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MOBIL OIL CORPORATION

RESEARCH DEPARTMENT

TECHNICAL MEMORANDUM NO. 67-4

MEASUREMENT OF C_3^+ CONTENT OF OFFGAS FROM THE GAS-COMBUSTION
RETORT AND POTENTIAL METHODS OF RECOVERY

ANVIL POINTS OIL SHALE RESEARCH CENTER

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in Recycle Gas By:

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MEASUREMENT OF C₃⁺ CONTENT OF OFFGAS FROM THE GAS-COMBUSTION
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MEASUREMENT OF C₃⁺ CONTENT OF OFFGAS FROM THE GAS COMBUSTION RETORT AND POTENTIAL METHODS OF RECOVERY

I. INTRODUCTION

During the early part of 1965, a concentrated effort was undertaken to improve material balances in general, and organic carbon balances in particular, around Retort No. 1. During the course of this work it was determined that the retort vent gas stream contained at least 1 lb/MSCF of propane and heavier hydrocarbons.

It was felt that the quantity and approximate composition of the hydrocarbon material carried in the retort gas streams should be defined. If recoverable, the material represented additional oil yield per ton of raw shale processed. Even if the material were not recoverable, the information would be necessary for precise material balance calculations.

Beginning early in 1966, a large amount of work was carried out by the analytical laboratory to determine the propane and heavier hydrocarbon content of retort gas after removal of the shale oil mist. Experiments were conducted during the bulk of 1966, using Retort No. 2 gas streams as the feed source to cold-trapping equipment to determine the actual liquefiable hydrocarbon content retort gas.

During the course of the work to determine the quantity of hydrocarbons present in retort gas, additional work was undertaken to determine if processing of the gas for recovery of the hydrocarbons would be economically attractive. To this end, it was felt that rough economic screening of various processes would be sufficient to determine if any incentive existed for a comprehensive evaluation of recovery methods. Consequently, major effort was devoted to the evaluation of unit operations and unit processes that are common to broad ranges of processes rather than specific processes. For example, gas compression would be common to all processes operating under pressure. If gas compression were prohibitively expensive by itself, then all pressurized operations could be ruled out. Other types of operations and processes to be evaluated were cooling, absorption, and adsorption.

II. SUMMARY AND CONCLUSIONS

Cold-trapping of Retort No. 2 gas after mist removal indicates that the equilibrium retort gas contains about 2.5 lbs/MSCFDG of propane and heavier hydrocarbons. On a raw shale basis, this is equivalent to between 5 and 25% of raw shale Fischer Assay.

A typical composition of equilibrium retort gas has been developed based on the data obtained from the cold-trapping experiments and routine gas analyses performed by the analytical laboratory. This gas composition is given below.

| <u>Component</u> | <u>Mol %</u> |
|--------------------|--------------|
| H ₂ | 4.97 |
| N ₂ | 60.96 |
| CO | 3.59 |
| CO ₂ | 26.07 |
| C ₁ 's | 1.89 |
| C ₂ 's | 0.90 |
| C ₃ 's | 0.50 |
| C ₄ 's | 0.20 |
| C ₅ 's | 0.12 |
| C ₆ 's | 0.31 |
| C ₇ 's | 0.16 |
| C ₈ 's | 0.22 |
| C ₉ 's | 0.06 |
| C ₁₀ 's | 0.05 |
| Total | 100.00 |

Several conventional methods of hydrocarbon recovery from gases were screened to determine if any offered sufficient economic incentive to justify recovering part or all of the 2.5 lbs/MSCFDG present in retort gas. Gas compression was found to be excessively expensive (\$70 per barrel) for the amount of hydrocarbon recovered. Even isobaric cooling by indirect heat exchange with air resulted in a minimum oil cost of about \$7 per barrel. The use of activated carbon as an adsorbent for the recovery of the hydrocarbon material was investigated and ruled out as a result of large carbon requirements. Absorption of the material with lean oil does not appear promising as a result of the lean oil requirement of 25 to 50 barrels lean oil per barrel oil recovered.

The main deterrent to economical processing of retort gas is the low pressure, about 12 psia, at which it is available.

III. DETAILED DISCUSSION

A. Composition of Retort Gas

The work done on the composition and processing of retort gas is divided into two parts. These are (1) the determination of the propane and heavier hydrocarbon content and the composition of gas from Retort No. 2 and (2) schemes for recovering propane and heavier hydrocarbons from the retort gas.

1. Experimental Determination of C₃⁺ Hydrocarbons In Retort Gas

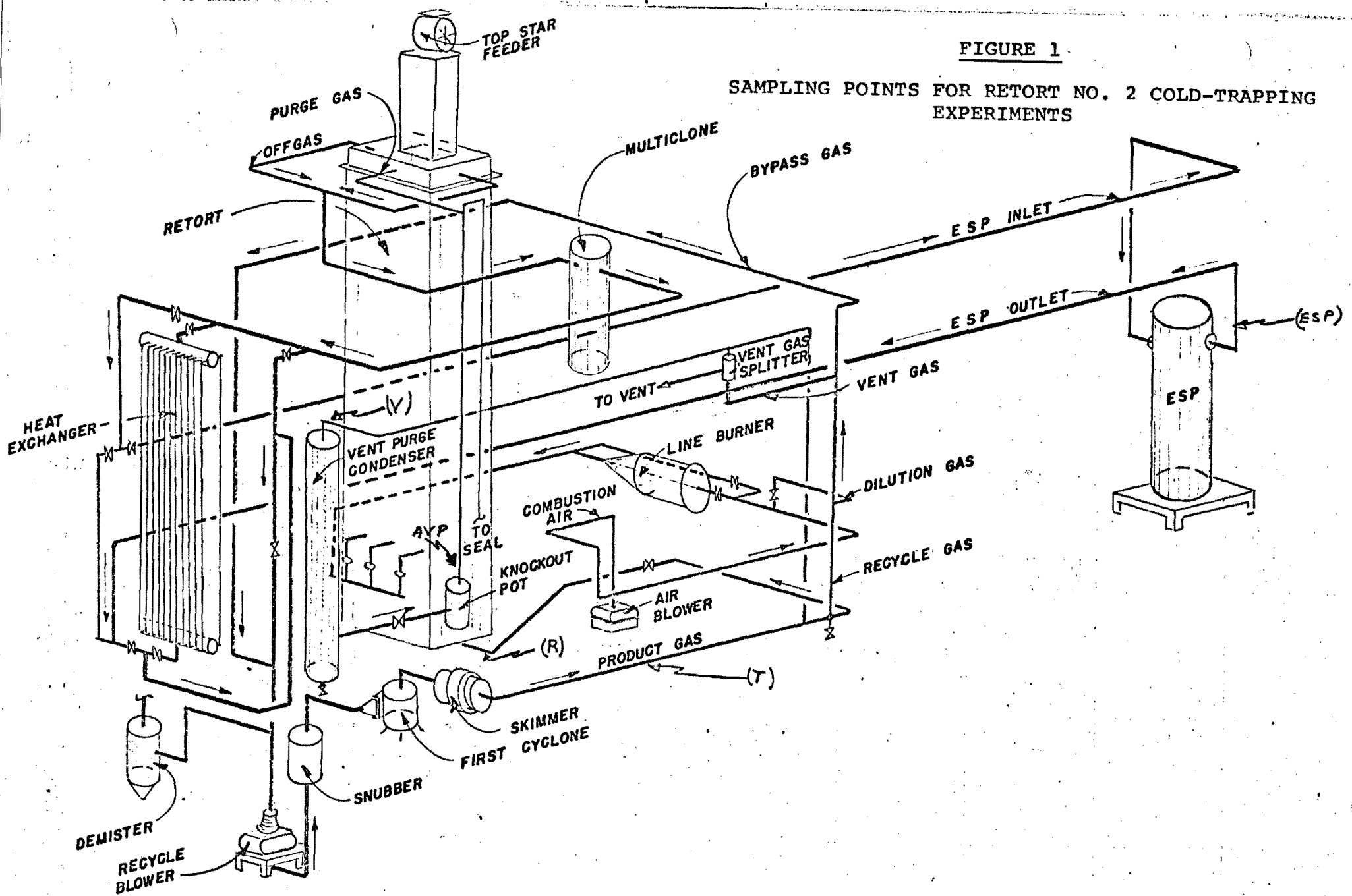
In February of 1965, extensive work was undertaken on Retort No. 1 to improve carbon balances. Several improvements were made in the gas sampling system during the course of this work. The major improvement was in physically enlarging the gas sampling equipment to sample and handle the large volume of gas required to obtain measurable quantities of oil. The improvements in the gas sampling system, along with more accurate measurements of air and vent gas rates, resulted in marked improvement in carbon balances. Also, cold-trapping of gas at the laboratory indicated about 1 lb/MSCFDG of condensable organic material.

At the beginning of 1966, additional cold-trapping experiments were carried out on Retort No. 2 at various points in the retort gas system. The sampling points are shown on Figure 1, a small isometric drawing of Retort No. 2 and its associated equipment and piping.

Figure 2 presents a schematic diagram of the equipment used for the cold-trapping experiments. Briefly, the experimental procedure involved passing gas in series through cooling coils and traps, one set of which was maintained at about 32 F by an ice bath, and one set of which was maintained at about -110 F by a dry ice-trichlorethylene bath. The volume of gas passed through the apparatus was determined by a wet-test meter located downstream from the -110 F trap. After a measured volume of gas was passed through the pre-weighed traps, they were warmed and reweighed, and the volumes of collected liquids were measured. The concentrations of propane and heavier hydrocarbon material and water in the gas were calculated from the amounts of material collected.

FIGURE 1

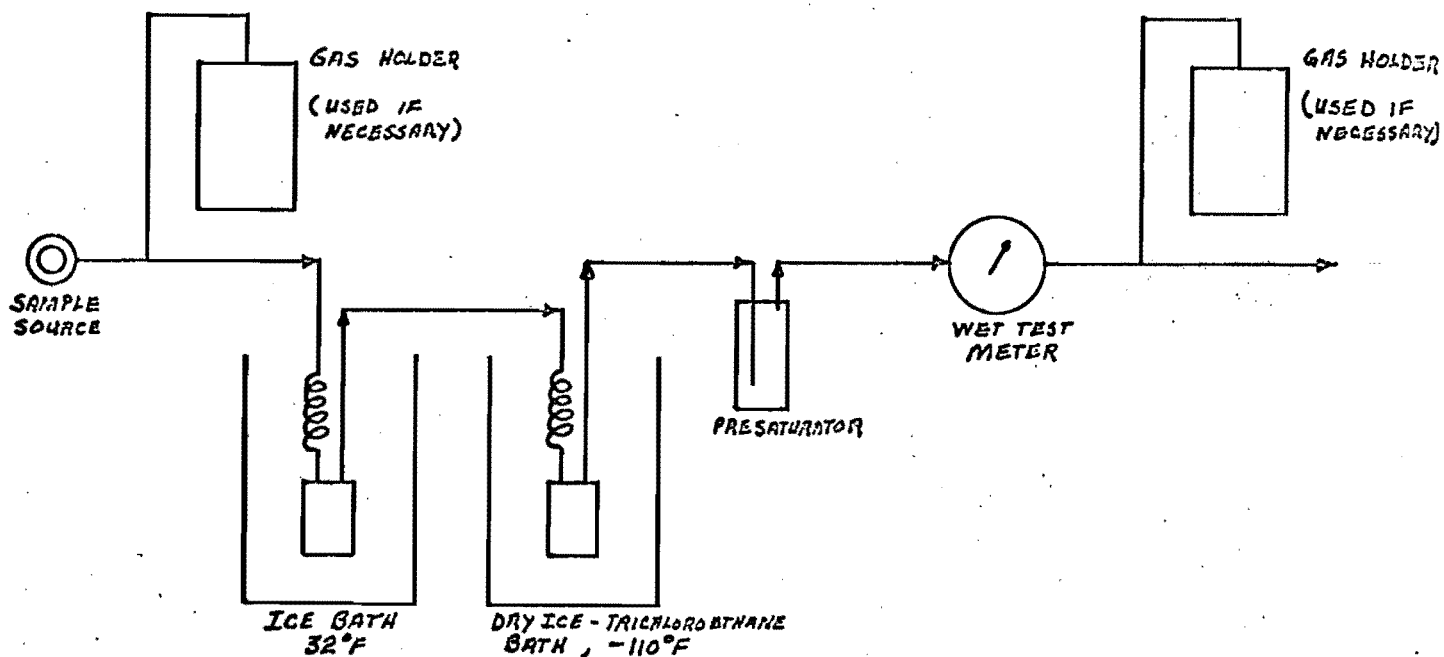
SAMPLING POINTS FOR RETORT NO. 2 COLD-TRAPPING EXPERIMENTS



ISOMETRIC OF NO. 2 RETORT PIPING

FIGURE 2

SCHEMATIC DIAGRAM OF EQUIPMENT USED IN COLD-TRAPPING EXPERIMENTS



The averaged results of all the cold-trapping experiments are summarized in Table 1. Since the data were acquired on retort runs made under varying conditions, and since the variability of the results is fairly large, individual data points are not presented. No attempt has been made to infer any effects of process changes from these data.

Examination of Table 1 leads to the following conclusions:

- (1) The quantity of water found in the -110 F trap does not check the amount of water that should be found, assuming that Raoult's Law applies. One possible reason for this non-agreement is that the water was frozen out in the inlet tubing to the -110 F trap and was not collected in the trap even though the tubes were warmed and drained into the trap. Another possible explanation is that the water was entrained out of the trap. A third possibility is that some water was counted as oil.
- (2) The pounds hydrocarbon per MSCFDG collected in the -110 F trap appears to be fairly constant, as would be expected.
- (3) The vent purge condenser does, by observation, remove some of the heavier hydrocarbons and mist (if present). Based on the data in Table 1, however, it does not appear to be very effective.
- (4) The gas sample stream sent to the laboratory does appear lean with respect to heavy hydrocarbons. Heavy hydrocarbon deposition in the flow tubing is the probable explanation for this result.

Analyses have been performed on the liquid hydrocarbon material obtained from both the 32 F trap and the -110 F trap. Results of these analyses are presented in Tables 2 and 3.

2. Composition of Gas Phase

An approximate composition of equilibrium single phase gas has been calculated based on measured gas compositions, the composition of liquids obtained from the 32 F and -110 F traps during the cold-trapping experiments, and measured gas-oil ratios.

TABLE 1

SUMMARY OF RESULTS OF COLD-TRAPPING EXPERIMENTS ON RETORT GAS

| Sample Point | Total Gas (T) | Laboratory Sample (L) | After Vent Purge (AVP) | Recycle Gas (R) | Precip. (ESP)* | Vent Gas (V) |
|---|---------------|-----------------------|------------------------|-----------------|----------------|--------------|
| No. of Data Points | 13 | 4 | 5 | 1 | 3 | 1 |
| # Oil/MSCFDG Collected in 32° F Trap | 0.72 | 0.11 | 0.49 | 0.51 | 0.70 | 0.77 |
| # Oil/MSCFDG Collected in -110° F Trap | 2.06 | 1.01 | 2.31 | 1.94 | 1.63 | 1.52 |
| Total # Oil/MSCFDG | 2.78 | 2.02 | 2.80 | 2.45 | 2.33 | 2.29 |
| # H ₂ O Collected in -110 F Trap | | | | | | |
| Theo. # H ₂ O Leaving 32 F Trap | .485 | .422 | .586 | .882 | 1.37 | .63 |

*Required Use of a Vacuum Pump

TABLE 2

ANALYSES BY MOBIL'S PAULSBORO LABORATORY ON CONDENSATE FROM 32 F TRAP
Sample Taken During Run B817I

| <u>Type</u> | <u>Mole %</u> |
|--|---------------|
| Paraffins | 28.6 |
| Mono olefins + Monocycloparaffins | 31.6 |
| Cyclo olefins + Dicycloparaffins + Diolefins | 13.1 |
| Cyclodiolefin + Dicycloolefin | 13.2 |
| Alkyl benzenes | 10.2 |
| Indans + Tetralins | 2.5 |
| Naphthalenes | <u>0.8</u> |
| Total | 100.0 |
| Average Molecular Weight (Total Sample) | 124.3 |

APPROXIMATE CARBON NUMBER DISTRIBUTION (MOLE %)

| <u>Carbon Number</u> | <u>Paraffins</u> | <u>Alkylbenzenes</u> |
|--------------------------|------------------|----------------------|
| 5 | 1.2% | -- |
| 6 | 1.6 | 1.1% |
| 7 | 1.9 | 1.7 |
| 8 | 3.8 | 2.9 |
| 9 | 10.4 | 2.4 |
| 10 | 5.1 | 1.1 |
| 11 | 2.8 | 0.6 |
| 12 | 1.2 | 0.3 |
| 13 | <u>0.6</u> | <u>0.1</u> |
| Total | 28.6% | 10.2% |
| Average Molecular Weight | 127.8 | 112.0 |

Butane and lighter ends were probably lost by evaporation when the liquid was charged to the mass spectrometer through the heated galium disc.

TABLE 2 (CONTINUED)

APPROXIMATE MOLAR CARBON NUMBER
DISTRIBUTION OF OLEFINS
Composite Sample Taken During Run B966

| <u>Carbon No.</u> | <u>Monoolefins</u> | <u>Cycloolefins Plus Diolefins</u> | <u>Cyclodiolefins</u> |
|-------------------|--------------------|--|-----------------------|
| 4 | 2.2 | -- | -- |
| 5 | 3.7 | 0.7 | -- |
| 6 | 4.1 | 1.8 | -- |
| 7 | 3.1 | 2.0 | -- |
| 8 | 3.8 | 2.0 | 2.6 |
| 9 | 4.8 | 2.7 | 3.4 |
| 10 | 4.1 | 2.4 | 2.9 |
| 11 | <u>2.1</u> | <u>1.0</u> | <u>1.5</u> |
| Totals | 27.9 | 12.6 | 10.4 |

TABLE 2 (CONTINUED)

ORGANIC COMPOUND TYPE ANALYSIS

| | | |
|-------------------------|--------|------|
| Para. Mol Wt and C. No. | 134.10 | 9.4 |
| Arom. Mol Wt and C. No. | 111.30 | 8.4 |
| Dcyp. Mol Wt and C. No. | 137.45 | 10.0 |

| <u>Compound Type</u> | | <u>Vol %</u> | <u>Wt %</u> | <u>Mole %</u> |
|-------------------------|--------------|--------------|--------------|---------------|
| Paraffins | 11.59 | 31.5 | 29.4 | 28.5 |
| Mono Cyclo Paraffins | 2.30 | 5.7 | 5.8 | 5.7 |
| Mono Olefins | 11.36 | 30.2 | 28.4 | 27.9 |
| Di Cyclo Paraffins | 0.35 | 0.8 | 0.9 | 0.8 |
| Cy Olefins + DI Olefins | 5.09 | 11.8 | 12.5 | 12.5 |
| Cn H(2N-4) | 4.25 | 8.8 | 10.3 | 10.4 |
| Alkyl Benzenes | 4.45 | 8.5 | 9.4 | 10.9 |
| Indanes + Tetralins | 1.16 | 2.4 | 2.9 | 2.8 |
| Naphthalenes | 0.16 | 0.3 | 0.4 | 0.4 |
| Total | 40.71 | 100.0 | 100.0 | 99.9 |

Approx. Paraffin
Carbon No. Distribution

| | | | | |
|---------------------------|------|-----|-----|-----|
| C ₅ Paraffins | 0.06 | 0.1 | 0.1 | 0.2 |
| C ₆ Paraffins | 0.35 | 0.7 | 0.6 | 0.9 |
| C ₇ Paraffins | 0.62 | 1.4 | 1.2 | 1.5 |
| C ₈ Paraffins | 1.49 | 3.6 | 3.2 | 3.7 |
| C ₉ Paraffins | 3.40 | 9.0 | 8.2 | 8.4 |
| C ₁₀ Paraffins | 3.22 | 9.1 | 8.7 | 7.9 |
| C ₁₁ Paraffins | 1.68 | 5.1 | 5.0 | 4.1 |
| C ₁₂ Paraffins | 0.54 | 1.8 | 1.8 | 1.3 |
| C ₁₃ Paraffins | 0.22 | 0.8 | 0.8 | 0.5 |

Approx. Alkyl Benzene
Carbon No. Distribution

| | | | | |
|-------------------------------|-------|-----|-----|-----|
| Benzene | 0.48 | 0.6 | 0.7 | 1.2 |
| Toluene | 0.73 | 1.2 | 1.3 | 1.8 |
| C ₈ Alkyl Benzene | 1.25 | 2.3 | 2.5 | 3.1 |
| C ₉ Alkyl Benzene | 1.20 | 2.4 | 2.7 | 2.9 |
| C ₁₀ Alkyl Benzene | 0.42 | 1.0 | 1.1 | 1.0 |
| C ₁₁ Alkyl Benzene | 0.21 | 0.5 | 0.6 | 0.5 |
| C ₁₂ Alkyl Benzene | 0.10 | 0.3 | 0.3 | 0.3 |
| C ₁₃ Alkyl Benzene | 0.06 | 0.2 | 0.2 | 0.1 |
| Wt PC Combined Hydrogen | 13.68 | -- | -- | -- |

TABLE 3

COMPONENT ANALYSIS OF -110 F LIQUID CONDENSATE
 Combined Samples From Runs B875, B876, B877

| Component | Wt. % | Component | Wt. % |
|-----------------------------|-------|---|--------|
| C ₂ = | 0.03 | 1-c-2-t-4TMCyC ₅ } | 0.79 |
| C ₂ = | Trace | 2MC ₇ | |
| CO ₂ | 0.18 | 4MC ₇ | |
| C ₃ = | 0.12 | 3,4DMC ₆ } | 0.44 |
| C ₃ = | 0.21 | 3M3EC ₅ | |
| iC ₄ | 0.02 | 1,1,3-t-4TetMCyC ₅ | 0.02 |
| nC ₄ | 1.23 | 1,1DMCyC ₅ } | 0.04 |
| 1-C ₄ = | 1.16 | 2,2,5TMC ₆ | |
| 1-C ₄ = | 1.34 | 1-t-4DMCyC ₅ | 0.02 |
| t-2-C ₄ = | 0.47 | 1-c-3DMCyC ₅ | 0.02 |
| iC ₅ | 0.88 | 2,2,4-TMC ₆ | 0.01 |
| C-2-C ₄ = | 0.42 | 1-M-t-2-ECyC ₅ } | 0.11 |
| nC ₅ | 4.35 | 1-M-1-ECyC ₅ | |
| 1,3C ₄ = | 1.00 | 1-t-2-DMCyC ₅ } | 0.03 |
| 1-C ₅ = | 2.35 | 1-c-2-c-3TMCyC ₅ } | |
| CyC ₅ | 0.75 | 1-c-4-DMCyC ₅ } | 0.05 |
| 2M-1-C ₄ = | 0.82 | 1-t-3-DMCyC ₅ } | |
| t-2-C ₅ = | 0.03 | nC ₆ | 3.0 |
| 2MC ₅ | 1.60 | 3,3-DM-1-C ₄ = | 0.20 |
| C-2-C ₅ = | 0.43 | 2-M-2-C ₅ = | 0.30 |
| 2-M-2-C ₄ = | 0.59 | CyC ₅ = | 0.40 |
| 2,2DMC ₄ | 4.60 | 3-M-1-C ₅ = | 0.55 |
| 2,3DMC ₄ | 0.16 | 4-M-1-C ₅ = | 0.74 |
| 2MC ₅ | 1.5 | 4-M-c-2-C ₅ = | 0.23 |
| 3MC ₅ | 0.54 | 2,3DM-1-C ₄ = | 0.16 |
| nC ₆ | 5.7 | 4-M-t-2-C ₅ = | 0.34 |
| MCyC ₅ | 0.59 | 2-M-1-C ₅ = | 0.27 |
| 2,2DMC ₅ | 0.04 | 1-C ₆ = | 6.4 |
| 2,4DMC ₅ | 0.03 | 2-E-1-C ₄ = | 0.11 |
| Benzene | 6.3 | c-3-C ₆ = | 0.31 |
| CyC ₆ | 0.27 | t-3-C ₆ = | |
| 1,1DMCyC ₅ | 0.02 | 3MCyC ₅ = | |
| 2MC ₆ | 0.16 | 2M2C ₅ = | 0.55 |
| 2,3DMC ₅ | 0.59 | t-2-C ₆ = | |
| 3MC ₆ | 0.51 | 3-M-c-2-C ₅ = | 0.70 |
| 1-c-3DMCyC ₅ | 0.08 | C-2-C ₆ = | 0.34 |
| 1-t-3DMCyC ₅ | 0.15 | 3-M-t-2-C ₅ = | 0.30 |
| 1-t-2DMCyC ₅ | 0.19 | 2,3DM-2-C ₄ = | 0.34 |
| nC ₇ | 4.8 | C ₇ = | 0.38 |
| 1-c-2-DMCyC ₅ | 0.09 | C ₇ = | 0.30 |
| MCyC ₆ | 0.43 | C ₇ = | 0.31 |
| 1,1,3TMCyC ₅ | 0.01 | 1-MCyC ₅ = | 1.1 |
| EtCyC ₅ | 0.50 | Other C ₇ = & C ₈ = | 13.3 |
| 2,5DMC ₆ | 0.02 | C ₉ Paraffins | 1.9 |
| 2,4DMC ₆ | 0.01 | C ₁₀ Paraffins | 0.8 |
| 1-t-2-c-4TMCyC ₅ | 0.01 | C ₁₁ Paraffins | 0.3 |
| 1-t-2-c-3TMCyC ₅ | 0.02 | C ₈ Alkyl Benzenes | 1.1 |
| Toluene | 3.2 | C ₉ Alkyl Benzenes | 0.4 |
| 1,1,2TMCyC ₅ | 0.07 | C ₁₀ Alkyl Benzenes | 0.2 |
| 2,3DMC ₆ } | 0.35 | C ₈ + Olefin & Diolefins | 12.2 |
| 2M3EC ₅ } | | C ₈ + Naphthenes | 4.4 |
| | | Total | 102.38 |

Approximate average molecular weight = 94

A typical routine gas analysis by the analytical laboratory for the components CO₂ through ethane-ethene is presented in Table 4.

The calculation procedure used to develop the gas composition is given below:

- Step 1. The component analysis of -110 F liquid, presented in Table 3, was simplified by aggregating all compounds with the same number of carbon atoms. Unseparated C₈⁺ olefin and diolefins and C₈⁺ naphthenes were then split into C₈'s, C₉'s and C₁₀'s⁺ in the ratio of the relative concentration of the separated C₈'s, C₉'s and C₁₀'s.
- Step 2. Vapor-liquid distribution ratios (K-values) and the carbon number distribution generated in Step 1, were used to estimate the concentration of C₃⁺ components in -110 F equilibrium vapor. K-values used were those for normal paraffins.
- Step 3. The average of the gas analyses from Runs B817U, B866, B870, B876, and B901 presented as Table 4 was used as an estimate of the concentration of C₂⁻ components in the -110 F equilibrium vapor.
- Step 4. The concentration generated in Steps 2 and 3 were joined, and the results normalized to provide a complete H₂ through C₁₀⁺ composition of -110 F equilibrium vapor.
- Step 5. Gas and liquid, with compositions as generated by Steps 1 and 4, were mathematically recombined. The recombination ratio used was 2.05 pounds hydrocarbon per MSCFDC. This is the average of all gas-liquid ratio determinations, for the -110 F trap, made by the analytical laboratory.
- Step 6. Using the composition generated in Step 5, K-values were used to estimate an equilibrium liquid composition at 32 F. $\sum x_i$ for the calculation was 0.70 instead of 1.0. (In view of the rather arbitrary apportionment of the unseparated C₈⁺ material and the assumption that the

TABLE 4

RETORT GAS COMPOSITION AS OBTAINED BY ROUTINE ANALYSIS
AVERAGE OF RUNS B817U, B866, B870, B876, B901

| <u>Component</u> | <u>Measured Vol %</u> |
|---------------------------------|---------------------------|
| CO ₂ | 26.2 |
| N ₂ + O ₂ | 61.2 |
| CH ₄ | 1.9 |
| CO | 3.6 |
| H ₂ | 5.0 |
| C ₂ 's | 0.9 |
| Others* | <u>1.2</u> |
| | 100.0 |

*Determined by difference

aggregated compounds behaved as normal paraffins, this result was deemed satisfactory.) These component concentrations were then normalized.

Step 7. Gas and liquid, with compositions as generated by Steps 5 and 6, were mathematically recombined. The recombination ratio used was 0.51 pound hydrocarbon per MSCFDG. This is the average of all gas-liquid ratio determinations for the 32 F trap made by the analytical laboratory.

The results of these calculations are presented in Table 5.

During January of 1966, a number of gas analyses were made for hydrocarbon components C₁ through C₅. The average of these determinations covering 18 retort runs, is presented in Table 6.

Comparison of the calculated component concentrations for the C₁ through C₅ hydrocarbons with the experimentally determined concentrations shows reasonable agreement for all components except propane. Consequently, the value of the propane concentration was increased to 0.5 mole % based on the data in Table 6, and the composition renormalized. The results are presented in Table 7. Concentrations given for the components H₂ through C₅'s appear to be very reasonable. Concentrations of C₆⁺ components are not as firmly fixed.

B. Potential Processing of Retort Gas to Recover C₃⁺ Hydrocarbons

1. General Bases for Evaluation

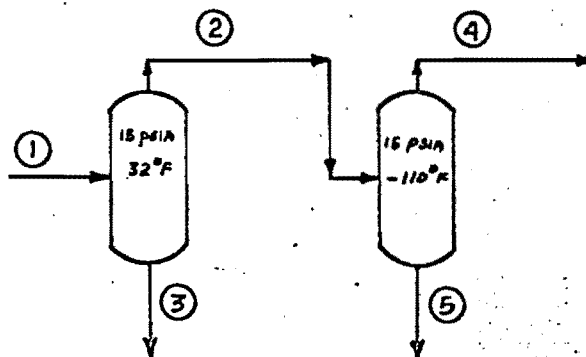
A number of conventional type processing schemes can be considered for the recovery of the heavier hydrocarbons present in the retort equilibrium gas phase. Schemes that have been considered are:

- (1) Compression
- (2) Cooling
- (3) Compression plus cooling
- (4) Adsorption
- (5) Absorption

If we consider a 50,000 barrel per day shale oil plant processing 85,000 tons per day of raw shale with a vent gas production of 5,000 SCFDG per ton raw shale,

TABLE 5

SUMMARY OF COMPLETE RESULTS FROM CALCULATIONS OF RETORT GAS COMPOSITION



Actual pressure was 12.5 to 13.5 psia.

"K" values used were those at 15 psia.

| Stream No. | 1 | | 2 | | 3 | | 4 | | 5 | |
|-----------------------|---------|--------|---------|--------|---------|--------|---------|--------|---------|--------|
| | Mol % | Wt % | Mol % | Wt % | Mol % | Wt % | Mol % | Wt % | Mol % | Wt % |
| H ₂ | 4.99 | 0.32 | 5.00 | 0.32 | -- | -- | 5.04 | 0.33 | -- | -- |
| N ₂ | 61.22 | 54.57 | 61.33 | 54.92 | 0.20 | 0.05 | 61.84 | 56.28 | -- | -- |
| CO | 3.60 | 3.21 | 3.60 | 3.22 | -- | -- | 3.63 | 3.30 | -- | -- |
| CO ₂ | 26.18 | 36.66 | 26.22 | 36.90 | 1.06 | 0.39 | 26.43 | 37.80 | 0.41 | 0.2 |
| C ₁ 's | 1.90 | 0.97 | 1.90 | 0.97 | 0.02 | -- | 1.92 | 1.00 | -- | -- |
| C ₂ 's | 0.90 | 0.86 | 0.90 | 0.86 | 0.07 | 0.02 | 0.91 | 0.89 | Trace | Trace |
| C ₃ 's | 0.09 | 0.13 | 0.09 | 0.13 | 0.03 | 0.01 | 0.08 | 0.11 | 0.62 | 0.3 |
| C ₄ 's | 0.20 | 0.37 | 0.20 | 0.37 | 0.24 | 0.12 | 0.13 | 0.24 | 8.86 | 5.5 |
| C ₅ 's | 0.12 | 0.28 | 0.12 | 0.28 | 0.56 | 0.34 | 0.02 | 0.05 | 12.72 | 10.0 |
| C ₆ 's | 0.31 | 0.85 | 0.30 | 0.83 | 7.43 | 5.39 | Trace | -- | 36.08 | 33.9 |
| C ₇ 's | 0.16 | 0.51 | 0.14 | 0.45 | 11.46 | 9.67 | Trace | -- | 16.76 | 18.3 |
| C ₈ 's | 0.22 | 0.80 | 0.16 | 0.58 | 35.17 | 33.82 | -- | -- | 19.76 | 24.6 |
| C ₉ 's | 0.06 | 0.24 | 0.03 | 0.12 | 19.06 | 20.59 | -- | -- | 3.29 | 4.6 |
| C ₁₀ 's | 0.05 | 0.23 | 0.01 | 0.05 | 24.70 | 29.60 | -- | -- | 1.68 | 2.5 |
| Total | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 |
| Moles Mol Stream 1 | 1.00000 | | 0.99844 | | 0.00155 | | 0.99023 | | 0.00819 | |

TABLE 6

AVERAGE C₁ - C₅ HYDROCARBON CONCENTRATIONS IN RETORT GAS

| <u>Component</u> | <u>Mol %</u> |
|-------------------|--------------|
| C1 | 2.08 |
| C2's | 1.08 |
| C3's | 0.50 |
| C4's | 0.11 |
| C5's | <u>0.20</u> |
| Total | 3.97 |
| Other Components* | <u>96.03</u> |
| Total | 100.00 |

*Other components not determined

TABLE 7

APPROXIMATE COMPOSITION OF RETORT GAS

| <u>Component</u> | <u>Most Probable Concentration, Mol %</u> |
|--------------------|---|
| H ₂ | 4.97 |
| N ₂ | 60.96 |
| CO | 3.59 |
| CO ₂ | 26.07 |
| C ₁ 's | 1.89 |
| C ₂ 's | 0.90 |
| C ₃ 's | 0.50 |
| C ₄ 's | 0.20 |
| C ₅ 's | 0.12 |
| C ₆ 's | 0.31 |
| C ₇ 's | 0.16 |
| C ₈ 's | 0.22 |
| C ₉ 's | 0.06 |
| C ₁₀ 's | <u>0.05</u> |
| Total | 100.00 |

a vent gas rate of 425 MMSCFDG per day is available for processing. Additionally, if the recycle gas rate is assumed to be 15,000 SCFDG per ton raw shale, and this gas is also processed, a total of 1,700 MMSCFDG per day is available for processing. Figure 3 shows the barrel per day of oil which might be recovered as a function of the pounds hydrocarbon per MSCFDG recovered from retort gas.

2. Gas Compression

One of the major blocks to the processing of retort gas is that it is available at low pressure and saturated with water. Table 8 indicates the actual gas rates in cubic feet per day, as a function of pressure, associated with the processing of vent gas only, 425 MMSCFDG per day.

The approximate theoretical work required to compress 425 MMSCFDG per day of vent gas available at 130 F, 12 psia and saturated with water vapor is shown on Figure 4. Also shown on Figure 4, is the work requirement to compress the total gas flow of 1,700 MMSCFDG per day to the same pressure levels.

Figure 5 indicates the approximate total cooling load on intercoolers and aftercoolers as a function of final discharge pressure. This cooling load is composed of the following items:

- (1) Cooling load required to cool the dry gas to 130 F.
- (2) Latent heat of condensation of water condensed upon cooling the gas to 130 F at the prevailing pressure.
- (3) Cooling load required to cool the water vapor remaining in the gas to 130 F.

Table 9 presents heat exchanger surface area requirements based on the following assumptions: (1) air cooled exchangers are used to provide cooling from 335 F to 130 F; (2) the effective ΔT is 90 F; (3) an overall average heat transfer coefficient of 10 Btu/hr-ft²-°F can be obtained for the total load.

Flash calculations using the gas composition previously given in Table 7, indicate that the molar gas-liquid ratio at 36 psia and 130 F is about 3,500 moles gas per mole of liquid. This molar ratio should result in the recovery of about 169 barrels of oil

FIGURE 3

OIL PRODUCTION FROM RETORT GAS AS A
FUNCTION OF RECOVERY

Basis: 85,000 T/D Raw Shale
5,000 SCFDG/TRS Vent Gas Rate
15,000 SCFDG/TRS Recycle Gas Rate

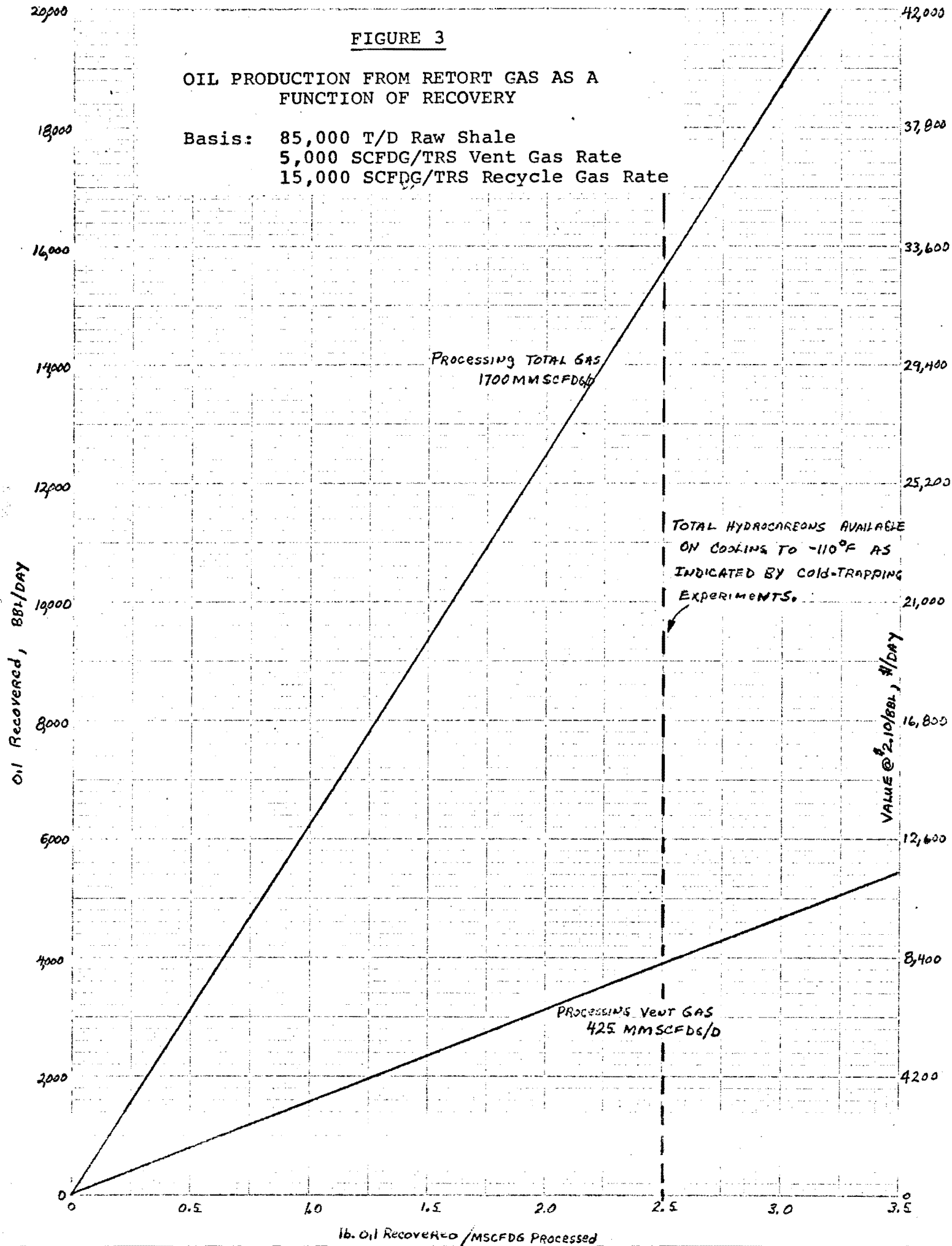


TABLE 8

ACTUAL GAS RATES AS A FUNCTION OF PRESSURE FOR VENT GAS PROCESSING

Vent gas rate: 425 MMSCFDG/D

Temperature: 130 F

Saturated with water at 130 F and 12 psia

| <u>Pressure,</u> <u>psia</u> | <u>Vent Gas Rate</u> <u>ACF WG/D</u> | <u>Mol %</u> <u>Dry Gas</u> |
|---------------------------------|---|--------------------------------|
| 12 | 739.7 MM | 81.5 |
| 14.7 | 579.6 MM | 84.9 |
| 20.0 | 406.8 MM | 88.9 |
| 36.0 | 214.1 MM | 93.8 |
| 60.0 | 125.2 MM | 96.3 |
| 108.0 | 68.4 MM | 97.9 |
| 200.0 | 36.6 MM | 98.9 |
| 324.0 | 22.5 MM | 99.3 |

FIGURE 4

THEORETICAL WORK REQUIREMENT FOR COMPRESSION OF RETORT GAS

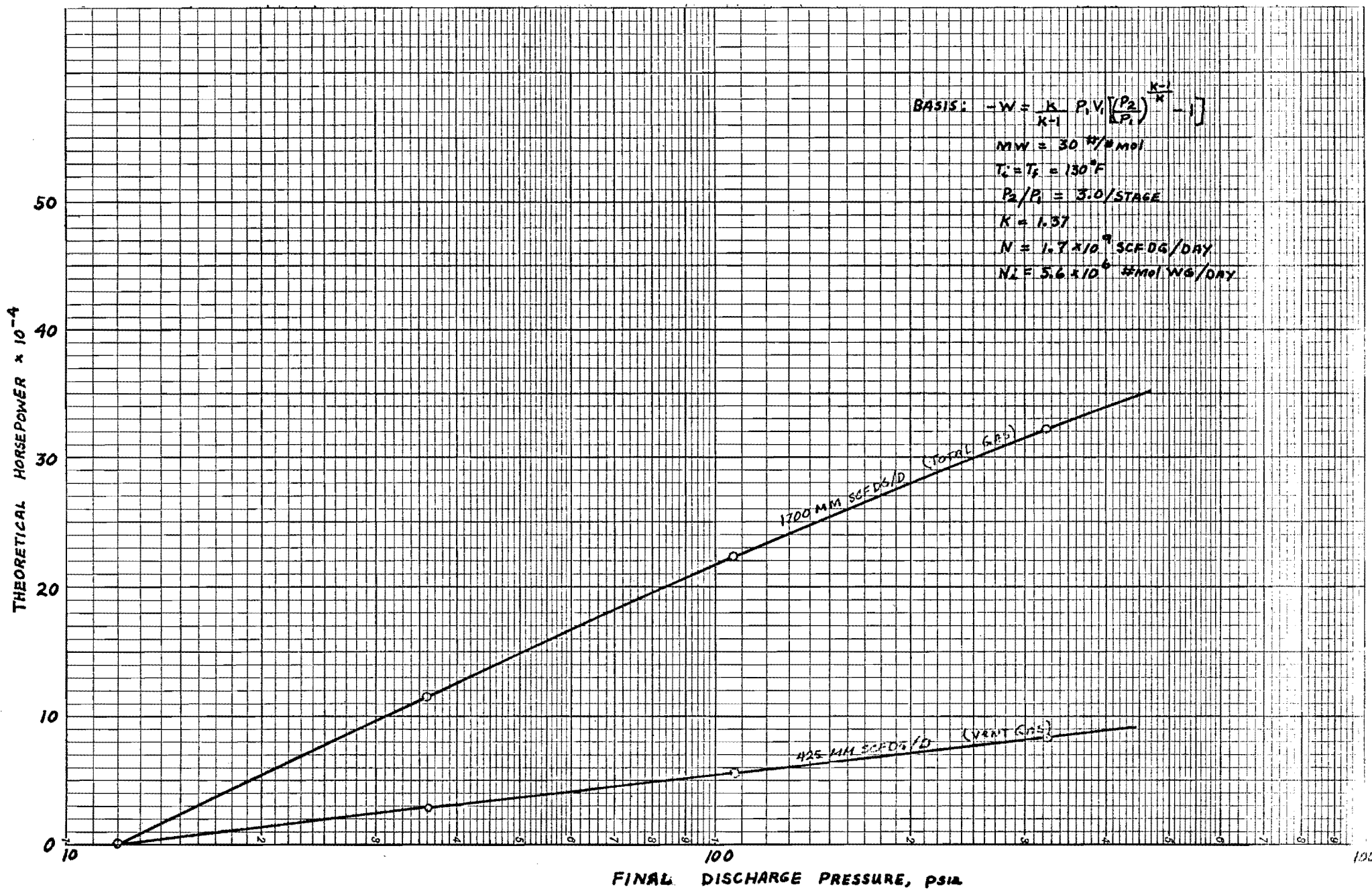


FIGURE 5

APPROXIMATE COOLING LOADS ASSOCIATED WITH COMPRESSION OF RETORT GAS

Basis: Initial Temperature = Final Temperature = 130 F
Saturated With Water at 130 F, 12 psia

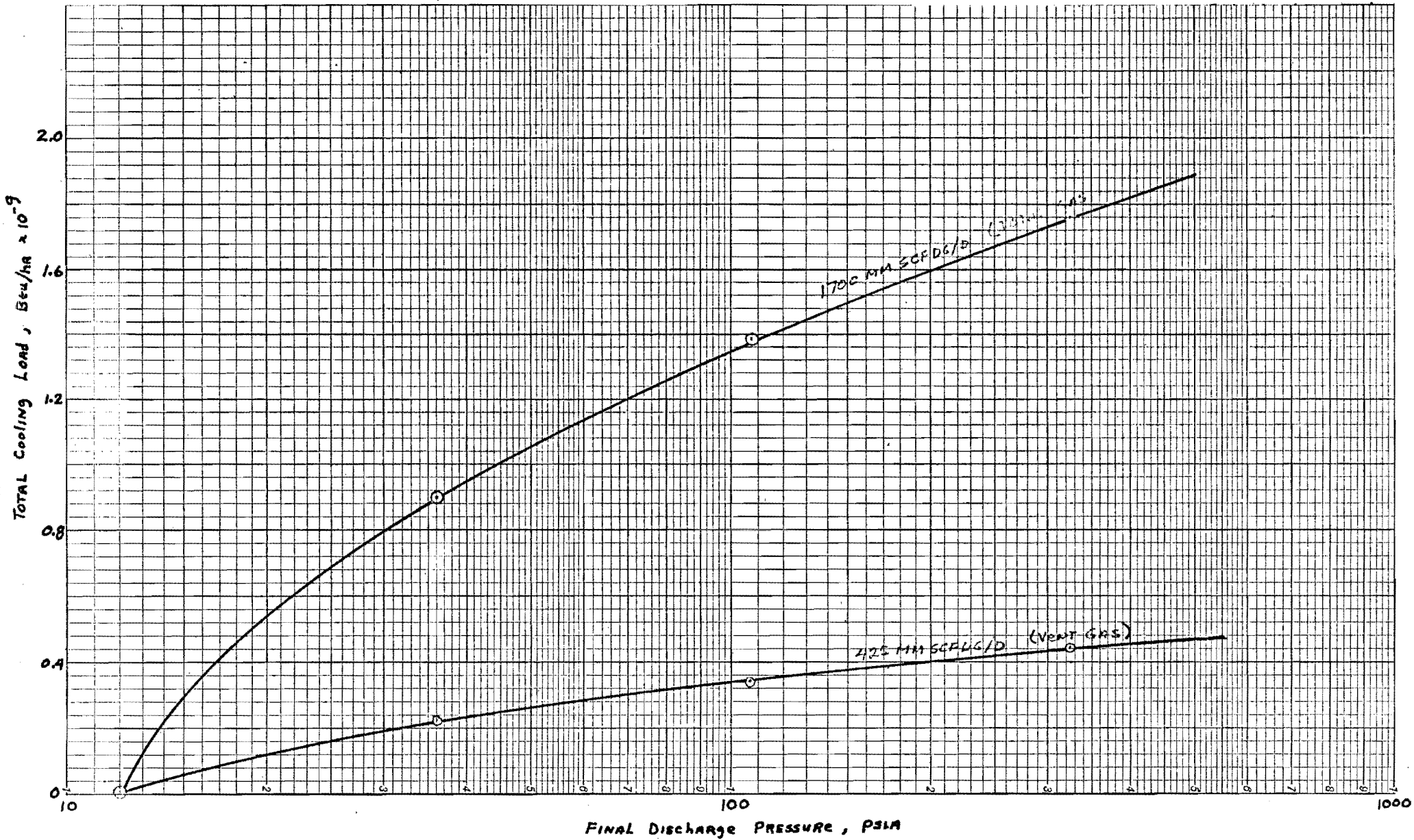


TABLE 9APPROXIMATE COOLER SURFACE REQUIRED TO COOL VENT AND RECYCLE
GAS STREAMS TO 130 F AFTER COMPRESSION

| <u>Pressure,</u> <u>psia</u> | <u>Total Cooling</u> <u>Load, Btu/hr</u> | <u>Area Required,</u> <u>Ft²</u> | <u>Total Cooling*</u> <u>Load, Btu/hr</u> | <u>Area Required,</u> <u>Ft²</u> |
|---------------------------------|---|--|--|--|
| 12 | 0 | 0 | 0 | 0 |
| 36 | 225 X 10 ⁶ | 2.5 X 10 ⁶ | 900 X 10 ⁶ | 10.0 X 10 ⁶ |
| 108 | 346 X 10 ⁶ | 3.8 X 10 ⁶ | 1384 X 10 ⁶ | 15.2 X 10 ⁶ |
| 324 | 441 X 10 ⁶ | 4.9 X 10 ⁶ | 1764 X 10 ⁶ | 19.6 X 10 ⁶ |

*Assumes saturation is maintained

per day by processing the vent gas stream of 425 MMSCFDG per day or about 675 barrels of oil per day if the total gas stream of 1,700 MMSCFDG per day were compressed.

Economically, if compressors are valued at \$20.00 per horsepower, compressor operating costs at \$0.02 per MSCF, and cooler surface at \$5.00 per square foot, the cost of the oil recovered would be about \$73.60 per barrel. (Bases: two year construction time, 15 year life, 50% Federal Income Tax, SY depreciation, 10% DCF rate of return.) Cost calculations were not made at higher pressures since the cost would be even higher.

To determine if compression was justified in conjunction with any subsequent processing scheme, it was assumed that a total maximum hydrocarbon content of three pounds per MSCF was present and that this material was all recovered by compression to 36 psia and recooling to 130 F. On this basis, the oil cost dropped to \$2.51 per barrel. This essentially eliminates from consideration all processes which require a high pressure feed.

3. Gas Cooling

Isobaric cooling of the retort gas from 130 F to 90 F will provide approximately the same "K" value improvement as compression to 36 psia with cooling to 130 F. A cooling load of about 160 MM Btu per hour is obtained for cooling the vent gas (425 MMSCFDG per day) to 90 F; a load of about 648 MM Btu per hour is obtained for cooling the total gas (1,700 MMSCFDG per day). Assuming air cooled heat exchangers operating with an effective ΔT of 30 F and an overall heat transfer coefficient of 10 Btu/hr-ft²-°F, about 540,000 square feet of surface would be required to cool the total gas stream. Valuing the heat transfer surface at \$5.00 per square foot, and assuming no other investment or operating costs, this results in a recovered oil cost of about \$6.90 per barrel. This is still about three times its actual value.

4. Gas Compression Plus Cooling

Gas compression with subsequent additional cooling past the 130 F level was not pursued since both operations are prohibitive individually.

5. Adsorption

The use of adsorbents such as silica gel, the synthetic zeolites, the activated aluminas, and the activated carbons has increased markedly in recent years for the recovery of hydrocarbons from lean gas streams. Most of these adsorbents can be eliminated from consideration for the recovery of hydrocarbons from retort gas on the basis of their preferential adsorption of water. Equilibrium retort gas saturated at 12 psia and 130 F contains about 10.8 pounds H₂O per MSCFDG. The maximum hydrocarbon content is about 3.0 pounds hydrocarbon per MSCFDG. This means that about 75% of the desiccant bed would be used for water removal and only 25% for hydrocarbon removal, if desiccants with a preferential adsorption for water are used. The silica gels, synthetic zeolites, and activated aluminas can be eliminated from further consideration on this basis.

Activated carbon has a preferential adsorption for hydrocarbons. Consequently, the use of this adsorbent was investigated to determine if an activated carbon plant was economically feasible.

Assuming that the plant would consist of three fixed beds, with one bed adsorbing, one bed cooling, and one bed regenerating, the vessel size and carbon loading were fixed by the maximum gas velocity consideration of 50 feet per minute based on empty vessel cross section. The cross sectional area required for each vessel to handle the vent gas stream of 425 MMSCFDG per day was calculated to be 10,300 square feet. For a 15-foot bed height, the mass of carbon required for each vessel is about 5,000,000 pounds for a total of 15,000,000 pounds carbon. (If the beds operate on a one-hour cycle, the adsorbate loading is about 1 pound per 100 pounds carbon. This is quite reasonable in view of the very low hydrocarbon partial pressure and should be obtainable.) The regeneration heat load required to heat the bed from 130 F to 500 F is about 500 MM Btu per hour. The lower quality activated carbons can probably be obtained in the \$0.25 pound range for very large quantities. Assuming an initial plant investment of \$7,000,000, including carbon, carbon replacement every two years as an operating expense, and fuel at \$0.20 per MM Btu, the cost of recovering 4,760 barrels per day (3 pounds hydrocarbon per MSCFDG) of oil from 425 MMSCFDG per day of vent gas is about \$2.28 per barrel. If less

than 100% recovery were obtained or the carbon beds deactivated rapidly, this cost would increase greatly.

It is doubtful, however, that activated carbon would last for two years in view of the fact that the retort gas contains large quantities of unsaturated hydrocarbons.

The use of a moving bed adsorption process was also investigated. For reasonable sized carbon particles ($d_p = 0.1$ inch), minimum fluidization velocity calculations indicate a vessel size equal to that of the retort if the total gas stream of 1,700 MMSCFDG per day were processed. Consequently, this approach was not pursued further.

6. Absorption

A brief look was taken at the case of a single stage absorption process, for example a venturi scrubber, to determine approximate lean oil circulation requirements for the recovery of 50% of the C_6 component and all of the heavier components in the equilibrium gas. Using completely denuded lean oil, a circulation rate of about 25 to 30 barrels lean oil per barrel of oil recovered was obtained. This oil requirement is not excessively high. However, high energy requirements necessary to strip the lean oil appear to make absorption less than a break-even operation. Detailed vapor-liquid equilibrium calculations with heat and material balances (preferably done by computer) would be necessary to adequately define the energy and equipment requirements.

Vapor-liquid equilibrium calculations, based on contacting the retort offgas (mist plus gas) with lean oil, yield approximately the same result. The lean oil requirement is somewhat higher 40 to 50 barrels lean oil per barrel incremental oil recovered, as a result of the simultaneous removal of mist from the gas stream.