

A LABORATORY-PILOT PLANT CORRELATIVE  
STUDY OF THE COKING OF HEAVY RESIDUAL OILS

By

BILLY E. STEINKUHLER

Bachelor of Science

Indiana Technical College

Fort Wayne, Indiana

1948

Submitted to the Faculty of the Graduate School of  
the Oklahoma Agricultural and Mechanical College  
in Partial Fulfillment of the Requirements  
for the Degree of  
MASTER OF SCIENCE

1950

OKLAHOMA  
AGRICULTURAL & MECHANICAL COLLEGE  
LIBRARY

JAN 17 1951

A LABORATORY-PILOT PLANT CORRELATIVE  
STUDY OF THE COKING OF HEAVY RESIDUAL OILS

BILLY E. STEINKUHLER

MASTER OF SCIENCE

1950

THESIS AND ABSTRACT APPROVED:

*Leo Gawin*

\_\_\_\_\_  
Thesis Adviser

*Charles L. Nickalls*

\_\_\_\_\_  
Faculty Representative

*R. C. McIntosh*

\_\_\_\_\_  
Dean of the Graduate School

266843

#### ACKNOWLEDGEMENT

The author gratefully acknowledges the advice and helpful criticism of Dr. Leo Garwin during the course of this investigation. Appreciation is expressed to the School of Chemical Engineering of the Oklahoma Institute of Technology for the facilities provided to carry out this work.

The author also wishes to take this opportunity to express appreciation to Dr. N. K. Anderson of the Deep Rock Oil Corporation, Cushing, Oklahoma, for the privilege of participating in the pilot plant operation, for the copy of the CDR pilot plant report, for the residual oil samples, and for information on the coke density determination.

## TABLE OF CONTENTS

	<u>Page No.</u>
ABSTRACT .....	1
INTRODUCTION .....	2
FEED STOCKS USED .....	6
A. Pilot Plant	
B. Laboratory	
CDR PILOT PLANT .....	8
A. Equipment	
B. Operation	
C. Sampling and Testing	
LABORATORY INSTALLATION .....	13
A. Equipment	
B. Operation	
C. Analytical Procedure	
RESULTS .....	24
A. Pilot Plant	
B. Laboratory	
DISCUSSION .....	25
A. Pilot Plant	
B. Laboratory	
C. Correlations	
SUMMARY .....	33
RECOMMENDATIONS .....	35
BIBLIOGRAPHY .....	36
APPENDIX	
Table I - Summary of Average Pilot Plant Results .....	38
Table II - Summary of Laboratory Run Data .....	39
Table III - ASTM Distillations of Liquid Products of All Standard Laboratory Runs .....	41
Method for Estimating Product Distribution on Loss-Free Basis in Laboratory Coking Installation .....	42
Equations for the Calculation of the Specific Gravity and the Total Weight of Gas Produced in the Laboratory Cok- ing Installation .....	43
Table IV - Sample Laboratory Run Sheet .....	44
Sample Laboratory Calculations .....	45
Nomenclature .....	46



## LIST OF FIGURES

	<u>Page No.</u>
1. Flow Diagram of CDR Pilot Plant .....	9
2. Details of Coking Unit .....	16
3. Flow Diagram of Laboratory Coking Installation .....	17
4a. Photograph of Coking Unit Assembled .....	18
4b. Photograph of Coking Unit Disassembled .....	18
5. Photograph of Laboratory Coking Installation .....	19
6. Photograph of Coking Unit (Shielded), Condenser, and Liquid Receiver .....	20
7. Typical Laboratory and Pilot Plant ASTM Distillation Curves of Liquid Produced from Vis-breaker Tar .....	31
8. Typical Laboratory and Pilot Plant ASTM Distillation Curves of Liquid Produced from Thermal Tar .....	31
9. Typical Laboratory and Pilot Plant ASTM Distillation Curves of Liquid Produced from Virgin Asphalt .....	31
10. Laboratory Coke Yield versus Maximum Coking Temperature ....	32
11. Laboratory Gas Yield versus Maximum Coking Temperature .....	32
12. Laboratory Liquid Yield versus Maximum Coking Temperature ..	32
13. Laboratory Coke Density versus Maximum Coking Temperature ..	32

## ABSTRACT

A laboratory-pilot plant correlative study of the coking of three heavy residual oils has been carried out with a Knowles type oil-coking oven of 17 sq. ft. floor area for the pilot plant operation and a crucible, set in a heating chamber, for the laboratory unit.

Pilot plant equipment, operation, and results are described and discussed. High grade metallurgical coke was made consistently in the pilot plant oven.

A laboratory coking installation consisting of a coking unit, a condenser, and a product accumulation system was developed. Operating temperatures up to 1550°F. were investigated in the laboratory unit with very low material losses in coke, liquid, and gas products.

When the laboratory coking data for the various temperatures were extrapolated to the maximum pilot plant coking temperatures, very good correlations of liquid, gas, and coke yields and coke densities were obtained. Comparisons of the quality of the liquid produced from a given feed stock were, in general, good.

As the temperature of laboratory coking is increased, the coke density is increased while the coke yield is decreased. This is accompanied by an increase in gas yield and a slight decrease in liquid yield. The quality of the liquid is not affected noticeably by the maximum coking temperature.

## INTRODUCTION

Interest in the production of high grade metallurgical coke has grown recently due to present and anticipated market conditions. High grade metallurgical coke is used for electrode manufacture (particularly by the aluminum industry), carbon motor brushes, crucibles, dry cells, abrasives, and many other similar applications. At present, the most widely used method of production is the calcination of raw or refinery coke.<sup>10</sup> This process is a two-step operation involving the production of raw petroleum coke by common refinery coking methods and the calcination of the raw coke in rotating kilns maintained at approximately 2700°F. Most of the volatile content of the raw coke is driven off, leaving almost pure carbon. The chief disadvantages of this process are the high material losses and the high costs of handling and processing.

In 1931, the Tidal Refining Company of Drumright, Oklahoma, reported on the commercial production of high grade coke (real density = 1.8) in a Knowles coking-oven unit.<sup>11</sup> This was essentially a batch-type unit, consisting of a conventional tube-still preheater, a charge system, a battery of six Knowles ovens, a fractionating column, and coke-handling equipment.

The Knowles oven, as described by Tidal, had floor dimensions of 10 ft. by 30 ft. The coke bed usually reached an average depth of 6 to 8 inches. This type of coke bed permitted a high rate of heat flux per unit volume of coke, allowing the driving off of the volatile fractions of the coke and the production of a high density (high per cent fixed carbon) coke. The floor, sides, and arched roof were lined with alumina or carborundum refractory. Two doors at each of the 10 ft. ends of the oven could be raised, allowing a hydraulic ram to push the coke from the oven. Heat was supplied by gas burners at each end of the oven, each burner being enclosed in a 6 inch by 8 inch combustion tunnel. These tunnels led to a common flue



under the center of the oven which carried the combustion gases to a stack. The residual oil charge was fed through two openings at the top of the oven. The vapors were taken off through a vapor outlet main, quenched with gas oil, and fractionated.

The charge stock (1500 bbls./day) for the Tidal oil-coking unit was a blend of 91.8% topped crude (11.5°A.P.I. gravity) and 8.19% cracked tar (6.5°A.P.I. gravity). The charge stock was preheated (800°F.) and fed to the ovens (floor temperature of 2350-2400°F.) in cycle for a charge period of 5 hours, 20 minutes followed by a gas-off or drying period of 2 hours. The oven was operated under a vacuum of 1/2 to 3/4 inches of water. The vapor (810-1000°F.) from the oven was quenched by cold gas oil and fractionated. The bottom product was gas oil. The overhead condenser liquid product was gasoline distillate. The wet gas was processed in a recovery plant. Pushing out coke and cleaning up took 40 minutes, completing an oven cycle of 6 hours. Serious trouble was not encountered with coking in the tube-still preheater. However, serious trouble with carbon-black formation and coking in the vapor system was encountered. This may have been caused by two factors, the very high initial oven floor temperature and air leakage into the oven.

The following tables contain some typical product yields and analyses from Tidal's unit:

<u>Overall Yield (Wt.%)</u>	
Gasoline (44.0°A.P.I.) ----	7.93
Gas oil (20.9°A.P.I.) ----	55.02
Gas (1.0 sp. gr.) ----	16.93
Coke -----	16.72
Loss -----	0.70
Total -----	100.00

<u>Coke Analysis</u>	
Sp. gr., apparent ----	1.2
Sp. gr., true -----	1.8
Moisture, % -----	0.6
Fixed carbon, % -----	94.8
Ash, % -----	1.8
Volatile, % -----	2.8



In 1933, the Atlantic Refining Company reported on a commercial Knowles coking unit.<sup>7</sup> Information was limited to specific operating and cost data. The plant had a capacity of 6,000 bbls./day of residual oil charge. Operation was similar to that of the Tidal unit. This report noted a correlation between carbon residue values of charging stocks and yields of coke.

In 1937, the Lubrite Refining Company reported on a modification of previous Knowles units in that a fuel oil reduction unit was used.<sup>2</sup> Thermal cracked tar (10-12°A.P.I.) was fed to a bubble tower after preheating to a high temperature. The light ends of the hot tar flashed off and were removed overhead. The bottoms (1-2°A.P.I.) were fed to four Knowles ovens operating in cycle. An operating cycle of 6 hours consisted of a charging time of 1.75 hours, a drying time of 3 hours, and a coke removal and door sealing time of 1.25 hours.

The only commercially successful continuous coking process is the delayed-coking process.<sup>6</sup> Due to the relatively low coking temperature and large volume of coke, this process produces a coke of high volatile content (raw coke) unsuitable for direct use as high grade metallurgical coke. The residual oil is heated to about 910°F. and charged to a coking drum where the coke is deposited by contained heat. The hot vapors (780°F.) are removed to a fractionating system. Three coking drums operate in cycle to provide for continuous operation. Coke produced by the delayed-coking process can be converted to high-density coke by calcination.

In 1944, Berry and Edgeworth-Johnstone reported on an investigation of the effect of temperature and time upon petroleum coking.<sup>4</sup> Results of this investigation indicated that the coking process could be regarded as taking place in four stages, corresponding to the production of pitch, semi-pitch, asphaltic coke, and carboid coke. Petroleum coke was defined as a disperse system of graphite-like crystallites of pure carbon embedded in

an organic matrix. Coke produced by cracking and by external coking units (delayed-coking) was considered to be chiefly asphaltic coke. Coke produced by batch coking in Knowles ovens was considered to be almost entirely carboid coke. Carboid coke has a greyer color, a greater strength, and lower volatile content than asphaltic coke. The four stages of coking were found to be dependent upon temperature and time. The quantity and quality of coke produced was also shown to depend upon these variables.

In 1945, Berry and Edgeworth-Johnstone reported on the production of compact nonporous coke by subjecting mixtures of pulverized coke and residuum or cracked asphalt to secondary coking.<sup>5</sup> For the production of strong nonporous coke under conditions of rapid heating, two requirements were found necessary. The volatile content of the primary coke should not exceed 7%, and the calculated volatile content of the mixture of coke and binder should not exceed 22%.

In 1949, Godfrey L. Cabot, Inc., of Boston, Massachusetts, and the Deep Rock Oil Corporation of Tulsa, Oklahoma, carried out a joint pilot plant investigation to determine if the broad oven coking process could produce economically from residual oils a maximum amount of high grade coke and, as by-products, gas, gasoline, and a stock suitable for catalytic cracking.<sup>1</sup> The pilot plant was constructed and operated at Deep Rock's Cushing, Oklahoma, refinery and was known as the CDR pilot plant.

The present laboratory scale investigation was undertaken to attempt to correlate the CDR pilot plant results with laboratory bench scale data and thus possibly permit the prediction of large scale operating results with any charge stock from laboratory tests on such charge stocks. The laboratory study consisted, first, of the development of suitable equipment, second, the carrying out of batch coking operations under various conditions, and, third, the analysis of the products produced.

## FEED STOCKS USED

### A. Pilot Plant.

1. Vis-breaker tar. This heavy residual oil was the bottoms stream of a viscosity-breaking unit. Only one batch of this tar was used in the pilot plant. The Conradson carbon residue as determined in the Deep Rock laboratory was 15.3%.

2. Deep Rock thermal tar. This feed stock was the bottoms stream of a Dubbs thermal cracking unit and was produced by the Deep Rock refinery at Cushing, Oklahoma. Different batches of this tar were used during the course of the pilot plant operation. This accounts for some variation in the analyses. The Conradson carbon varied from 13.5 to 14.0%.

3. Deep Rock virgin asphalt. This feed stock was the bottoms stream of a vacuum fractionator and was produced by the Deep Rock refinery. Several different batches of this tar were used during the course of the pilot plant operation. This again accounts for some variation in the analyses. The Conradson carbon varied from 18.5 to 21.9%.

Table I gives complete feed stock tabulations.

### B. Laboratory.

1. Vis-breaker tar. This tar was identical with that used in the pilot plant operation. It was secured directly from the pilot plant storage tank. The Conradson carbon value was checked and found to be 15.4%.

2. Deep Rock thermal tar. This feed stock was not identical with that used in the pilot plant operation as it was obtained from the Dubbs cracking unit several weeks after pilot plant operation had ceased. The Conradson carbon value was 16.4%. However, the gravity, sulphur, ash, viscosity,



and characterization factor can be assumed to be reasonably close to the pilot plant stock.

3. Deep Rock virgin asphalt. This stock was again not identical with the equivalent in the pilot plant operation. However, the Conradson carbon value was found to be 19.8%. This checked within the range of values given for the pilot plant stock. The gravity, sulphur, ash, and viscosity can also be assumed to be very close to the values for the corresponding pilot plant stock.

## CDR PILOT PLANT

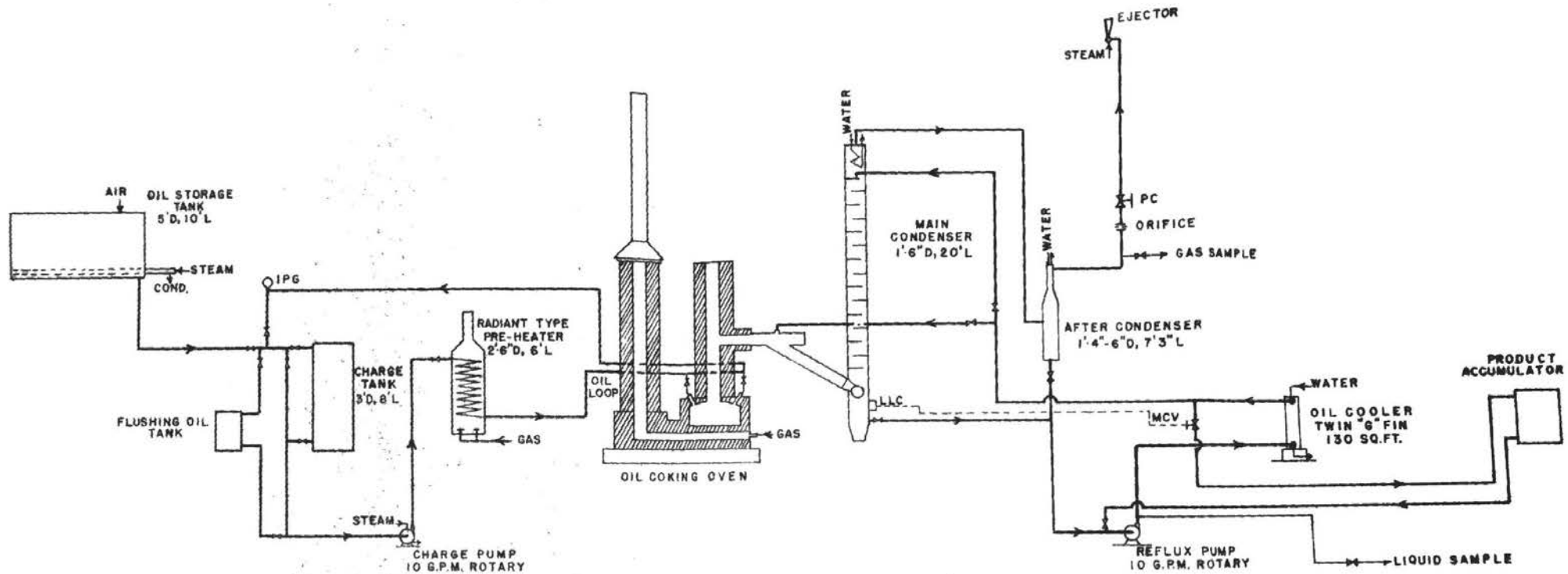
A. Equipment. The plant consisted of a feed storage, preheat, and charge system which could handle heavy residual oils, a pilot plant broad oven of the Knowles-type design (17 sq. ft. floor area), a reflux tower, a condenser, tanks to collect liquid products, and necessary auxiliaries (meters, instruments, etc.). Figure 1 gives a flow diagram of the pilot plant.

1. Feed storage and charge tank. The feed storage consisted of three 40-barrel tanks, each equipped with bayonet-type steam heaters. Steam traced, movable feed lines connected the storage tanks to the charge tank which was provided with a steam coil. Steam at 125 pounds was used for heating throughout the plant.

2. Feed system. The feed system comprised, in addition to the charge tank, a 10 gpm rotary pump and a gas fired coil-type preheater. All transfer lines were steam traced and insulated. Oil entered the oven through two 1/4 inch Hauck linear discharge-type valves. The feed line pressure was controlled by a valve in the recycle line.

3. Oven. The oven consisted of four gas fired flues connected to an exhaust stack and a coking chamber directly above the flues which connected to a condensing system. Each of the flues was provided with a 530,000 B.t.u./ hr. natural gas burner. The coking chamber and combustion flues were lined with carborundum brick. The two oil inlet ports were mounted diagonally opposite each other in the arch of the coking chamber. The chamber was provided with two mortar-filled steel doors with cable winches for lifting. The top of the coking chamber stack was fitted with a heavy alloy machine-fitted cap which was opened and closed by a lever and chain system.

Figure 1  
Flow Diagram of CDR Pilot Plant



**LEGEND**  
 IPG INDICATING PRESSURE GAUGE  
 LLC LIQUID LEVEL CONTROL  
 MCV MOTOR CONTROL VALVE  
 PC SYSTEM PRESSURE CONTROL VALVE



4. Main condenser. The main condenser, vertical, was 18 inches in diameter and contained sixteen perforated baffle plates spaced at approximately 1 foot. Reflux connections were provided in the top of the condenser to provide wash for the plates. A liquid level control valve in the bottom of the condenser regulated the flow of liquid to the product accumulator tank. A small water coil was also installed in the top of the condenser.

5. After condenser. The after condenser consisted of a short section of 6 inch pipe containing a 3/8 inch pipe water coil. The bottom of this condenser widened to provide approximately 10 gallons storage capacity. An entrainment separator consisting of a length of 6 inch pipe containing small pebbles followed the after condenser.

6. Reflux system. A 10 gpm rotary pump was provided for refluxing light oil through a cooler and up to the top of the main condenser. A small amount of light oil was sent also into the vapor main to quench the hot coking vapors. The cooler consisted of one twin "G" fin section (130 sq. ft.). The oil passed through the annular or finned section while water was used as the cooling medium. Two tanks were used for the accumulation of the liquid product.

7. Pressure control system. The non-condensable gases were measured by an orifice and were exhausted by a 2 inch steam ejector. The ejector was used for the safe disposal of the gas. A gate valve was located between the orifice and ejector and was fitted with an extension handle. It served as a pressure control for the system.

8. Coke handling. A hand coke pusher was provided for removing the coke from the oven. A coke cart was constructed so as to fit under the lip of the oven to catch the coke as it fell. A hose was provided for quenching the coke with water.

9. Temperature measurements. Most of the temperature measurements were made with chromel-alumel thermocouples. Higher temperatures were measured by a Leeds and Northrup optical pyrometer.

B. Operation. A run consisted of a charging period, a de-gassing period, and a calcining period. The oven was first brought to a floor temperature of 1500°F. The oil charge was preheated to 550°F. by circulation through the preheater, the charging loop and back to the charge tank. The two oven doors were lowered into place and sealed with asbestos rope and fire clay.

After preparation of the condensing system, the charging period was started by opening the charging valves and regulating the feed line pressure. For about 5 to 10 minutes the coking vapors were allowed to pass out the open oven stack. When carbon black disappeared from the smoke issuing from the stack, the stack damper was shut, and circulation of reflux was started. The pressure on the system was regulated manually to get a small plume of smoke from a 1/4 inch hole in the cap of one of the oven peep-sights. Oil was charged at the desired rate until the entire charging period was completed.

At the close of the charge period the oven inlet valves were closed and the preheater shut off. De-gassing then took place for 0.5 to 1.5 hours. When the gas production was practically completed, the condensing system was shut down, and the oven stack damper was opened. The coke was then calcined at the desired temperature and the run terminated.

C. Sampling and testing. The coke pulled from the oven was water-quenched, dried, and weighed. A representative sample of the coke was tested by both the Cabot and Deep Rock laboratories for real density by a kerosene immersion method.

The liquid collected in the accumulating tanks was gaged. Spot and composite liquid samples were taken during each run. A.P.I. gravity measurements and A.S.T.M. distillations on liquid samples were made by the Deep Rock Laboratory. The A.S.T.M. distillation data were reported as: I.B.P. to 400°F. (gasoline), 400°F. to cracking (gas oil), and residue (recycle stock). Hempel distillations to obtain the 400°F. Hempel gasoline fraction were made on several selected runs.

Spot gas samples were taken in drums by water displacement. The exhaust temperature of the gas was about 90 to 100°F. The gas was noticeably wet. Complete Podbielniak analyses were made on four spot samples for each of five runs. Specific gravities were calculated from Podbielniak analyses.



## LABORATORY INSTALLATION

A. Equipment. The laboratory coking installation consisted of a coking unit, a condenser, a liquid product receiver, a gas meter, a gas receiver, and a gas sampling system.

The coking unit consisted of a Skidmore crucible (Fisher No. 8-190, 180 ml. capacity) set in a mild steel, open top cylindrical heating chamber. A No. 3 wide-form Coors porcelain crucible containing the residual oil charge was set in the Skidmore crucible. The Skidmore crucible was constructed of sheet iron, and its cover was constructed of cast iron. A yoke and thumb screw clamped the cover to the crucible. The factory-fabricated crucible, when fitted with an asbestos gasket, developed serious coking vapor leaks. The cover was then machined, but, again, when fitted with either asbestos or copper gaskets, the crucible developed serious leaks. A tight metal-to-metal seal was obtained by grinding the cover and crucible together with a mixture of glycerine and emery powder. This stopped vapor leaks for short periods of time. Warping of the crucible due to thermal expansion, however, soon caused bad leaks to recur. When the cover was spring loaded from the yoke with a spring  $1/2$  inch in diameter and 1 inch long, warping and serious vapor leakage were greatly reduced. A new spring was used for each run.

The vapor line consisted of a 2 inch length of  $1/4$  inch outside diameter and  $3/16$  inch inside diameter brass tubing brazed to a  $2\ 1/2$  inch length of copper tubing of similar outside and inside diameters. This vapor line connected the coking crucible to the condenser tube by means of a flare fitting which screwed to a reducer fitting ( $1/4$  inch tubing to  $1/2$  inch pipe).

The heating chamber consisted of a short section of a 3 inch standard pipe coupling with a circular section of  $1/4$  inch steel plate welded to the bottom to form a cylindrical crucible. The bottom of the chamber was covered with approximately  $3/8$  inch of fine sand. The chamber was insulated with

a 1/2 inch layer of asbestos cement.

A 20 gage chromel-alumel thermocouple extended through a 3/16 inch drilled opening in the side of the chamber just above the sand layer to within about 1/8 inch of the coking crucible. A Hoskins pyrometer was used to indicate the temperature. The thermocouple-pyrometer combination was calibrated as a unit against a standard thermocouple, itself previously calibrated at several fixed points.

The entire coking unit was surrounded by a thin gage, sheet steel, cylindrical section 6 5/8 inches in diameter and 9 inches high. The bottom end of this was completely open while the other end had a hole 3 1/2 inches in diameter which served as a chimney to vent the burner gases. Appropriate slots were cut in the side of the cylinder allowing it to be placed around the coking unit. With the shield, there was a material reduction in radiation and convection losses.

The heating chamber was supported by two ring stand supports and a refractory ring of the dimensions specified in the Conradson carbon residue test, A.S.T.M.-D 189-46.<sup>3</sup> Heat was supplied by three natural gas burners, two Fisher No. 3-900 and one Fisher No. 3-902, each having approximately 7,500 B.t.u./hr. output.

The condenser was of the conventional A.S.T.M. distillation type (D 158-41).<sup>3</sup> It was equipped with circulating cooling water and a steam heating coil constructed from copper tubing.

The liquid product receiver consisted of a Berzelius beaker (100 ml. capacity) connected to the condenser tube by means of a No. 10 rubber stopper. A thermometer extended through the stopper into the vapor space. Rubber tubing and glass fittings connected the liquid receiver to a precision wet test meter equipped with a thermometer and manometer indicating the system

pressure. The meter sealing liquid was distilled water saturated with gas from several preliminary runs. Rubber and glass tubing connected the wet test meter to two Florence flasks, each having a 6000 ml. capacity, which served as gas holders, the gas displacing a saturated solution of NaCl in water. A thermometer extended into one of the gas holders.

Regulation of the pressure on the system was accomplished by a glass and rubber tubing siphon, the discharge end of which was submerged in an overflow weir of variable elevation. This variable level overflow weir consisted simply of an Erlenmeyer suction flask (250 ml. capacity) connected by a clamp to a ring stand support. The Erlenmeyer flask could be raised or lowered as desired. A length of rubber tubing connected to the side outlet of the flask transferred the overflow salt solution to suitable receivers. The pressure was maintained at atmospheric to 0.2 inch water vacuum at the meter.

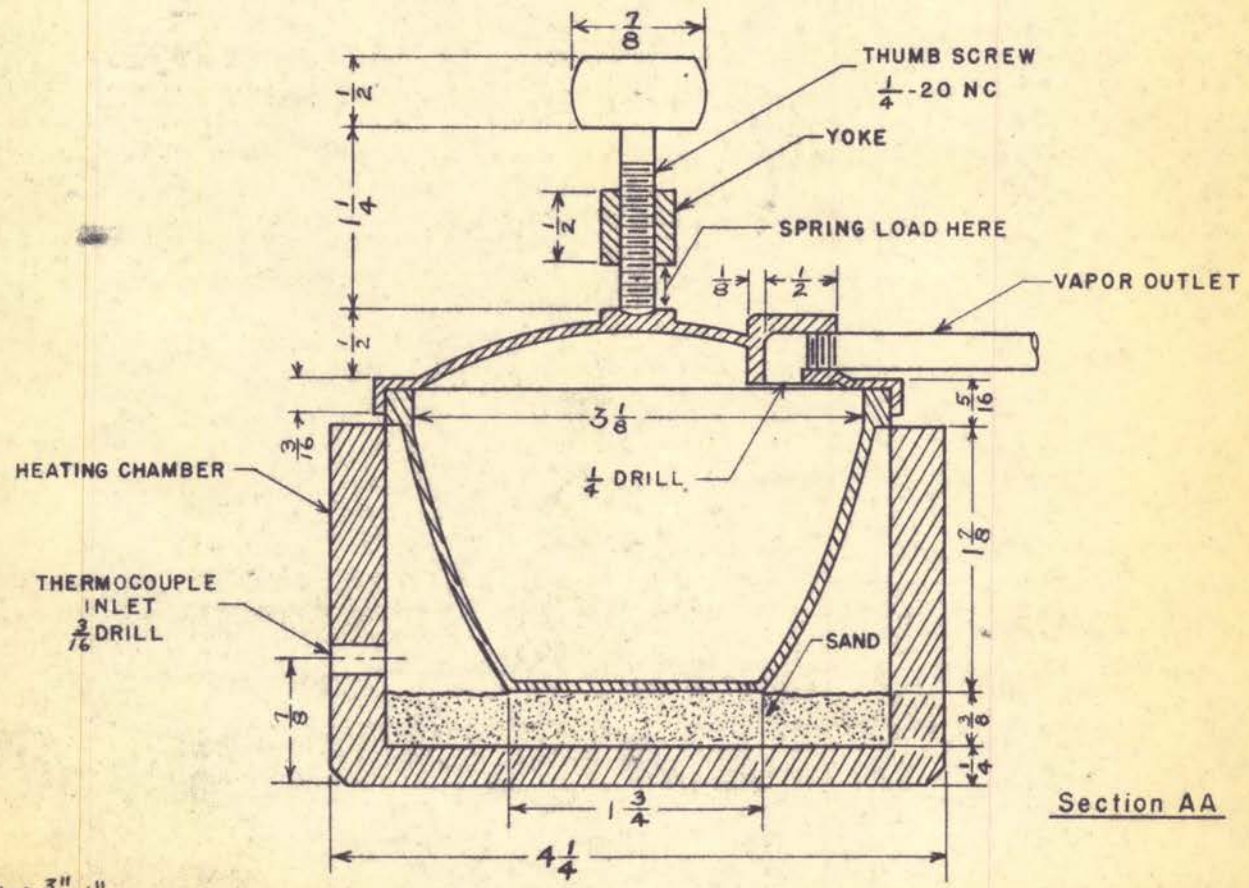
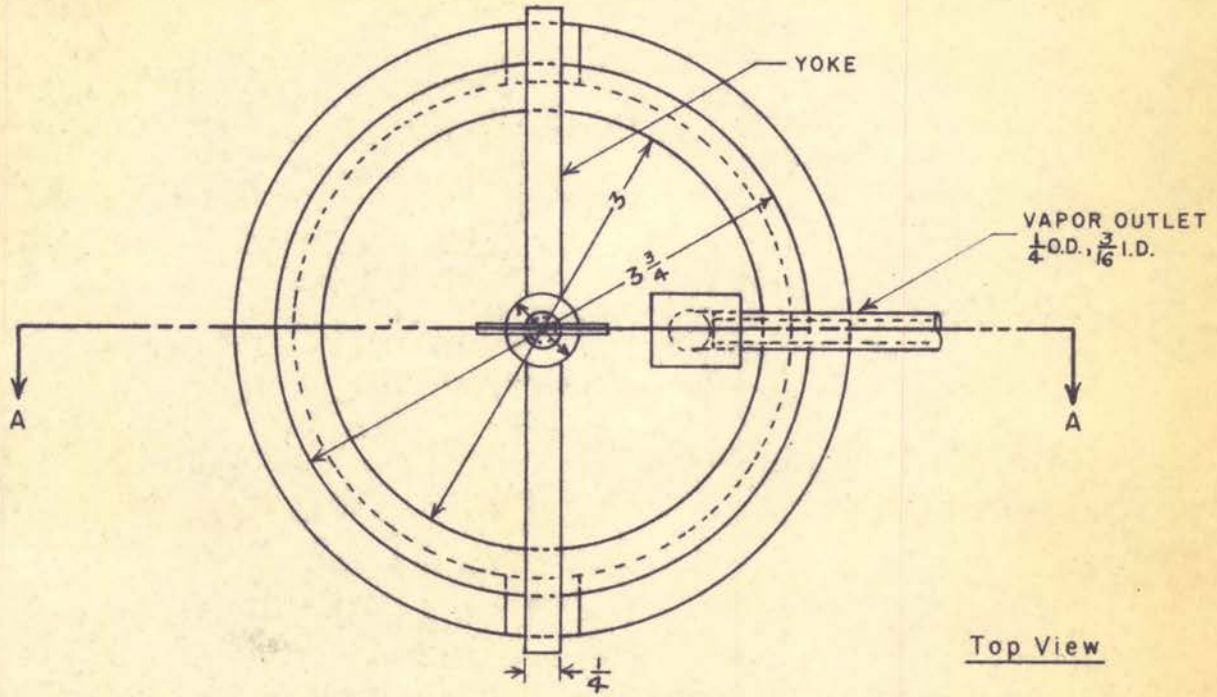
The gas gravity sampling apparatus consisted of a pyrex gas balloon (208.5 ml. capacity) which was connected to the gas holders by a silica gel drying U-tube, rubber tubing, and glass fittings. Evacuation of the gas balloon to about 1 mm. mercury absolute pressure prior to sampling was accomplished by a Hy-Vac pump.

Figure 2 shows the details of the coking unit. A flow diagram of the entire coking installation is given in Figure 3.

Figure 4a is a photograph of the coking unit assembled, while Figure 4b shows the coking unit disassembled. Figure 5 is a photograph of the entire laboratory coking installation. Figure 6 is a photograph of the coking unit (shielded), the condenser, and the liquid receiver.

B. Operation. Solids and liquids were weighed on an analytical balance to  $\pm 2.5$  mg. Gas volumes were read directly from the precision wet test meter.

Figure 2  
Details of Coking Unit



Scale:  $\frac{3}{4}'' = 1''$



Figure 3  
Flow Diagram of Laboratory  
Coking Installation

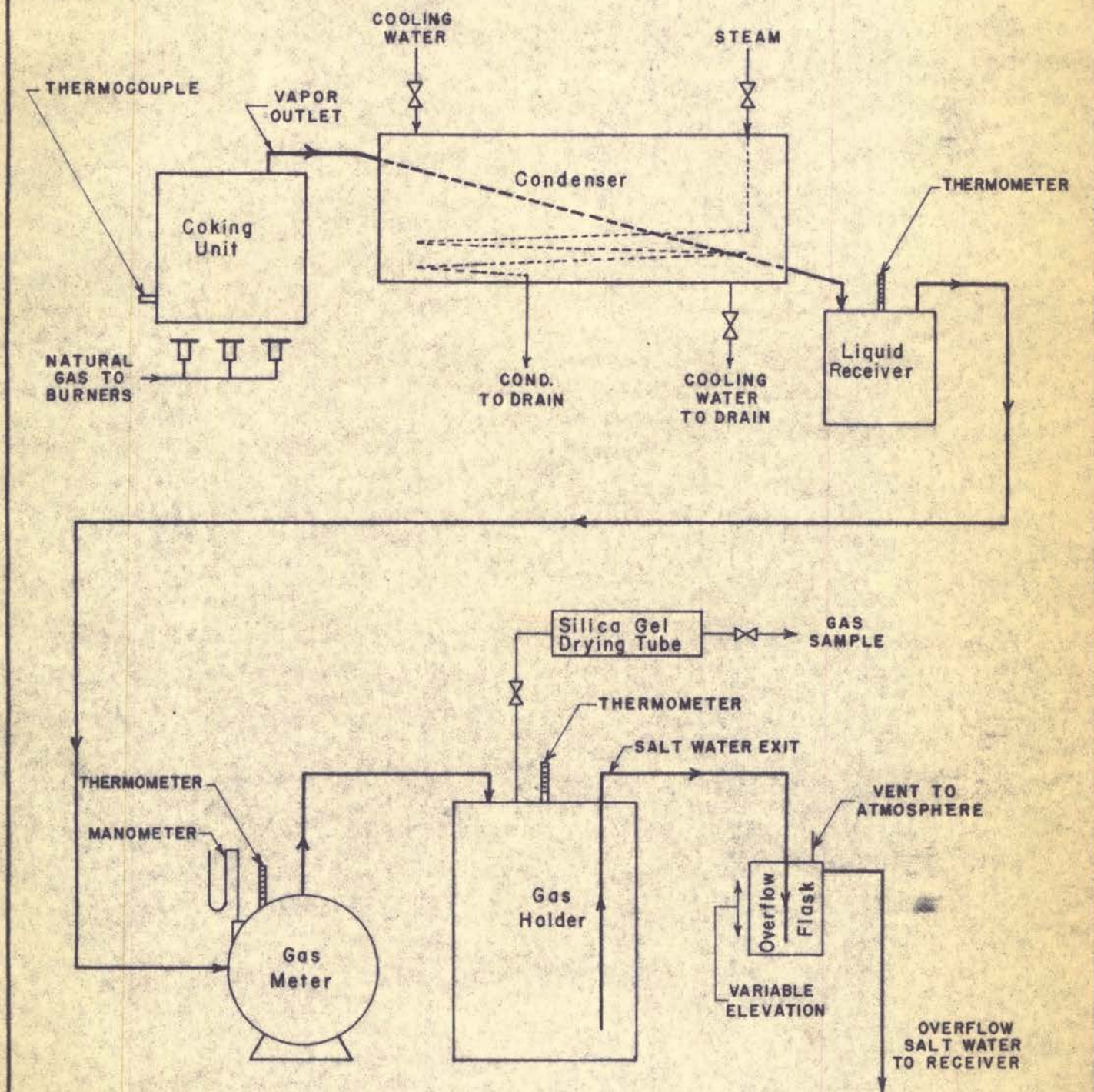




Figure 4a

Photograph of Coking Unit Assembled



Figure 4b

Photograph of Coking Unit Disassembled



Figure 5

Photograph of Laboratory Coking Installation

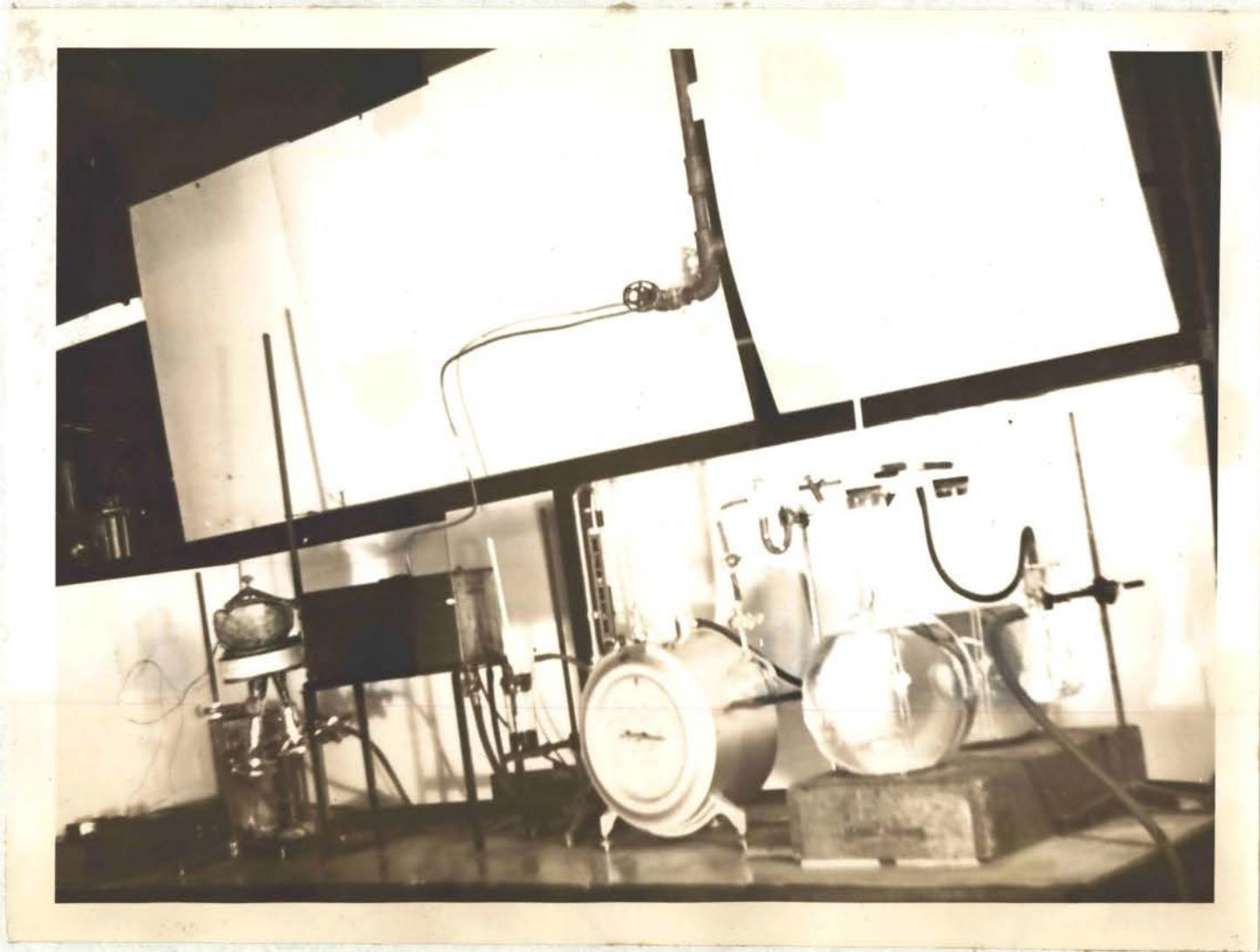
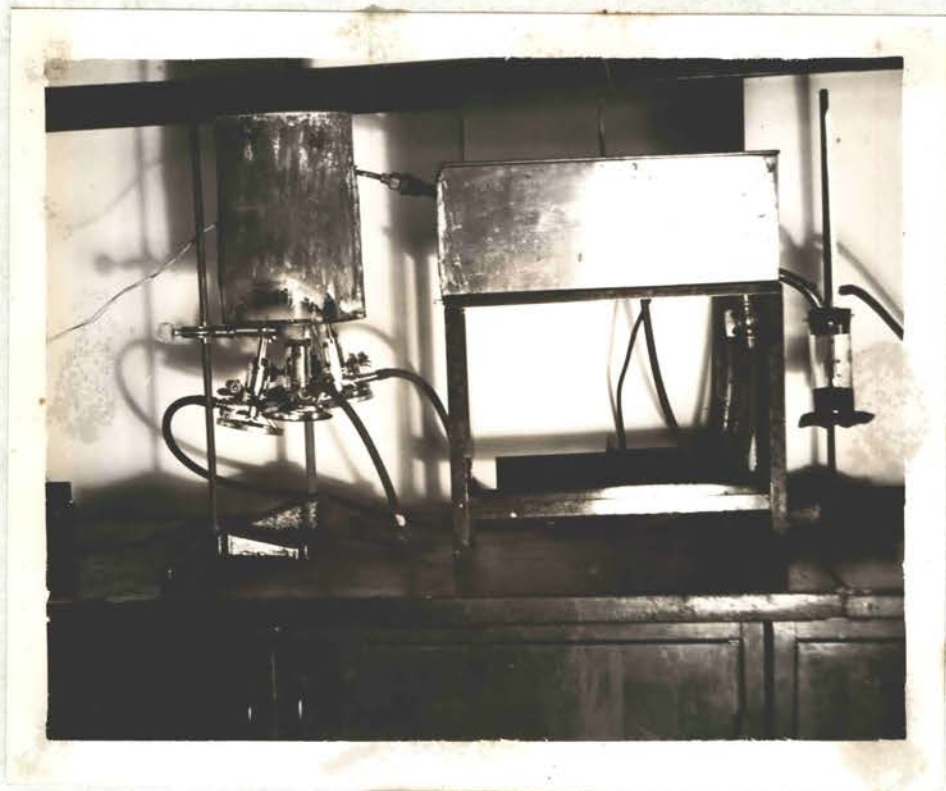


Figure 6

Photograph of Coking Unit (Shielded),  
Condenser, and Liquid Receiver





A standard type of run was developed from the results of the preliminary runs (1-11). It consisted of a preheating period, a coking period, and a blasting period.

A 50-gram sample of the residual oil was weighed in a No. 3 wide-form porcelain crucible, which was then placed in the Skidmore coking crucible. The coking crucible cover was fitted in place and spring loaded. The vapor line was connected to the condenser tube. The Fisher gas burners were lighted and the coking crucible preheated. Meanwhile, water was circulated through the condenser, the gas holders filled with salt water, and the pressure control siphon system manipulated to give a pressure within the range of atmospheric to 0.2 inch water vacuum at the gas meter.

The appearance of the first drop of liquid condensate in the liquid receiver signified the beginning of the coking period. The pressure was closely maintained as the liquid and gas make proceeded. The gas burners were so regulated as to allow the proper coking time and temperature (see below).

When the liquid make was practically completed, the blasting period was started and the coke blasted to the desired maximum temperature. This temperature was then maintained until the gas make was completed, at which time the gas burners were shut off.

The condenser water circulation was shut off, and the steam heating coil was turned on. The condenser water was allowed to boil for approximately 10 minutes to insure that viscous liquid drained completely from the condenser tube.

The coke and liquid were weighed and stored in sealed glass flasks. A gas sample was taken and weighed to determine its specific gravity.

The standard runs for the vis-breaker tar and Deep Rock thermal tar consisted of 1/2 hour preheating to 1000°F., 1/2 hour coking at

1000 to 1200°F., and 1 hour blasting.

Due to frothing, the Deep Rock virgin asphalt was coked directly in the Skidmore crucible. A 50-gram sample was used. One run was made using a 20-gram sample in a porcelain crucible. No significant difference in product distribution was noted. The standard run for virgin asphalt consisted of 1/3 hour preheating to 900°F., 1/2 hour coking at 900 to 880°F., 1/2 hour coking at 900 to 1200°F., and 1 hour blasting.

All runs were made with maximum coking temperatures of 1200°F., 1350°F., and 1520 to 1550°F.

### C. Analytical Procedure.

1. Feed stocks. The Conradson carbon residue value was determined for each of the feed stocks as described in A.S.T.M. -D 189-46.<sup>3</sup>

2. Coke. The real density of the coke was determined by a Cabot kerosene immersion method. The coke sample was crushed to pass a 100 mesh screen, dried in a ventilated oven for at least 1 hour at 105°C. and cooled in an ordinary desiccator.

Kerosene of known specific gravity at a definite temperature is required for this test. A 25 ml. pycnometer was weighed, filled with distilled water and weighed, dried and then filled with kerosene and weighed. All operations were carried out at 25°C. The specific gravity of the kerosene was calculated by the following equation:

$$\text{Specific gravity of kerosene} = \frac{e - a}{b - a}$$

where a = weight of empty pycnometer.

b = weight of pycnometer and distilled water.

e = weight of pycnometer and kerosene.

For the coke density determination, about 2 grams of the pulverized coke was weighed in the pycnometer. The pycnometer was then about half-filled with the standardized kerosene. The pycnometer was placed in a pyrex vacuum desiccator for 1 hour under a vacuum of about 715 mm. of mercury

relative to about 740 mm. of mercury barometer reading. When air bubbles were no longer apparent, the vacuum was released. The pycnometer was filled with kerosene and cooled slightly below 25°C. The thermometer was inserted. The pycnometer was warmed slowly to 25°C., capped and weighed. The real density was calculated by the following equation:

$$\text{Real density} = \frac{c - a}{b - a - \frac{d - c}{\text{sp.gr. of kerosene}}} \quad (2)$$

where  $c$  = weight of pycnometer and coke.

$d$  = weight of pycnometer, coke, and kerosene.

3. Liquid. A.P.I. gravity measurements were made as described in A.S.T.M.-D 287-39.<sup>3</sup> A.S.T.M. distillations were made as described in A.S.T.M.-D 158-41<sup>3</sup> with one modification: 50-ml. samples were used instead of 200-ml. samples. The A.S.T.M. distillation data were divided into three portions, I.B.P. to 400°F., 400°F. to cracking, and residue. Complete distillation data are presented in Table III.

4. Gas. The gas was collected at approximately 70 to 75°F. and appeared to be very dry. The specific gravity was determined by a gas balloon evacuation method as follows:

A calibrated glass balloon of known capacity (208.5 ml.) equipped with a capillary tube and ground glass stopcock was evacuated to about 1 mm. mercury absolute pressure by a Hy-Vac air pump and weighed. The gas sampling system and silica gel drying tube were purged by allowing the gas balloon to fill with gas from the gas holders. The gas balloon was again evacuated and filled with a fresh gas sample. The barometric pressure and gas holder temperature were recorded. The filled gas balloon was weighed and the specific gravity calculated by equations (3) to (8). (See Appendix).

## RESULTS

A. Pilot Plant. Forty-eight pilot plant runs yielding material balances, product qualities, and operational data were made. Table I presents the best process data available from the CDR pilot plant while it was operating near maximum capacity to produce maximum liquid recovery and high density coke from vis-breaker tar, thermal tar, and virgin asphalt.

B. Laboratory. Eighteen standard laboratory runs were made, six on each of the three feed stocks. Duplicate runs were made at each of three maximum coking temperatures, and the liquid and coke samples were mixed for tests. Material balances, product qualities, and operational data of these standard runs are presented in Table II. Table III gives the complete A.S.T.M. distillation data of the liquid products.

Preliminary runs were made to secure operating characteristics and to permit the setting up of a standard coking procedure. These were runs 1-11, 13, and 15 on vis-breaker tar, runs 20-21 on thermal tar, and runs 28-31 on virgin asphalt. The results of these preliminary runs are not reported.

The product distributions were converted to a loss-free basis by a method described in the Appendix. A sample laboratory run sheet and sample calculations are also given in the Appendix.

Typical A.S.T.M. distillation curves of laboratory and pilot plant liquid products from all three charge stocks are given in Figures 7, 8, and 9.

Laboratory coke yields from all three stocks are shown as a function of maximum coking temperature in Figure 10. Similar yield plots for gas and liquid are given in Figures 11 and 12.

The real density of the coke produced in the laboratory as a function of maximum coking temperature is shown in Figure 13.



## DISCUSSION

A. Pilot Plant. High grade metallurgical coke was made consistently in the pilot plant oven. The coke yield for a given feed stock was found to be approximately equal to the Conradson carbon residue value of the stock.

Carbon black formation in previous Knowles coking units had been a serious problem. However, by operating the pilot plant oven at a proper initial floor temperature and by maintaining a positive pressure on the oven to prevent air leakage into the oven, this problem was eliminated. At an initial oven floor temperature of 1500°F. or lower, the formation of carbon black at the start of a run necessitated only a 5 to 10 minute purging period. Carbon black formation was quite serious with initial floor temperatures above 1500°F.; at 1800°F., the system was rendered inoperable.

The most serious operational difficulty encountered in the pilot plant operation was that of oven door leaks. These leaks accounted for some of the high losses.

Some trouble was caused by tar frothing into the vapor line, but proper feed charging procedure remedied this. The only effective pilot plant controls were the initial oven floor temperature and the rate of oil feed to the oven. Variation of heat output of the oven gas burners had little effect on the coking process due to the high heat content of the oven refractory.

Table I indicated losses of 4 to 7% of the charge for the pilot plant process. These losses were probably due mainly to door leaks, floor leaks and vapor purging at the start of a run, and vapor losses during calcination.

B. Laboratory. The highest temperature attained in the laboratory coking unit was 1550°F. The coking temperature was controlled effectively by regulation of the gas and air ports of the burners. Higher temperatures in the coking unit would have been desirable during the blasting operation, as high density coke must be produced at temperatures higher than 1550°F.

However, the coking unit, as designed, was not suited mechanically for maximum temperatures very much higher than 1500°F. At 1500°F., the iron coking crucible scaled badly due to oxidation. Warping of the crucible rim due to thermal strains was also evident. This had a tendency to cause serious vapor leaks. Vapor leaks were stopped quite effectively, however, by machining and grinding the crucible and crucible cover to a tight metal-to-metal seal and by spring loading of the cover from the yoke, as described previously. Asbestos gaskets (plain or impregnated with water glass) and copper gaskets were not effective in preventing vapor leaks.

The vapor line withstood the operating conditions very well. However, a vapor line of larger cross-sectional area would have been more desirable. During the first portion of the actual coking period, the volume of coking vapor produced was extremely large. The small vapor line definitely caused a fairly high back pressure to develop in the coking crucible. This pressure had a tendency to appreciably increase vapor leaks during the initial coking period. Coking or polymerization of coking vapors in the vapor line or condenser tube was never observed.

While operating with vis-breaker tar and thermal tar, trouble was not encountered with frothing of the tar into the vapor line and condenser tube, regardless of the severity of the cracking conditions. However, when virgin asphalt was being coked, the problem of frothing and subsequent plugging of the vapor line was serious. Evidently, this frothing was caused by the more rapid cracking of virgin asphalt, as this stock is very susceptible to thermal cracking, having never been previously subjected to any cracking conditions. The rapidly evolved coking vapor probably caused the liquid asphalt to become violently agitated. This caused froth to be generated. By carrying out the major coking portion of the run at a lower temperature (880°F.-900°F.), this problem was eliminated. Also, this asphalt was coked

in the iron Skidmore crucible to allow more volume. When the liquid production was practically completed, it was safe to begin raising the coking temperature gradually to 1200°F. and then to blast to the desired maximum temperature.

The plugging of the vapor line due to tar frothing can be very dangerous, since the heat content of the heating chamber can cause the coking to continue for a few minutes after the burners are shut off. However, the spring-loaded yoke and crucible cover will allow the coking vapors to be immediately vented to the air and thus prevent high pressures from building up in the coking crucible, although a slight fire hazard does thereby exist. Due to the obvious hazards of mechanical failure caused by excessive pressure, coking crucible lids which are fastened solidly with threaded connections or bolts are not recommended.

The conventional A.S.T.M. distillation condenser equipped with the steam heating coil proved very satisfactory. All liquid drained completely into the liquid receiver. The non-condensable gas from the liquid receiver appeared to be very dry, as drops of condensate were never observed in any portion of the gas recovery system.

The methods of gas metering, gas accumulating, and gas sampling were satisfactory. Precautions were taken to see that air did not contaminate the gas meter or gas sample drying tube between runs.

Losses of 0.1 to 1.8% of charge were encountered in the standard runs. The losses were in most cases due to vapor leaks from the coking crucible. These losses are represented as liquid and gas, for the coke was weighed directly in the crucible in which it was produced, reducing the possibility of loss at this source. The liquid was weighed directly in the liquid receiver.

The coking crucible had sufficient capacity for only a 50-gram charge. This resulted in the production of about 30 to 35 grams of liquid, depending

upon the charge stock. In order to analyze the liquid, it was necessary to combine the liquid from two runs made under the same conditions. A larger coking crucible permitting the use of larger charges would have been desirable. The liquid and gas recovery system had sufficient capacity for at least a 100-gram charge.

C. Correlation. A rough comparison of the overall product distributions between the pilot plant and laboratory runs can be made by direct inspection. The results correspond reasonably well. A more refined and valid comparison, however, results when the laboratory yield data (obtained in the range of 1200-1550°F.) are extrapolated to the temperatures at which the pilot plant operations were conducted. When this is done the following percentage points deviations are obtained:

	% Yield in Pilot Plant minus % Yield in Laboratory (Extrapolated)		
<u>Stock</u>	<u>Coke</u>	<u>Liquid</u>	<u>Gas</u>
Vis-breaker tar	- 0.2%	-1.6%	+1.8%
Thermal tar	- 1.5	±0.0	+ 2.7
Virgin asphalt	+ 1.8	±0.0	- 1.2
Average absolute deviation	±1.2	±0.5	±1.9

This correspondence represents quite a satisfactory correlation, particularly when it is noted that the thermal tar and virgin asphalt were not identical for the two investigations, as explained previously.

When the laboratory coke density data are extrapolated (by straight lines) to the temperature at which the pilot plant coke was calcined, the following deviations in real density were obtained:



<u>Stock</u>	<u>Pilot Plant Coke Density minus Laboratory Coke Density (Extrapolated)</u>
Vis-breaker tar	+0.04
Thermal tar	-0.01
Virgin asphalt	<u>+0.05</u>
Average absolute deviation	<u>± 0.03</u>

This, again, shows a remarkably good correlation.

A study of Figures 7 and 8 indicates a good comparison between the distillation curves for the liquid produced by the pilot plant and laboratory from vis-breaker tar and thermal tar. However, Figure 9 indicates a marked difference in the case of the virgin asphalt. The laboratory coking unit produced a much lower boiling and lower specific gravity liquid. This may be due in part to lower laboratory condensing temperature and the drier laboratory gas. A small amount of light liquid was probably exhausted in the pilot plant gas. It is quite possible, however, that a good part of the discrepancy is due to differences in the charge stock.

The specific gravities of the laboratory gas were slightly lower than those of the corresponding pilot plant gas. This is probably due to the drier laboratory gas.

In the laboratory investigation, the maximum coking temperature of the run did not noticeably affect the quality of the liquid. This is explained by the fact that the liquid make was nearly completed before 1200°F. As the temperature was increased past 1200°F., the additional product was mostly gas, formed at the expense of coke.

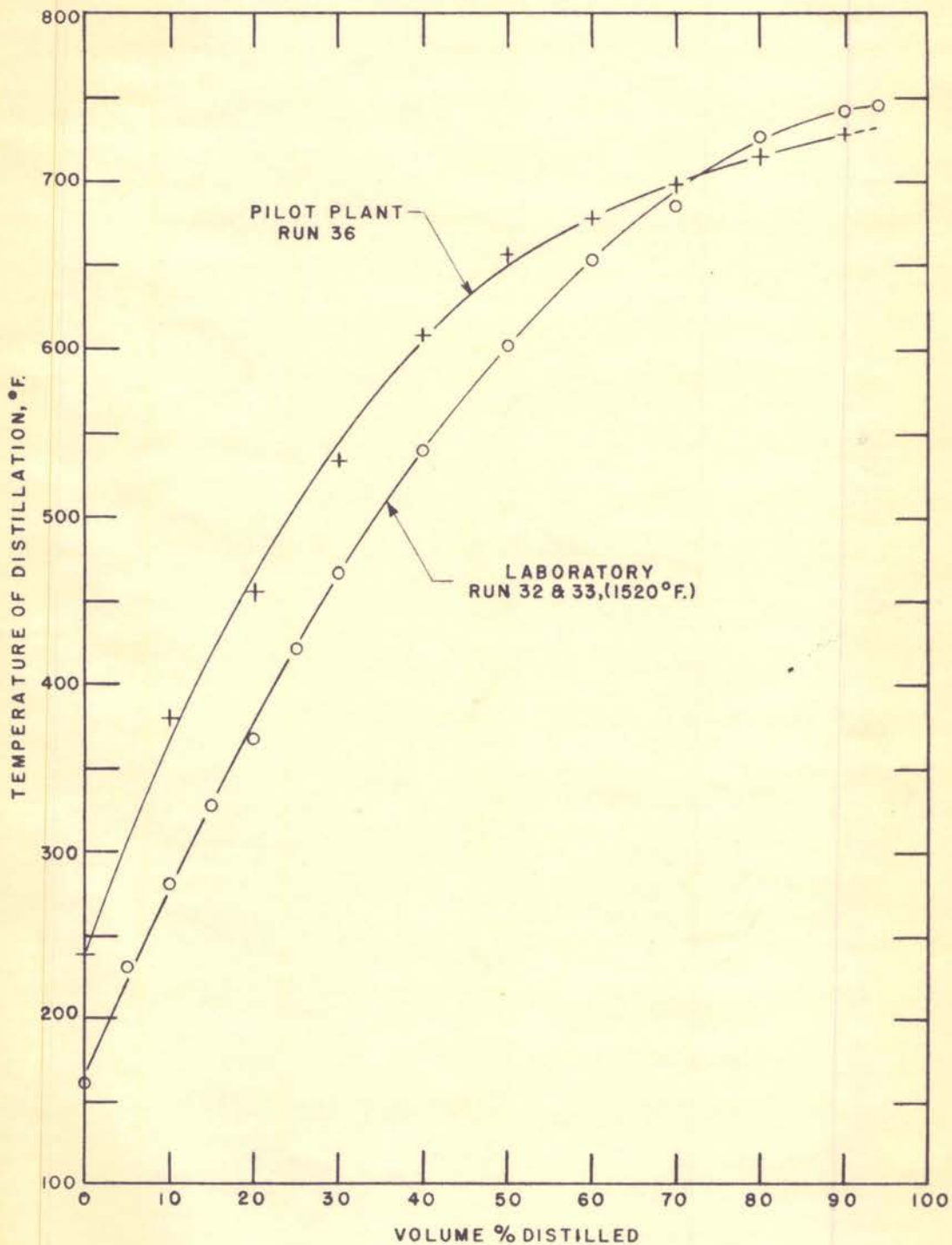
Maximum coking temperature had no appreciable effect on the gravity of the gas produced in the laboratory. The highest temperatures produced slightly lighter gas due to more severe cracking.

Laboratory coke yields decreased as the blasting temperature increased. Conradson carbon residue values compared reasonably close to coke yields at 1520 to 1550°F., the greatest deviation occurring in the case of virgin

asphalt. This may be explained by the fact that the Conradson carbon test was difficult to run on the virgin asphalt due to the standard rate at which the temperature must be raised in the test. This resulted in frothing and, therefore, a lower Conradson carbon value.

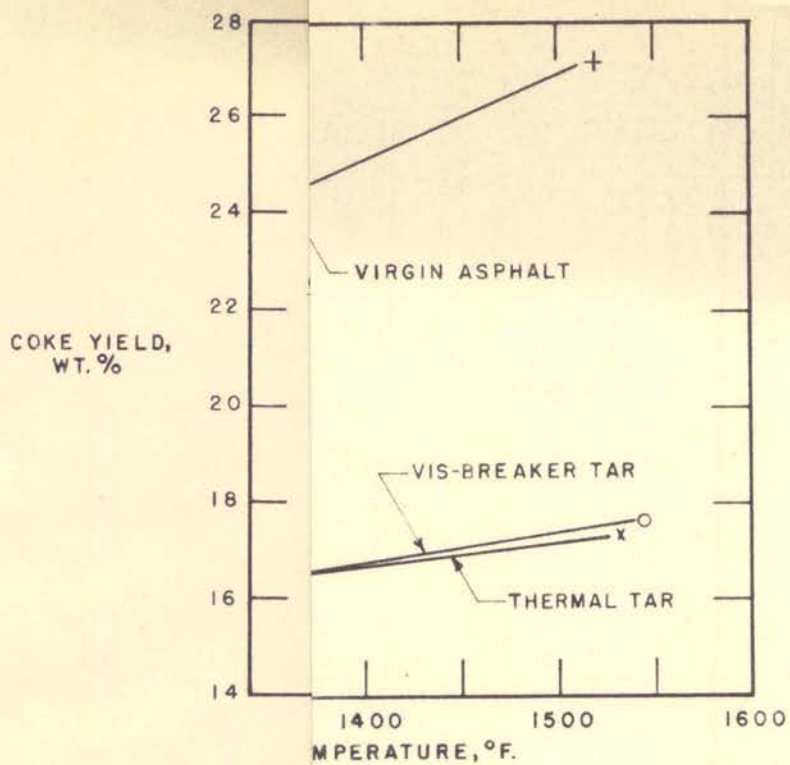
Liquid yields decreased slightly as the maximum coking temperature increased. Gas yields increased noticeably as the temperature increased.

Figure 9  
Typical Laboratory and Pilot Plant A.S.T.M. Distillation  
Curves of Liquid Produced from Virgin Asphalt



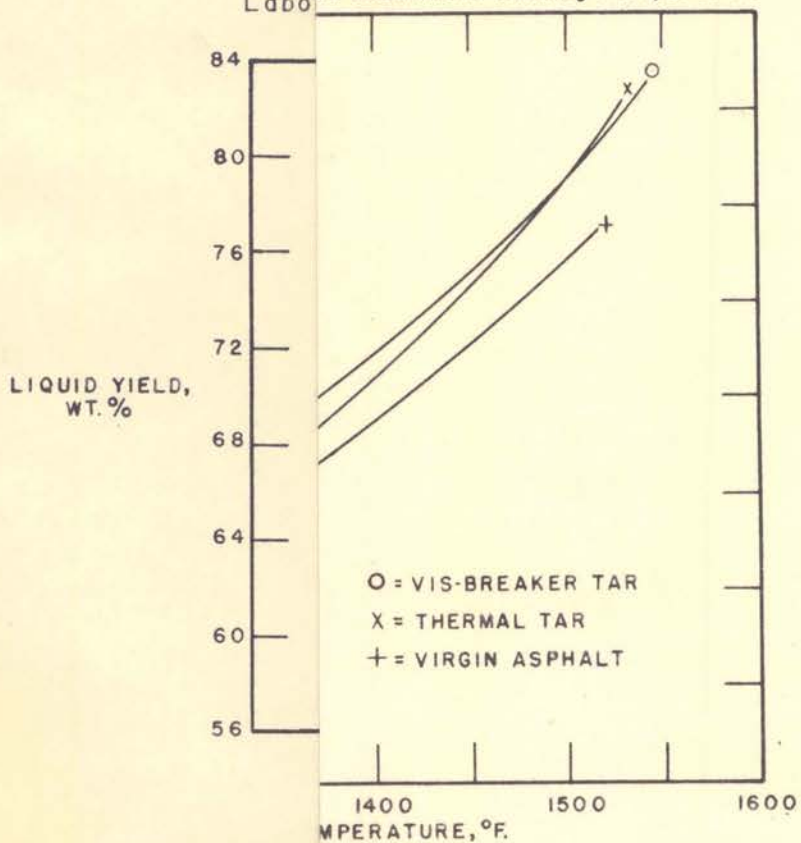
re 11

Lab Maximum Coking Temperature



re 13

Lab Maximum Coking Temperature





## SUMMARY

A laboratory-pilot plant correlative study of the coking of vis-breaker tar, thermal tar, and virgin asphalt has been made. The pilot plant results were obtained at the Cabot-Deep Rock pilot plant operated at Cushing, Oklahoma.

A Knowles oil-coking oven of 17 sq. ft. floor area was used in the pilot plant operation. The inherent operational difficulties involved with carbon black formation and tar frothing were eliminated by operating with a proper oil feed charging rate and an initial oven floor temperature of about 1500°F. Serious oven door leaks hampered operation at times. High grade metallurgical coke was made consistently.

A laboratory coking unit, consisting of a crucible set in an insulated heating chamber, was developed for temperatures of operation up to around 1550°F. Coking temperature was controlled by regulation of three Fisher gas burners. A good metal-to-metal seal between the cover and crucible was found to be an effective method of decreasing vapor leaks from the coking crucible. Spring loading of the crucible cover against the crucible was also found important. Coking or polymerization in the vapor line was never observed. However, virgin asphalt frothed badly if coked at too high a temperature. By coking under temperature conditions of 880 to 900°F., serious frothing was eliminated in this case.

Straight line extrapolation of the laboratory yields at various temperatures to the maximum pilot plant coking temperature for each of the three feed stocks resulted in quite satisfactory correlations, with average absolute deviations varying from  $\pm 0.5$  to  $\pm 1.9$  percentage units. Extrapolation of laboratory coke density data to the maximum pilot plant coking temperature resulted in very good comparisons, with an average absolute deviation of  $\pm 0.03$  g/cc.

Laboratory operation was carried out with much lower losses than was pilot plant operation.

Liquid quality comparison between pilot plant and laboratory products was good except for the case of virgin asphalt. Here the laboratory liquid was lower boiling than the corresponding pilot plant liquid. Differences in the stock may account for this.

The maximum temperatures to which the coking was carried out in the laboratory varied from 1200 to 1550°F. Coke yield decreased and coke density increased as maximum coking temperature increased. There was a corresponding slight decrease in liquid yield, but liquid quality was practically unchanged. Gas yield increased noticeably as the temperature increased.

## RECOMMENDATIONS

Recommendations for further work on heavy residual oil coking in the laboratory are as follows:

1. The development of a more satisfactory coking crucible with greater charge capacity, smaller leakage tendencies, and a greater range of operating temperatures.
2. The investigation of the relationship between the volatile content of coke and its real density.

## BIBLIOGRAPHY

1. Anderson, M. K., Hall, A. L., and Jackson, J. B., Jr., "Cabot-Deep Rock (CDR) Report No. 6," Deep Rock Oil Corporation, Cushing, Oklahoma, 1949. (Portions of this report confidential).
2. Anonymous, *Petroleum Refiner*, 16, 53 (1937).
3. "A.S.T.M. Standards on Petroleum Products and Lubricants," pp. 117, 128, 201, American Society for Testing Materials, Philadelphia, 1948.
4. Berry, A. G. V. and Edgeworth-Johnstone, R., *Ind. Eng. Chem.*, 36, 1140 (1944)
5. *Ibid*, 37, 551 (1945)
6. Diwocky, R. J., *Oil & Gas J.*, 37, 131 (1933).
7. Foster, A. L., *Nat. Petroleum News*, 25, 26 (1933).
8. Jones, D. H., *Oil & Gas J.*, 34, 113 (1935).
9. Perry, J. H., "Chemical Engineers' Handbook," 3rd Edition, pp. 149, 411, McGraw-Hill Book Company, New York, 1950.
10. Watkins, J. C., *Chem. Met. Eng.*, 44, 153 (1937)
11. Ziegenhain, W. T., *Oil & Gas J.*, 30, 16 (1931).



**APPENDIX**

TABLE I

## Summary of Average Pilot Plant Results

Basic Run	48	45	43
Comparison Runs	34,35,36	46,47	42
<u>Feed Stock</u>	<u>Virgin Asphalt</u>	<u>Vis-breaker Tar</u>	<u>Thermal Tar</u>
Gravity, °API	8.4	8.6	8.6-9.2
Conradson Carbon, wt.%	18.5-21.9	15.3	13.5-14.0
Sulphur, wt.%	1.13	0.96	0.88
Ash, wt.%	0.075-0.08	0.03	0.38-0.49
Viscosity, SUS @ 210°F		150-155	180-240
Viscosity, SFS @ 250°F	900		
Characterization factor		10.95	11.05
<u>Cycle</u>			
Charge Period, hrs.	4.0	4.0	4.0
De-gas Period, hrs.	1.2	0.6	0.9
Calcining Period, hrs.	2.0	1.6	2.0
<u>Operating Conditions</u>			
<u>Temperatures, °F</u>			
Oven Floor, initial	1500	1500	1500
Feed Preheat	560	550	560
Coke	875-up	850-up	800-up
Vapor, average	830	870	810
Total Charge, lbs.	1910	1910	1890
" " gals.	227	227	224
<u>Material Balance</u>			
Gas, wt.% on charge	19	8	9
Liquid " "	53	72	73
Coke " "	21	14	14
Loss " "	7	6	4
<u>Product Inspections</u>			
<u>Liquid</u>			
Gravity, °API	26.4	15	16.5
Vol.% @400°F, Hempel	19	7.5	6.5
Vol.% @400°F ) by	11	3	3
% 400°F-cracking )ASTM	82	86	87
% Residue )Dist.	7	11	10
<u>Gas</u>			
Average Mol. Wt.	26.0	24.0	24.0

TABLE II

## Summary of Laboratory Run Data

Run No.	12	19	17	18	14	16	22	23	26	27
<u>Feed Stock</u>	←----- Vis-breaker Tar -----→						←----- Thermal Tar -----→			
<u>Temperatures, °F</u>										
Initial Coking	980	990	1020	1040	1010	990	1010	1020	1020	1020
Maximum Coking	1540	1550	1350	1350	1200	1200	1535	1535	1350	1350
Condensate Receiver	84	79	79	82	76	83	79	76	74	78
<u>Product Distribution</u>										
Coke, Wt.% of Charge	15.2	15.0	15.5	15.4	15.8	16.0	16.4	16.4	16.8	16.7
Liquid, " " " "	76.6	77.2	77.6	77.5	78.3	78.4	76.0	76.2	76.3	76.4
Gas, " " " "	6.4	7.6	5.8	5.6	4.5	5.3	7.3	7.2	6.8	6.7
Loss, " " " "	1.8	0.2	1.1	1.5	1.4	0.3	0.3	0.2	0.1	0.2
<u>Product Distribution on Loss-Free Basis</u>										
Coke, Wt.% of Charge	15.2	15.0	15.5	15.4	15.8	16.0	16.4	16.4	16.8	16.7
Liquid, " " " "	77.2	77.3	78.0	78.0	78.8	78.5	76.1	76.3	76.3	76.5
Gas, " " " "	7.6	7.7	6.5	6.6	5.4	5.5	7.5	7.3	6.9	6.8
<u>Product Inspections</u>										
Coke Density, g/cc	1.72		1.53		1.44		1.71		1.51	
Liquid										
Gravity, °A.P.I.	16.5		16.2		16.1		17.0		16.9	
A.S.T.M. Distillation										
Vol.%, IBP-400°F	7		6		6		7		7	
Vol.%, 400°F-Cracking	81		82		81		78		77	
Vol.%, Residue	12		12		13		15		16	
<u>Gas</u>										
Specific Gravity	0.72	0.82	0.82	0.80	0.74	0.85	0.70	0.74	0.84	0.81
Average Molecular Wt.	20.8	23.8	23.8	23.3	21.4	24.6	20.4	21.6	24.2	23.5

TABLE II (Cont.)

Summary of Laboratory Run Data								
Run No.	24	25	32	33	37	38	35	36
<u>Feed Stock</u>	Thermal Tar		←———— Virgin Asphalt —————→					
<u>Temperatures, °F</u>								
Initial Coking	1010	1020	905	880	920	920	900	920
Maximum Coking	1200	1200	1525	1520	1350	1350	1200	1200
Condensate Receiver	79	76	77	78	81	84	78	76
<u>Product Distribution</u>								
Coke, Wt.% of Charge	16.9	17.1	23.8	23.5	24.9	25.1	26.6	26.7
Liquid, " " " "	77.3	77.4	58.5	58.7	60.4	60.2	61.4	61.6
Gas, " " " "	4.9	5.0	16.0	16.2	14.4	13.9	11.0	11.2
Loss, " " " "	0.9	0.5	1.7	1.6	0.3	0.8	1.0	0.5
<u>Product Distribution on Loss-Free Basis</u>								
Coke, Wt.% of Charge	16.9	17.1	23.8	23.8	24.9	25.1	26.6	26.7
Liquid, " " " "	77.6	77.6	59.1	59.2	60.5	60.5	61.7	61.8
Gas, " " " "	5.5	5.3	17.1	17.3	14.6	14.4	11.7	11.5
<u>Product Inspections</u>								
Coke Density, g/cc	1.41		1.64		1.50		1.40	
Liquid								
Gravity, °A.P.I.	16.7		33.0		32.9		33.1	
A.S.T.M. Distillation								
Vol.%, IBP-400°F	7		23		22		22	
Vol.%, 400°F-Cracking	77		71		70		71	
Vol.%, Residue	16		6		8		7	
<u>Gas</u>								
Specific Gravity	0.74	0.78	0.82	0.83	0.84	0.84	0.83	0.84
Average Molecular Wt.	21.4	22.7	23.8	23.9	24.4	24.4	24.2	24.4



TABLE III

ASTM Distillations of Liquid Products  
of All Standard Laboratory Runs

(Temperature, °F. vs. Vol. % Distilled)

Lab Run No.	12 & 19	14 & 16	17 & 18	22 & 23	24 & 25	26 & 27	32 & 33	35 & 36	37 & 38
Vol. % Distilled									
I.B.P.	235	240	240	228	235	226	160	169	164
5	366	375	370	346	353	349	232	235	232
10	465	470	466	468	477	468	281	282	282
15	534	530	540	543	554	538	328	336	336
20	568	561	572	596	590	585	368	381	379
25	605	602	613	624	615	612	422	442	440
30	618	633	625	647	645	634	468	480	478
35	630	650	644	668	662	650	497	518	523
40	652	668	662	683	675	670	540	550	554
45	665	684	686	696	682	690	575	581	588
50	684	695	698	705	700	702	604	606	618
55	697	703	706	715	712	711	628	635	640
60	709	709	712	723	718	718	654	654	659
65	716	718	714	730	722	724	670	668	674
70	726	735	718	736	732	730	686	690	695
75	732	743	722	741	741	735	712	715	713
80	737	750	726	743	750	738	727	724	718
85	742	754	730	745			736	742	738
90	744						743	752	744

METHOD FOR ESTIMATING PRODUCT DISTRIBUTION ON  
LOSS-FREE BASIS IN LABORATORY COKING INSTALLATION

The losses in the laboratory coking unit as finally developed were quite low. They varied from 0.1 to 1.8% by weight of the charge. Since the coke was weighed directly in the crucible in which it was produced, it was assumed that no coke was lost and that the loss figures represented the vapor leaks from the coking crucible.

In order to apportion these losses between liquid and gas make, the results of pairs of standard runs, each pair made under different temperature conditions and with each run of a pair having different losses, were evaluated. The following is an example, using vis-breaker tar:

Temp. Run No.	1200°F.		1350°F.		1540-1550°F.	
	14	16	17	18	12	19
Coke, %	15.8	16.0	15.5	15.4	15.2	15.0
Liquid, %	78.3	78.4	77.6	77.5	76.6	77.2
Gas, %	4.5	5.3	5.8	5.6	6.4	7.6
Loss, %	1.4	0.3	1.1	1.5	1.8	0.2
$\Delta$ Loss	-1.1		+0.4		-1.6	
$\Delta$ Gas	+0.8		-0.2		+1.2	
$\Delta$ Liquid	+0.1		-0.1		+0.6	
$\Delta$ Gas/ $\Delta$ Loss	0.73		0.50		0.75	
$\Delta$ Liquid/ $\Delta$ Loss	0.09		0.25		0.38	

$$\text{Average Gas Loss} = \frac{0.73 + 0.50 + 0.75}{3} \times 100 = 66\% \text{ of } \Delta \text{ Loss}$$

$$\text{Average Liquid Loss} = \frac{0.09 + 0.25 + 0.38}{3} \times 100 = 24\% \text{ of } \Delta \text{ Loss}$$

Assuming that the fractions of the total loss represented by the individual liquid and gas losses are constant and independent of the loss, two-thirds of the total loss was assigned to gas and one-third to liquid.

When the adjustments are made as described above, the loss-free data given in Table II are obtained. The degree of reproducibility of the adjusted results is quite good. This lends some support to the validity of the adjustment technique.

EQUATIONS FOR THE CALCULATION OF THE SPECIFIC GRAVITY AND  
THE TOTAL WEIGHT OF GAS PRODUCED IN THE LABORATORY COOKING INSTALLATION

The perfect gas law was assumed to apply. Assuming the wet test meter to saturate the gas with water vapor, the metered volume was corrected to that of gas at dry standard conditions of 32°F. and 1 atmosphere as follows:

$$V_g = \frac{18.33 V_m (P - P_w)}{T_m} \quad (3)$$

In calculating the specific gravity, a correction was made for approximately 0.34 liters of dry air assumed to have been in the system at the start of a run. The fraction of air in the gas holder was calculated by the following equation:

$$y_a = \frac{0.220 P}{V_g T_{gh}} \quad (4)$$

The density of the dry gas on an air-free basis at standard conditions was calculated as follows:

$$D_g = \frac{\frac{7.41 w_g T_{gh}}{P} - 1.293 y_a}{1 - y_a} \quad (5)$$

The total weight of gas was calculated from:

$$W_g = V_g D_g \quad (6)$$

The specific gravity referred to air and the average molecular weight were calculated from:

$$\text{Sp.Gr.} = \frac{D_g}{1.293} \quad (7)$$

$$\text{MW} = 29.0 (\text{Sp.Gr.}) \quad (8)$$

TABLE IV

## Sample Laboratory Run Sheet

Run No. 23

Feed Stock: Thermal tar, 50 g  
 Object: Coke to 1500°F ±

Date: March 31, 1950  
 Barometer: 736.4 mm Hg

<u>Time</u>	<u>t<sub>c</sub></u> (°F)	<u>t<sub>lr</sub></u> (°F)	<u>t<sub>m</sub></u> (°F)	<u>V<sub>m</sub></u> cu. ft.	<u>Remarks</u>
0800	75	75	75.5	0.000	Started preheating.
0815	670	--	----	-----	Turned on condenser water.
0830	980	--	----	-----	
0832	1020	74	75.5	0.002	Started coking (first drop condensate).
0840	1040	73	75.5	0.012	Rate of liquid make high.
0845	1060	72	75.0	0.036	Rate of liquid make slowing.
0850	1120	72	75.0	0.070	Liquid make almost finished.
0900	1220	74	75.0	0.100	Started blasting. Shielded coking unit.
0915	1435	76	75.0	0.127	
0930	1490	78	75.1	0.143	
0945	1520	79	75.2	0.150	
1000	1530	79	75.4	0.153	Terminated run. Shut off condenser water. Turned on steam to condenser.
1015					Turned off steam. Sampled gas. t <sub>gh</sub> = 79°F, w <sub>g</sub> = 0.1820 g
1030					Collected and weighed liquid. Wt. of liquid = 38.105 g
1100					Cooled coke in desiccator and weighed. Wt. of coke = 8.180 g

## SAMPLE LABORATORY CALCULATIONS

Run No. 23

A. Coke, wt.% of charge.

$$\text{Weight of charge} = 50.000 \text{ g}$$

$$\text{Weight of coke} = 8.180 \text{ g}$$

$$\text{Per cent coke} = \frac{8.180 \text{ g}}{50.000 \text{ g}} \times 100 = 16.4$$

B. Liquid, wt.% of charge.

$$\text{Per cent liquid} = \frac{38.105 \text{ g}}{50.000 \text{ g}} \times 100 = 76.2$$

C. Gas, wt.% of charge and specific gravity.

Substituting in equation (3):

$$V_g = \frac{(18.33) (0.153) (736.4 - 22.2)}{535} = 3.744 \text{ liters}$$

Substituting in equation (4):

$$y_a = \frac{(0.220) (736.4)}{(3.744) (539)} = 0.084$$

Substituting in equation (5):

$$D_g = \frac{\frac{(7.41) (0.1820) (539)}{736.4} - (0.084) (1.293)}{1.000 - 0.084} = 0.955 \text{ g/liter}$$

$$W_g = (0.955 \text{ g/liter}) (3.744 \text{ liter}) = 3.58 \text{ g}$$

$$\text{Per cent gas} = \frac{3.58 \text{ g}}{50.000 \text{ g}} \times 100 = 7.2$$

$$\text{Sp.Gr.} = \frac{0.955}{1.293} = 0.74$$

$$MW = 29.0 (0.74) = 21.5$$



## NOMENCLATURE

$D_g$  = density of gas on air-free basis at standard conditions, grams/liter.

$MW$  = molecular weight

$P$  = barometric pressure, mm. mercury.

$p_w$  = vapor pressure of water at gas meter temperature, mm. mercury.

Sp.Gr. = specific gravity of gas referred to air.

$t_c$  = coking temperature, °F.

$t_{gh}$  = gas holder temperature, °F.

$t_{lr}$  = liquid receiver temperature, °F.

$T_{gh}$  = gas holder temperature, °R.

$T_m$  = wet test meter temperature, °R.

$V_g$  = volume of dry gas at standard conditions, liters.

$V_m$  = volume of wet gas at meter conditions, cu. ft.

$W_g$  = total weight of dry gas produced, grams.

$w_g$  = weight of 208.5 ml. of dry gas at gas holder conditions, grams.

$y_a$  = volume fraction of air present in gas holder.

Subscripts

a = air

c = coke

g = dry gas

gh = gas holder

lr = liquid receiver

m = wet test meter

Typist - Evelyn Steinkuhler