short means that there is very little refluxing. But there is not enough evidence to indicate that either one of the first two reasons are primarily responsible and it will have to be a combination of the two that is responsible.

The two peaks formed during start-up lead to the idea that, for a given shale and air rate, the retort may operate at one of two possible steady states.

If it is assumed that the retort has an oxygen feed rate of X_o units per minute, to operate at steady state all or some specified fraction of X_o must be utilized in combustion. To achieve the utilization of X_o, X_f units per minute of fuel are required. If the fuel rate is less that X_f, the combustion zone would move up in the retort; or if the fuel rate is greater than X_f, the combustion zone sould move down in the retort.

When X_f (fuel required for steady state) is greater than that supplied by the coke left from kerogen decomposition, the difference must be made up to achieve a steady state. If the retort is operated with the combustion zone near the top of the retort, the length of the retorting zone may be insufficient to produce complete retorting. In the upper region, the unconverted kerogen can serve as fuel to achieve the steady state when oxygen is in excess. The upper region combustion of unconverted kerogen produces a decrease in yield which is shown by the recovery data from figure 27. If the retort is operated with the combustion zone further down in the retort, the kerogen conversion can go to completion, but there is increased refluxing of oil. The refluxed oil can now be burned to serve as fuel for the excess oxygen, and a steady state can be achieved. It can be seen from run No. 3-10 that there is a pronounced decrease in the oil yield for higher refluxing.

The steady state at the top or upper portion of the retort is stable. For small changes in the oxygen rate, parallel changes in the fuel rate for a constant shale rate are produced. The stability of the upper steady state can be demonstrated by slightly decreasing the oxygen rate. The decreased oxygen rate produces an excess fuel rate. The excess fuel rate causes the retorting zone to move down in the retort. The downward movement of the combustion zone increases the length of the retorting zone. The increased length of the retorting zone produces less unconverted kerogen as fuel.

The steady state in the lower end of the retort is unstable. It can be shown that, for a small change in the oxygen rate, there is an opposite change in the fuel rate and therefore an unstable steady state. The instability of lower zone operation can be shown be increasing the oxygen rate slightly. The increased oxygen rate means that the fuel rate is insufficient. The insufficient fuel rate causes the combustion zone to move up the retort. The movement up the retort shortens the distance between the retorting zone and the off-gas line and thus reduces refluxing. The decreased refluxing means less fuel from the refluxed oil, and hence the combustion zone is accelerated upwards.

The oil-quality results clearly demonstrate a lighter hydrocarbon product is produced by lowering the zones. But the source of the lighter product is not completely available. It cannot be said whether the increased light product is due to secondary cracking, boil-off of the lighter products, or the change in the length of time for retorting by lowering the zones.

The naphtha fraction is most clearly related to the distance between the retorting zone to the off-gas line. The distance and the naphtha fraction have a correlation coefficient of 0.96 and a population correlation coefficient of 0.75. The naphtha yield does not fit such a straight line. The naphtha yield follows more the type of recovery of the total yield. The naphtha yield would show that, in the upper region of operation, its increase could be due to reboiling and secondary cracking. However the decrease in naphtha yield from run No. 3-10 shows that reboiling of the primary naphtha does not proceed far enough to begin the cracking of the heavier fraction. The two regions of operation and yield show that cracking will take place in the upper region but not in the lower region. Further it could be said that, in the upper region, refluxed oil is carried down by adhering to the shale particles; but as the refluxing increases, the refluxed oil becomes too excessive for it all to adher, and it begins to flow down over the shale.

The retort recovery data appears to fall into two characteristic regions: the region near the top where losses are due to combustion of unconverted kerogen and the region lower in the retort where losses are due to combustion of refluxed oil. The individual and total losses are demonstrated by figure 34.

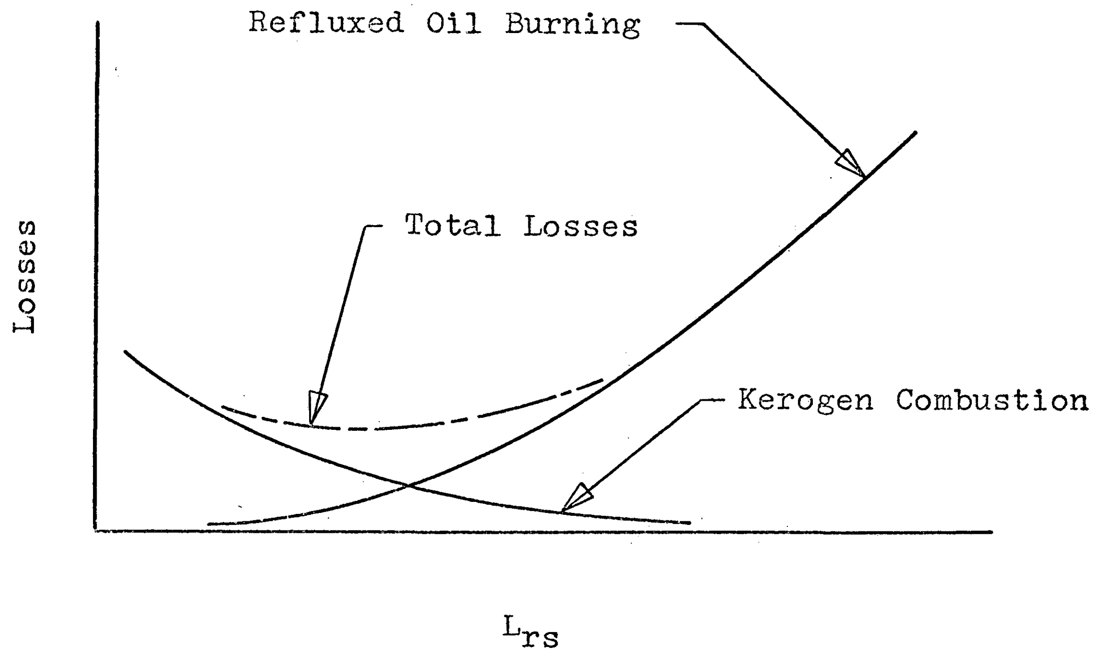


Fig. 34 Delineation of Losses

CONCLUSIONS AND RECOMMENDATIONS

It is concluded from the results that:

1. It is possible that the combustion retort with gravity feed can have two steady states where one is stable and the other is unstable.
2. The naphtha fraction is linerly related to the distance between the retorting zone and the off-gas line. The naphtha fraction will vary from 4 to 9 percent in the first 4 ft of the retort.
3. If the distance between the retorting zone and the off-gas line is less than 1 ft, the losses will be as high as 1/3 of the recovery at 1 ft. The upper zone losses are due to combustion of kerogen.
4. If the distance between the off-gas line and the retorting zone is 4 ft, the losses will be 2/3 the recovery when the distance is 1 ft. The lower region losses are due to the combustion of oil.

It is recommended that:

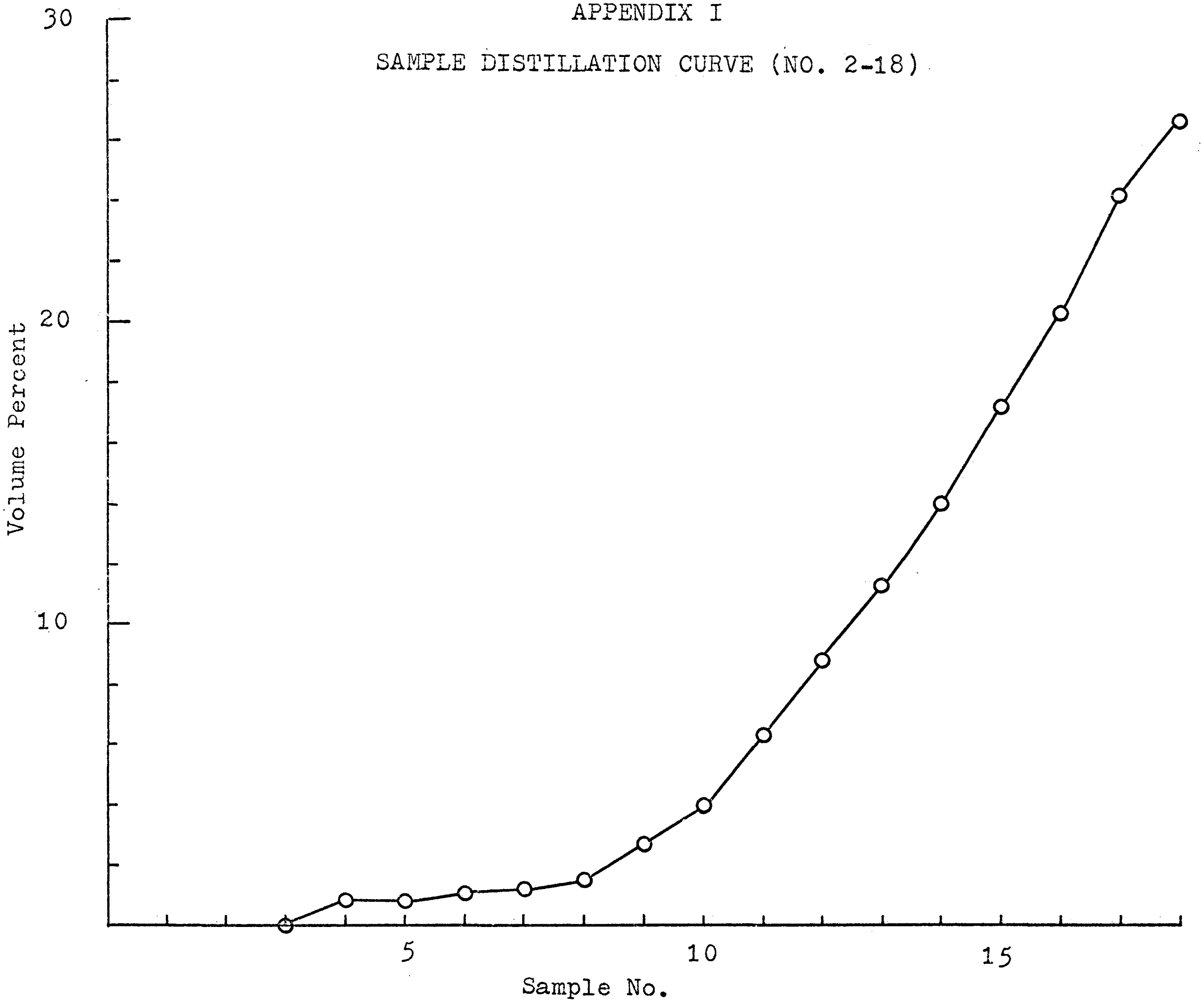
1. A study be made to prove the existence of

multiple steady states in order to establish more clearly the rate of refluxing, extent of reflux combustion, and extent of unconverted kerogen combustion.

2. A study be made of the transition region in figure 34 to establish the oxygen requirement to burn only coke and thus establish the amount of coke deposited for this particular retort.

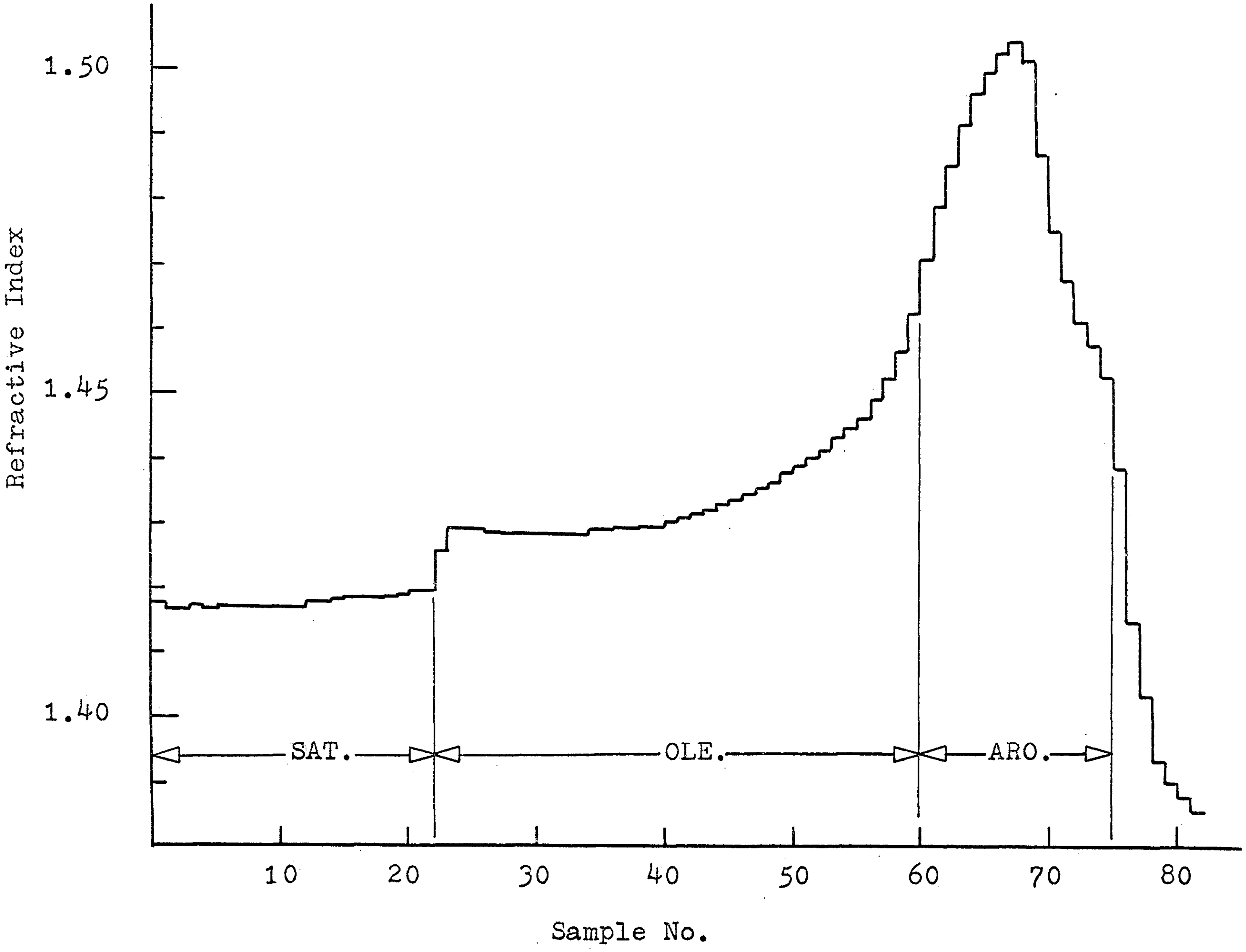
APPENDIX I

SAMPLE DISTILLATION CURVE (NO. 2-18)



APPENDIX II

SAMPLE ABSORPTO-GRAPH (NO. 2-18)



APPENDIX III

COMPARISON OF OIL QUALITIES FOR U.S. SHALES

			VISC.	DISTILLATION			HYDROCARBON ANALYSIS OF NAPHTHA		
	API	POUR POINT	SSU 100°F	UP TO 400°F	400 TO 600°F	RESID	SAT	OLE	ARO
NTU*	19.8	90	280	2.7	15.7	81.6	33	48	19
PUMPHERSON*	25.7	60	50	17.6	29.4	53.0	32	43	25
GAS FLOW*	16.0	70	660	1.5	12.8	85.7	27	42	31
ROYSTER*	19.7	90	230	4.9	13.2	81.9	31	49	20
GAS COMBUSTION*	18.6	85	310	4.4	14.6	81.0	27	51	22
1200°F HIGH TEMP.*	16.5	60	47	39.2	13.5	47.3	10	39	51
1500°F HIGH TEMP.*	1.6	5-	62	38.4	15.4	46.2	0	0	100
CSM INTERNAL COMB.	17-19	80	180-480	4.0-9.2	17.0-22.1	78.7-88.7	30	49	21

*Dinneen, Ball, and Thorne, 1952, pp. 2633-2634

APPENDIX IV

MATERIAL BALANCES (BASED ON RAW SHALE)

	2-18	2-28	3-10	3-25	3-28
IN:					
Shale	420	370	435	415	800
Air (cu ft)	(1193)	(1180)	(890)	(870)	(2830)
TOTAL (lb)	420	370	435	415	800
OUT:					
Spent Shale	356.5	304.0	408.5	365.0	697.0
Water	9.0	8.6	7.2	7.0	18.7
Oil	19.8	15.7	4.9	16.0	33.6
Gas (cu ft)	(2350)	(2900)	(1280)	(2050)	(5820)
C in CO_2 from Combustion	8.1	6.3	5.4	7.2	15.0
CO_2 from Carbonate Decomp	17.0	10.6	4.6	7.0	23.5
C in CO	1.2	0.4	0.3	0.1	1.6
Hydrocarbons	3.0	0.3	0.7	1.3	3.6
TOTAL (lb)	414.6	345.9	431.6	403.6	793.0
Unaccounted for (percent)	1.3	6.5	0.8	3.0	0.9

APPENDIX V

CARBON BALANCE RUN #3-28

IN:	
Shale	75.5
TOTAL	75.5 lb
OUT:	
Shale Ash	16.7
CO_2 from Combustion	15.0
CO_2 from Carbonate Decomposition	6.4
CO	1.6
Hydrocarbons (Off Gas)	2.9
Oil	21.8
TOTAL	63.4 lb

Unaccounted for 16%

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