

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Printed in the United States of America. Available from:
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161

NTIS price codes

Paper copy: **A04**

Microfiche copy: **A01**

**PHASE BEHAVIOR AND MINIMUM MISCIBILITY PRESSURES FOR
NITROGEN MISCIBLE DISPLACEMENT**

Topical Report

**By
Feliciano M. Llave
Ting-Horng Chung**

March 1987

Work Performed Under Cooperative Agreement No. FC22-83FE60149

**Prepared for
U.S. Department of Energy
Assistant Secretary for Fossil Energy**

**James W. Chism, Project Manager
Bartlesville Project Office
P.O. Box 1398
Bartlesville, OK 74005**

**Prepared by
IIT Research Institute
National Institute for Petroleum and Energy Research
P.O. Box 2128
Bartlesville, OK 74005**

TABLE OF CONTENTS

	<u>Page</u>
Abstract	1
Introduction.....	2
Phase Behavior Measurement.....	5
Experimental Equipment and Procedure.....	5
Experimental Results.....	7
Discussion.....	8
Phase Behavior Prediction.....	10
Equation of State Prediction and Discussion.....	10
Slim Tube MMP Determination.....	11
Experimental Apparatus.....	11
Experimental Procedure.....	12
System Preparation.....	12
Recombined Oil Preparation.....	12
Experimental Runs.....	13
Experimental Results and Discussion.....	14
Conclusion.....	17
References.....	17

TABLES

1. Measured liquid equilibrium compositions of nitrogen-hydrocarbon binary systems.....	20
2. Experimental results of ternary vapor-liquid equilibria.....	25
3. Experimental results of quaternary vapor-liquid equilibria.....	26
4. Lake Barre recombined oil compositions.....	27
5. Alaskan crude recombined oil compositions.....	28
6. Alaskan crude recombined oil compositions.....	29
7. Binary interaction parameter.....	30

ILLUSTRATIONS

1. Flow diagram for volumetric and VLE measurement apparatus.....	31
2. Liquid phase composition of N_2 - nC_7 binary system.....	32
3. Liquid phase composition for N_2 -normal decane system.....	32

ILLUSTRATIONS (continued)

	<u>Page</u>
4. Equilibrium phase composition for N ₂ -benzene binary system.....	33
5. Ternary C ₁ -nC ₄ -nC ₁₀ phase diagram.....	33
6. Ternary N ₂ -nC ₄ -nC ₁₀ phase diagram.....	34
7. Pseudoternary phase diagram of N ₂ -C ₁ -nC ₄ -nC ₁₀ system.....	34
8. Ternary phase diagram for N ₂ -C ₁ -nC ₁₀	35
9. Quaternary phase diagram for N ₁ -C ₁ -nC ₄ -nC ₁₀	36
10. Pseudoternary phase diagram of N ₂ -crude oil system.....	37
11. Psuedoternary phase diagram of N ₂ -crude oil system.....	38
12. Predicted psuedoternary phase diagram of N ₂ -crude oil system.....	39
13. Predicted psuedoternary phase diagram of N ₂ -crude oil system.....	40
14. Slim tube miscibility apparatus.....	41
15. Slim tube displacement test result.....	42
16. Oil recovery versus pressure.....	43
17. Ternary phrase diagram of N ₂ -C ₃ -nC ₁₀ system (calculated by PR equation of state).....	43
18. Oil recovery of nitrogen displacement in slim tube.....	44
19. Effect of light components on oil recovery.....	45
20. Effect of pressure and GOR on recovery.....	45
21. Reconstituted Lake Barre crude oil - percent oil recovery ⁷ versus pressure at 300° F.....	46
22. Oil recovery versus pressure.....	47
23. MMP and bubble point pressure versus GOR.....	48
24. Effect of temperature on MMP.....	49
25. MMP correlations.....	50
26. Recombined Alaskan crude oil - percent oil recovered versus pressure.....	51
27. Synthetic oil #1 - percent oil recovered versus pressure at 275° F..	52
28. Synthetic oil #2 - percent oil recovered versus pressure at 200° F..	53

NITROGEN MISCIBLE DISPLACEMENT METHOD

By Feliciano M. Llave* and Ting Horng Chung**

ABSTRACT

The phase behavior and minimum miscibility pressure (MMP) for nitrogen with light oils were studied. The phase behavior studies were performed on N_2 +hydrocarbon mixtures as well as N_2 +recombined oil systems at high pressures (above 4,000 psia). The synthetic oil system of $N_2+C_1+C_4+C_{10}$ was studied to approximate the phase behavior of crude oils with nitrogen and to investigate the effect of the presence of methane on phase behavior and N_2 MMP values. The phase behavior data are used in a computer simulator to match the slim tube displacement behavior and to provide an estimate of the MMP. The N_2 +recombined oil studies provide the complex behavior of multicomponent systems. Adjustment of parameters to predict the phase envelope has been made in order to use these parameters in equations-of-state (EOS) for predictions at various reservoir conditions. This provides a cross-check of the conditions of miscibility achieved during the slim tube experiments.

Experimental runs were performed in a slim tube apparatus to determine the MMP of stock-tank oils with nitrogen, recombined oils, and synthetic oils at pressures up to 10,000 psia and temperatures from 200° to 300° F. These experiments were performed using stock-tank oils with API gravities of 50.8° and 61.5°, recombined at different gas-oil ratios (GOR). The experimental results indicate the important contribution of the light and intermediate components of crude oil in decreasing the MMP and show the variation in oil recovery as a function of temperature. Similar N_2 MMP tests were performed on two synthetic mixtures containing $C_1, C_2, C_3, C_4, C_5, C_6, C_7, C_8, C_9, C_{10}$, and C_{12} . These studies will provide useful information for the implementation of the N_2 miscible displacement process.

* Research Engineer.
** Project Leader.

INTRODUCTION

Nitrogen has been widely used in oilfield operations for reservoir pressure maintenance, gas cycling, and gas lift. In recent years, the use of nitrogen for enhanced oil recovery has become an attractive method for some high-pressure reservoirs.

A thorough understanding of the phase behavior of the nitrogen gas and the crude oil is essential for application in enhanced oil recovery. The equilibrium phase diagram of nitrogen+crude oil systems can be used to establish whether a miscible or an immiscible condition will occur.

Ideally, the phase behavior of complex systems can be predicted by using equations of state (EOS) such as the Soave-Redlich-Kwong (SRK) or Peng-Robinson (PR) EOS. However, the use of an EOS for the prediction of these multicomponent systems may present a problem -- the lack of experimental phase behavior information needed to optimize these equations of state for more accurate predictions.

Most of the available literature related to this subject is on binary nitrogen-light alkane systems and includes binary system studies involving nitrogen and methane, ethane or propane which mainly concentrated on operations under cryogenic conditions. Most data in the literature for ternary and a few quaternary systems have concentrated on mixtures containing nitrogen and methane at low temperatures. Under these conditions, vapor-liquid equilibrium (VLE) and vapor-liquid-liquid equilibrium (VLLE) information have been reported.

Intermediate and high temperature studies involving nitrogen with alkanes ranging from butanes up to octanes¹⁻⁹, and the aromatics benzene^{10,11} and toluene,^{12,13} have been reported. Only a few data are available for systems containing components heavier than n-decane.¹⁴⁻¹⁶ The ternary study by Azarnoosh et al.¹⁷ presented the nitrogen+methane+n-decane VLE data at high temperatures and pressures. Data for nitrogen-containing quaternary and multicomponent systems under such conditions are scarce.

To understand the complex behavior of nitrogen+crude oil multicomponent systems, an initial study of systems containing three or four components can be helpful. These simpler systems would serve as the basis for understanding the behavior of multicomponent systems through analysis of simpler systems

represented by light, intermediate, and heavy components. Information generated from these VLE studies will help to determine binary interaction parameters in equations of state for more accurate representation of nitrogen + crude oil phase behavior.

This report presents results on the equilibrium compositions of binary, ternary, and quaternary systems of nitrogen+hydrocarbons at elevated pressures. The binary systems of nitrogen and n-heptane, n-octane, n-nonane, n-decane, n-dodecane, benzene and toluene were studied to provide additional VLE information on these binary systems and to check the consistency of the experimental techniques and procedures with data in the literature. The temperatures and pressures of this study are in the range of reservoir conditions. The ternary systems of methane+n-butane+n-decane and nitrogen+n-butane+n-decane were studied at 175° F and 4,000 psia to provide information on the phase diagram of the quaternary system of nitrogen+methane+n-butane+n-decane. This latter system exhibited the effect of methane on the behavior of the nitrogen + n-butane + n-decane mixture.

Phase behavior studies of recombined oil mixtures, which had stock-tank-oil gravities of 50.8° API (Alaskan crude) and 61.5° API (Lake Barre) were also performed. The phase diagram for the recombined Lake Barre crude oil with a GOR of 564 scf/bbl and the recombined Alaskan crude oil with a GOR of 250 scf/bbl were determined at 175° F and 4,000 psia. Both of these studies provided the opportunity to analyze the complexity of the phase behavior of a multicomponent mixture with nitrogen. The phase envelopes for these two systems were also compared to the predictions using the Peng-Robinson equation of state. A cross-check of the results from the slim tube test⁵ was also made. Phase envelopes were predicted for the two recombined oils at conditions that resulted in miscibility in the slim tube apparatus.

The important screening factor for the use of nitrogen in enhanced oil recovery is the minimum pressure for nitrogen to achieve miscibility with crude oil through a multiple contact process in porous media. The determination of the minimum miscibility pressure (MMP) of nitrogen with the oil would ensure miscibility at an operating pressure greater than the MMP at a specified reservoir temperature. The available literature data on the MMP of nitrogen with crude oils and synthetic oils are very scarce; therefore,

systematic slim tube tests were conducted to determine the MMP for N_2 miscible displacement. Two slim tube apparatus (one 64-ft long and another 120-ft long) were constructed for this purpose.

The first oil tested in the 64-ft slim tube was a propane-n-decane mixture (50 mole % C_3 + 50 mole % C_{10}) at 150° F and at pressures up to 7,000 psia. To determine compositional effects on the development of miscibility, a second mixture was then tested, with 80 mole percent propane and 20 mole percent n-decane. These displacement tests were also performed at the same temperature. The results determined the minimum propane fraction required in the oil for nitrogen to achieve miscibility.

The MMP was also determined for nitrogen and a stock-tank oil from West Bradley field, Grady County, OK, with an API gravity of 61.5°. The 64-foot displacement tests were conducted at 200° and 300° F and pressures from 5,000 to 7,000 psia. The same stock-tank oil was then reconstituted with propane (propane-oil ratio was 1,662 scf/bbl) and tested at the same operating conditions as the stock-tank oil. To further analyze the effect of the light and intermediate components in achieving nitrogen miscibility, methane, ethane, propane, and butane were used as solution gas components. The results indicate that the light and intermediate components (C_1 - C_5) in the oil are important for nitrogen to achieve miscibility at low pressures and that nitrogen requires a longer displacement distance to achieve multiple contact miscibility (MCM).

A 120-foot slim tube apparatus was constructed for the study of the recombined crude oils and synthetic oils. This apparatus provided a longer multi-contact length and a higher allowable operating pressure than the 64-ft slim tube. The MMP of nitrogen with the stock-tank oil of the Lake Barre crude (61.5° API gravity) was studied at 279° F. A slug injection scheme using a 0.1-PV slug of the solution gas followed by nitrogen drive was also performed at 279° F. The results showed a drastic decrease in MMP by injecting a hydrocarbon gas slug before N_2 injection. A series of slim tube tests using the Lake Barre oil, recombined with a solution gas at various gas-oil ratios (84, 247 and 564 scf/bbl) was performed at three temperatures, 225° , 279° , and 300° F. This provided a parametric analysis of the MMP as a function of oil composition and temperature.

The recombined oil of an Alaskan crude (API gravity 50.8°) was studied at 250° and at 300° F. The first batch of the recombined Alaskan oil was made using a solution gas composition which was the same as that for the Lake Barre recombined oil studies. A second batch of mixture was then made using a solution gas that was similar to that expected in the field. The results of the tests show the effect of the solution gas composition on the development of miscibility and oil recovery. Two synthetic oil mixtures containing C₁, C₂, C₃, C₄, C₅, C₆, C₇, C₈, C₉, C₁₀, and C₁₂ were also studied in this slim tube apparatus at temperatures from 200° to 300° F.

The phase behavior experiments and the slim tube experiments jointly provided the information for a better understanding of the mechanism by which nitrogen achieves miscibility with light oils. The phase behavior study provided the required information on the thermodynamic mixing aspect of the nitrogen+oil mixture, and the slim tube study determined the conditions under which nitrogen can achieve multi-contact miscibility with the oil.

PHASE BEHAVIOR MEASUREMENT

Experimental Equipment and Procedure

The experimental work was performed with an apparatus designed to facilitate sampling of both liquid and vapor phases at high pressures and temperatures by means of a flow switching technique. A schematic diagram of the experimental apparatus is shown in figure 1.

The VLE apparatus consisted of a 100-cm³ Ruska high-pressure, windowed PVT cell. The system was designed to handle high pressure studies (up to 6,000 psia). A Ruska magnetic pump was used to circulate each phase to ensure thorough mixing as well as to pump the fluid into the sampling valve for the chromatographic sampling. To obtain both liquid and vapor phase samples, a Valco switching valve was used to direct the flow of each phase. Sampling was done using an inline, high-pressure sampling valve with a volume of 1-5 μ l. The samples were analyzed on line with a gas chromatograph, which provided convenient, rapid, and accurate analysis of phase compositions. The apparatus was housed in an oven, temperature-controlled to $\pm 0.1^\circ$ F. Temperature was measured by means of a thermocouple connected to a digital temperature readout. Frequent thermocouple calibrations were made to ensure that no

temperature shifts occurred. System pressure was directly measured by means of a pressure transducer with an accuracy of ± 5 psia.

Compositions of the vapor and liquid samples were determined with a Hewlett-Packard 5890A gas chromatograph equipped with both thermal conductivity and flame ionization detectors. The chromatograph was equipped with a Porasil C column. Peak areas were determined using an HP 3392A electronic integrator.

The nitrogen used was Linde High Purity grade with a stated purity of 99.9 mole %. The methane used was an Ultra High Purity grade with a stated purity of 99.97 mole %. The propane and butane used were Instrument grade with a stated purity of 99.5 mole %. The solutes (n-heptane, n-octane, n-nonane, n-decane, benzene, and toluene) were all of stated purity of 99+ wt. % from Alfa Products. These materials were used without further purification.

The system was preflushed with n-pentane or petroleum ether and then dried under vacuum at 175° F. The system was then purged with nitrogen to remove remaining cleaning solvents and then evacuated overnight before the experiment was actually begun. On the experimental date, a measured amount of the heaviest hydrocarbon was injected into the PVT cell under vacuum. The secondary solvents (butane, and methane) were then added to the system when needed. Finally, the system was pressurized with nitrogen (or primary solvent) to the desired pressures. The magnetic circulation pump was then turned on to circulate the vapor phase to hasten the approach to equilibrium. Nitrogen was then introduced sparingly, to maintain the desired operating pressure, until the pressure stabilized.

After the system had reached equilibrium, vapor samples were collected in the sampling valve and carried by helium into the gas chromatograph for analysis. Sampling of the vapor phase continued until a stable compositional value was achieved (typically after three to four samples). Upon completion of the gas phase sampling, the switching valve was switched to liquid phase circulation to permit liquid phase sampling. The sampling lines were heated above the boiling point of the sample by means of electric heating coils to vaporize the liquid sample. Liquid phase sampling injections and analysis were repeated four or five times.

Experimental Results

The experimental results for the binary systems are given in table 1. These results cover a range of temperatures from 90° to about 212° F as well as pressures from 500 to 5,100 psia. The pressure-composition diagrams of some of these binaries are shown in figures 2 through 4. The liquid phase composition data from this experimental work were compared with literature data. As shown in the figures, the experimental work agrees well with the work of Legret et al.⁸ and Akers et al.⁷ for the N₂-C₇ system, Azarnoosh et al.¹⁴ for the N₂-C₁₀ system, and Miller et al.¹¹ for the N₂-benzene system. These comparisons provide an acceptable measure of the internal consistency of the experimental setup and procedure.

The results of the vapor-liquid equilibrium studies on the ternary systems of methane+n-butane+n-decane and nitrogen+n-butane+n-decane and the quaternary system of nitrogen+methane+n-butane+n-decane are given in tables 2 and 3 and shown in figures 5 through 7. No literature information was available for comparison for these systems. Figures 5 through 7 also show a comparison of the experimental results with the Peng-Robinson EOS predictions. The interaction parameters for the EOS were determined by the best fit of the binary data. As shown in the figures, deviations of the experimental and predicted results occurred near the critical region.

The phase envelope of a ternary system can be represented on a triangular phase diagram, but for quaternary or multicomponent systems, because of the extra degrees of freedom, the system components must be lumped into three pseudocomponents in order to be represented on the triangular phase diagram. In the study of the system of nitrogen+methane+n-butane+n-decane, the proportion of nitrogen to methane in the feed was fixed in equimolar ratio (1:1).

For the recombined oil mixtures, two stock-tank oils with API gravities of 50.8° (Alaskan crude) and 61.5° (Lake Barre) were used. The Lake Barre crude oil study was performed with a solution GOR of 564 scf/bbl at 175° F and 4,000 psia, and the Alaskan crude oil study, with a solution GOR of 250 scf/bbl at 175° F and 4,000 psia. The experimental results of these two crude oil studies are shown on the triangular phase diagrams in figures 10 and 11. These two figures also show a comparison of the experimental results with the Peng-Robinson EOS predictions.

For each of the ternary, quaternary, and recombined crude oil experimental runs, at least four samples of each phase were analyzed. The equilibrium compositions were determined by using both TCD and FID detectors, which were connected in series with the GC column. The nitrogen and methane compositions were determined using the TCD, while the other hydrocarbons were determined using the FID. The average uncertainty of the determined response factor was ± 0.5 percent.

Discussion

As shown in figure 9, the quaternary system of nitrogen+methane+n-butane+n-decane has four ternary system constituents: nitrogen+methane+n-decane, methane+n-butane+n-decane, nitrogen+n-butane+n-decane and nitrogen+methane+n-butane.

The system of nitrogen+methane+n-decane studied by Azarnoosh and McKetta at 160° F revealed a large two-phase region (fig. 8). Additional experimental runs were made on this system to check the consistency of the experimental work at the ternary level, which was previously confirmed with the binary studies. The nitrogen+n-decane and methane+n-decane binaries show two-phase behavior at 160° F and 4,000 psia. The nitrogen+n-decane binary exhibits a larger two-phase region than the methane+n-decane binary. This shows that increasing the methane composition in the ternary $N_2-C_1-n-C_{10}$ system decreases the size of the two-phase region.

For the ternary system of methane+n-butane+n-decane, the addition of n-butane to the methane+n-decane reduces the two-phase region. The limit of the phase envelope is at about 14 mole % of n-butane before the system becomes completely miscible at 175° F and 4,000 psia (figure 5). If the methane is completely replaced by nitrogen, the relative size of the two-phase region is larger, immiscible up to about 42 mole % of n-butane, as shown in figure 6. On the other hand, the ternary system of nitrogen+methane+n-butane is completely miscible at the same temperature and pressure. The addition of n-butane to the nitrogen+methane binary does not promote any two-phase regions at these conditions.

The quaternary system reflects all the effects of the constituent ternaries. In the limits of near negligible amounts of nitrogen in the feed, the predominant phase behavior is that of the small phase envelope

methane+n-butane+n-decane ternary system, while the phase boundary of nitrogen+n-butane+n-decane dominates the behavior at low methane concentrations. The phase envelope of the quaternary $N_2+C_1+C_4+C_{10}$ system can be represented by a pseudoternary phase diagram (fig. 7), which is shown as an inclined surface in figure 9. The addition of a fourth component to a ternary system produces a two-phase volume in a thermodynamic phase diagram, as shown in figure 9.

The recombined crude oil phase behavior studies using the two stock-tank oils, with API gravities of 50.8° and 61.5°, are presented in figures 10 and 11. The Lake Barre recombined oil mixture had a GOR of 564 scf/bbl, and the Alaskan crude had a GOR of 250 scf/bbl. Both of these measurements were made at 175° F and 4,000 psia. The compositions of these two recombined mixtures are presented in tables 4 and 5. These phase-behavior studies provided a means of checking the results of the slim tube displacement tests for these two sample oils. EOS prediction of the phase envelope of these two multicomponent mixtures are also shown in figures 10 and 11. From the results of the EOS prediction, the Lake Barre crude oil phase diagram indicates that at the experimental conditions, nitrogen cannot achieve miscibility through multiple contact with this crude oil. In a similar fashion, the phase diagram indicates that the nitrogen cannot achieve multiple contact miscibility (MCM) with the Alaskan crude oil at the given temperature and pressure. The results of the slim tube study will provide further information on the pressure and temperature requirement to achieve miscibility. To cross-check with the results of the slim tube experiments, phase diagrams of the two oils at different temperatures and pressures were constructed by EOS. The phase diagram for the Lake Barre crude was predicted at 225° F and at 5,000 and 6,000 psia. The phase diagram of the Alaskan crude was predicted at 300° F and at 6,000, 7,000 and 8,000 psia. Details of the prediction of the phase diagrams of the two recombined oil mixtures will be discussed in the following section.

PHASE BEHAVIOR PREDICTION

Equation of State Prediction and Discussion

The phase behavior of complex systems can be established by using cubic equations of state (EOS) such as the Soave-Redlich-Kwong (SRK)¹⁹⁻²⁰ or Peng-Robinson (PR) EOS.²¹ Research on phase behavior prediction using cubic EOS has gained wide acceptance in the industry because of the ease of use and acceptable accuracy these equations present.

One possible problem that equation of state prediction might face would be the lack of experimental phase behavior information needed to adjust the parameters in EOS for more accurate predictions, especially near the critical region. NIPER's research endeavor provides additional information on the phase behavior of simple systems leading to more complex multicomponents systems. The results of the binary, ternary, quaternary, and recombined crude oil systems have been previously presented in this report. The phase behavior prediction package used to fit and predict the phase diagrams utilizes the Peng-Robinson EOS to calculate the thermodynamic properties of the mixtures.

The binary interaction parameters used in the Peng-Robinson EOS were obtained either from the literature²² or by data fitting using the measured binary VLE data. A listing of these binary interaction parameters is presented in table 7. A comparison of the predicted phase envelope with the experimental results indicates good agreement for the methane+n-butane+n-decane system and the quaternary system of nitrogen+methane+n-butane+n-decane. However, the prediction for the ternary system of nitrogen + n-butane + n-decane shows a positive deviation in the region near the critical point (see fig. 7).

In the phase equilibrium calculations for recombined oil systems, a pseudoization technique was used. Several methods of representing the multicomponent system as pseudocomponents of hydrocarbons have been reported.²³⁻²⁵ A method for predicting critical properties of petroleum fraction has also been proposed.²⁶ In this study, the properties of each of the single carbon number groups have been treated as having the same critical properties as equivalent normal alkanes.

From results of the slim tube experiments, the Lake Barre recombined oil (GOR = 564 scf/bbl) has an MMP of about 4,850 psia at 225° F. The predicted phase diagrams at 225° F (fig. 12) showed that the nitrogen could achieve miscibility with this oil at pressures above 5,000 psia which was in agreement with the experimentally determined MMP for this mixture.

Another recombined oil mixture studied was that of Alaskan crude oil. The experimental work on this system was performed at 175° F and 4,000 psia. This mixture was recombined with the solution gas-B with a GOR of 250 scf/bbl. The EOS was tuned to match the equilibrium phase compositions. Figure 11 shows that the calculated two phase envelope had a slightly larger two-phase region compared to the experimental data. The EOS with the same parameters was used to generate the phase diagrams for the same system at 300° F and pressures of 6,000, 7,000, and 8,000 psia (fig. 13). The phase diagrams show that nitrogen can achieve miscibility with this recombined oil at of 7,000 psia and 300° F.

These two-phase behavior studies involving nitrogen-complex multicomponent crude oil systems provided information needed in the determination of conditions that will promote phase miscibility. The information gathered through this effort will provide tuning parameters for improved predictions of complex system phase diagrams.

SLIM TUBE MMP DETERMINATION

Experimental Apparatus

The experimental apparatus used for the slim tube displacement tests is illustrated in figure 14. One unit was a 64-foot slim tube, and the other was a 120-foot setup. Figure 14 shows the flow diagram for the 120-foot-long slim tube apparatus. The 120-foot slim tube apparatus utilized stainless steel tubes of 3/8-inch O. D. and 0.203-inch I. D. The tube was packed with silica sand of 140-200 mesh to simulate porous media. The porosity of this tube was 39 percent, and nitrogen permeability was 7 darcies, with a pore volume of 290 cm³. For this slim tube, the operating pressure was rated to 10,000 psig. The 64-foot slim tube utilized stainless steel tubes of 0.152-inch I.D. This tube was packed with sand of 60-100 mesh, which gave a porosity of 31.6 percent and permeability of 5 darcies. This unit was rated up to 7,000 psia and temperatures below 300° F. To facilitate observation of

the miscible conditions at the outlet of this tube, an inline sight glass was installed for experimental runs less than 6,000 psia. The oil and solvent gas injection was performed by means of a calibrated Temco positive-displacement pump. The effluent oil and gas were collected for the determination of the mass-balance and efficiency of the oil displacement by the solvent gas.

Experimental Procedure

The displacement experiments were performed at specified operating temperatures and pressures. The variation in the operating pressures permitted the determination of the minimum miscibility pressure.

The descriptions of the experimental procedures can be presented in three sections as follows:

System Preparation

The slim tube was initially flushed with 1.5 pore volume (PV) of toluene to eliminate residual materials present from the previous run. This was followed by flushing with about 1.5 PV of petroleum ether. Nitrogen gas was then purged through the coil to allow thorough drying. The apparatus was then evacuated to about 22-in. Hg. The oven temperature controller was then set to the desired experimental condition.

Recombined Oil Preparation

In situations where live oil was used, the stock-tank oil was recombined with solution gas in a 5-liter, high-pressure floating piston vessel (rated to 10,000 psia).

With the mixing vessel thoroughly cleaned, the unit was first completely filled with a pressure fluid (transmission oil) in one side, and the other side of the floating piston was evacuated. The next step was to inject the solution gas into the floating piston vessel at a pre-calculated pressure, until a known volume of transmission oil had been displaced. After a known amount of gas had been injected into the vessel, the stock-tank oil was pumped into the mixing vessel. The addition of the oil into the mixing vessel was accompanied by appropriate mixing using a rocking mechanical apparatus with the aid of stainless steel ball bearings inside the vessel. The volume of the

stock-tank oil to be added had been predetermined in order to establish the desired gas oil ratio (GOR). The mixture was then compressed to determine its bubble point pressure. The recombined oil mixture was then kept at pressures above the bubble point pressure.

Experimental Runs

When a live crude oil was to be used in the experiments, an oil miscible fluid (n-C₇ or n-C₁₀) had to be injected into the tube to build the pressure up to the testing pressure before the live oil was injected. This procedure prevented the flash of the live oil inside the slim tube. The requirement for the use of an oil miscible fluid ensured complete displacement of this fluid by the live oil after 1.5 PV injection. From the material balance of the injected and produced fluids, we determined the formation volume factor (FVF) for the live oil.

Once the slim tube was saturated with oil at the required experimental conditions, the displacing gas (nitrogen) was injected into the oil-saturated slim tube at a constant rate of about 200 to 500 ft/day (48 cm³/hr) by means of a high-pressure displacement pump. Beginning at the point of introducing the displacing gas into the slim tube, the amount of oil displaced and the gas produced were recorded as a function of time.

The experiment proceeded at the 48 cm³/hr rate until more than 1.2 PV of the displacing gas had been injected. When operating at lower pressures (less than 6,000 psia), it was possible to determine the point at which displacing gases passed through the output section of the slim tube by means of a sight glass. Through the sight glass, different kinds of phase behavior were observed at different pressures. These observations provided a first-hand tool in determining whether miscibility conditions were established. However, high-pressure operations eliminated the use of the sight glass setup. Therefore, under such extreme conditions, the experimental observation of the gas breakthrough (BT) point could not be made. The oil recovery was plotted versus equivalent hydrocarbon pore volumes of N₂ injected, as shown in figure 15. From this plot, we determined the BT point as well as the oil recovery at breakthrough and after 1.2 PV N₂ had been injected. These experiments were performed at different pressures until the MMP had been determined at the prevailing temperature. The MMP was determined from the oil recovery versus

pressure plot (fig. 16). The criterion for determining the MMP is the pressure at which there is a break in the slope of the recovery curve, with recovery levels near maximum (above 95 percent of OOIP).

Experimental Results and Discussion

The first oil tested in the 64-ft tube was a propane+n-decane mixture (in an equimolar ratio). The slim tube tests at 150° F and up to 7,000 psia showed that the nitrogen cannot achieve miscibility with this oil mixture. A second mixture was then made, with 80 mole % of propane and 20 mole % of n-decane. The displacement tests indicated that miscible displacement was established at 6,000 psia, whereas at 5,000 psia, immiscible displacement was observed. The MMP for this mixture would be about 5,500 psia. A ternary phase diagram (EOS prediction) of the N₂-C₃-C₁₀ system, figure 17, shows that the propane composition of the oil had to be at least 73 mole % in order for nitrogen to achieve miscibility at 150° F and 7,000 psia.

Slim tube tests were also performed on a stock-tank oil from West Bradley field, Grady County, OK., with API gravity of 61.5°. The 64-foot displacement tests were conducted at 200° and 300° F and pressures from 5,000 to 7,000 psia. The results indicated relatively low oil recoveries of less than 60 percent. Figure 18 show the increase of oil recovery as temperature increases. Sight glass observations indicate a clear interface between the oil phase and the displacing gas phase for all tests performed, which confirmed immiscible displacement under the operating conditions.

The same stock-tank oil was then reconstituted with propane (propane ratio was at 1,662 scf/bbl). When saturated with propane, the tests indicated recoveries greater than 90 percent at 4,000 psia and 250° F. The sight glass observations also showed a smooth phase transition without an interface occurring between the oil and the displacing gas front, clearly indicating that miscible displacement had been achieved. To further investigate the effect of the light and intermediate components in the development of nitrogen miscible displacement, methane, ethane, propane and butane were used as solution gas. Figure 19 shows that the oil recovery increases with more ethane or propane content in the oil. Methane and butane would increase oil recovery to a certain level before reaching a plateau. Since stock-tank oils would not contain significant amounts of intermediate components, the injected

nitrogen cannot vaporize enough light hydrocarbons from the dead oil to develop miscibility within the 64-ft length limit. These results indicate that the light and intermediate components (C_1 - C_5) in the oil are important for the nitrogen to achieve miscibility at low operating pressures, and that nitrogen requires a longer displacement distance to achieve multiple contact miscibility (MCM).

A 120-foot slim tube was then built for the study of the recombined crude oils and synthetic oils. A series of displacement tests was conducted using a Lake Barre field oil (61.5° API gravity), recombined with a solution gas-A (86.06 percent C_1 , 7.22 percent C_2 , 4.77 percent C_3 , 1.48 percent C_4 , and 0.47 percent C_5) at different GOR levels (84, 247 and 564 scf/bbl). Before the study of the recombined Lake Barre Crude, the stock-tank oil was studied at 279° F. The MMP for this stock-tank oil is about 9,400 psia. An injection scheme using a 0.1-PV slug of the solution gas followed by nitrogen was also tested at 279° F. Figure 20 presents the results of the stock-tank oil, 0.1-PV slug injection scheme and the recombined oil displacement at 279° F. Results indicate a drastic decrease of the MMP as a function of increase in GOR. At the same time, using the 0.1 PV slug injection scheme reduces the MMP by almost half, as compared with the displacement of stock-tank oil with straight nitrogen. Figures 21 and 22 present the results of the recombined Lake Barre crude displacement at 300° and 225° F, at different GOR levels. Figure 23 shows the MMP curve and bubble point pressure curve of the recombined oil as a function of the solution gas oil ratio (GOR). The MMP curves and the bubble point curve intersect at pressures above 4,000 psia, which will be the lower limit of the MMP for the sample oil. The temperature effect on the MMP is shown in figure 24 which shows that MMP slightly increases with temperature. A preliminary attempt was made to correlate the MMP as a function of a group parameter ($[C_2-C_5]/[MWC_{7+} \cdot (T)^{0.25}]$) given by Firoozabadi and Aziz.¹⁸ Figure 25 presents the results of the correlation. The figure shows the steeper slope of the MMP curve for the Lake Barre crude oil study compared to the Firoozabadi curve. Also note the relatively richer mixture, in terms of intermediate components, in the Firoozabadi correlations compared to the Lake Barre study.

The recombined oil mixture of an Alaskan crude, API gravity 50.8°, was studied at 250° F with two additional experiments performed at 300° F. The

solution gas-A was used for the recombination of this first set of experiments. This recombined oil had a solution GOR of 250 scf/bbl. The composition of this recombined oil is presented in table 5. A second batch of recombined oil mixture using a solution gas-B (5.64 mole % CO, 0.91 mole % N₂, 77.83 mole % C₁, 7.96 mole % C₂, 4.26 mole % C₃, 0.70 mole % i-C₄, 1.31 mole % n-C₄, 0.38 mole % i-C₅, 0.39 mole % n-C₅, 0.30 mole % C₆, 0.20 mole % C₇, 0.09 mole % C₈, 0.02 mole % C₉, and 0.01 mole % C₁₀) was prepared. The composition of this recombined oil is presented in table 6. This set of experiments was performed at 246° and at 300° F. The results of the second set of tests indicate a slightly lower recovery rate compared to that of the previous study using the solution gas-A. At 7,000 psia, the percent recovery was only about 75 and about 85 at 9,000 psi (recovery after 1.2 PV was injected). This indicates that miscibility was not achieved within the experimental pressure range. Experimental runs at 300° F were made for comparison with the previous runs at similar operating pressures. For the 300° F experiment, the recovery at gas breakthrough was estimated to be about 95 percent, indicating that the percent recovery after 1.2 PV injected would be greater than 95, slightly higher than that of the study using the solution gas-A. Figure 26 shows the results of the study for this recombined Alaskan crude.

Two synthetic oil mixtures were studied in the slim tube apparatus at a temperature range from 200° to 300° F. The results of the first mixture, containing 43.015 mole % C₁, 3.61 mole % C₂, 2.385 mole % C₃, 0.74 mole % C₄, 0.25 mole % C₅, and 0.50 mole % C₁₀, indicate a percent recovery of about 88 percent at 6,000 psia and about 93 percent at 8,000 psia. These tests were performed at 275° F. The plot in figure 27 shows the recovery versus pressure curve for this synthetic oil No. 1. The minimum miscibility pressure for this synthetic mixture is about 7,500 psia. The second batch of synthetic oil was studied at two temperature levels; 200° and 300° F. This mixture contained 53.66 mole % C₁, 4.50 mole % C₂, 2.98 mole % C₃, 0.92 mole % C₄, 0.31 mole % C₅, 13.12 mole % C₆, 4.95 mole % C₇, 4.94 mole % C₈, 4.87 mole % C₉, 4.87 mole % C₁₀, and 4.88 mole % C₁₂. Figure 28 presents results of the tests for this synthetic oil at 200° F. The plot indicates that the MMP for this mixture would be about 3,800 psia. In comparison, the EOS prediction presented in figure 29 indicates that the MMP would be about 3,900 psia.

CONCLUSIONS

1. The phase behavior information gathered from the binary, ternary and quaternary systems studied provides data to optimize EOS parameters for improved phase-behavior predictions.
2. The intermediate components (C_2-C_5) of the oil are important in allowing the N_2 to achieve miscibility with the oil. The N_2 displaces the oil through a stripping or vaporization process of the intermediate components.
3. Nitrogen can achieve miscibility with light oils at pressures higher than 4,000 psia. Injection of a solution gas slug before nitrogen injection can drastically reduce the MMP.
4. The nitrogen MMP decreases with the increase of solution gas oil-ratio. This indicates the strong effect of the volatile hydrocarbons in the oil on the miscibility pressure.
5. The nitrogen MMP slightly increases with temperature.
6. For the minimum miscibility correlation, the effect of the methane component of the oil needs to be included.

REFERENCES

1. Kalra, H., H. J. Ng., R. D. Miranda, and D. B. Robinson. Equilibrium Phase Properties of the Nitrogen-Isobutane System. *J. Chem. Eng. Data*, v. 23, No., 4, October 1978, p. 321.
2. Lehigh, W. R., and J. McKetta. Vapor Equilibrium in the Ethane-n-Butane-Nitrogen System. *J. Chem. Eng. Data*, v. 11, No. 2, April 1966, p. 180.
3. Akers, W. W., L. L. Attwell, and J. A. Robinson. Volumetric and Phase Behavior of Nitrogen-Hydrocarbon Systems; Nitrogen-n-Butane System. *Ind. Eng. Chem.*, v. 48, No. 12, December 1954, p. 2830.
4. Krishnan, T. R., H. Kalra, and D. B. Robinson. The Equilibrium Phase Properties of the Nitrogen-Isopentane System. *J. Chem. Eng. Data*, v. 22, No. 3, July 1977, p. 282.
5. Kalra H., D. B. Robinson, and G. J. Besserer. The Equilibrium Phase Properties of the Nitrogen-n-Pentane System. *J. Chem. Eng. Data*, v. 22, No. 2, April 1977, p. 215.

6. Poston, R. S., and J. McKetta. Vapor-Liquid Equilibrium in the n-Hexane-Nitrogen System. *J. Chem. Eng. Data*, v. 11, No. 2, July 1966, p. 364.
7. Akers, W. W., D. M. Kehn, and C. Kilgore. Volumetric and Phase Behavior of Nitrogen-Hydrocarbon Systems. *Ind. Eng. Chem.*, v. 46, December 1954, p. 2536.
8. Legret, D., D. Richon, and H. Renon. Vapor Liquid Equilibria up to 100 Mpa: New Apparatus. *AIChE J.*, v. 27, No. 2, March 1981, p. 203.
9. Wilcock, R. J., R. Battino, W. F. Danforth, and E. Wilhelm. Solubilities of Gases in Liquids II. The Solubilities of He, Ne, Ar, Kr, O₂, N₂, CO, CO₂, CH₄, CF₄, and SF₆ in 1-Octanol, n-Decane, and 1-decanol. *J. Chem. Therm.*, v. 10, No. 9, July 1978, p. 817.
10. Lewis, W. K., and C. D. Luke. Vapor-Liquid Equilibria of Hydrocarbons at High Pressures. *Ind. Eng. Chem.*, v. 25, July 1933, p. 725.
11. Miller, P., and B. F. Dodge. The System Benzene-Nitrogen Liquid-Vapor Phase Equilibria at Elevated Pressures. *Ind. Eng. Chem.*, v. 32, March 1940, p. 434.
12. Field, L. R., E. Wilhelm, and R. Battino. The solubility of Gases in Liquids. Solubility of N₂, O₂, CO, CO₂, CH₄, and CF₄ in Methyl Cyclohexane and Toluene at 283 to 313 K. *J. Chem. Therm.*, v. 6, No. 3, January 1974, p. 237.
13. Prausnitz, J. M., and P. R. Benson. Solubility of Liquids in Compressed Hydrogen, Nitrogen, and Carbon Dioxide. *AIChE J.*, v. 5, 1959, p. 161.
14. Azarnoosh, A., and J. J. McKetta. Nitrogen-n-Decane in the Two-Phase Region. *J. Chem. Eng. Data*, v. 8, October 1963, p. 494.
15. D'Avila, S. G., B. K. Kaul, and J. Prausnitz. Solubilities of Heavy Hydrocarbons in Compressed Methane and Nitrogen. *J. Chem. Eng. Data*, v. 21, No. 4, October 1976, p. 488.
16. Lin, H. M., H. Kim, and K. C. Chao. Gas-Liquid Equilibria in Nitrogen-n-Hexadecane Mixtures at Elevated Temperatures and Pressures. *Fluid Phase Equil.*, v. 7, 1981 p. 181.
17. Azarnoosh, A., and J. J. McKetta. Vapor-Liquid Equilibrium in the Methane-n-Decane-Nitrogen. *J. Chem. Eng. Data*, v. 8, October 1963, p. 513.
18. Firoozabadi, A., and K. Aziz. Analysis and Correlation of Nitrogen and Lean-Gas Miscibility Pressure. *SPE Reservoir Engineering*, v. 1, No. 6, November 1986, p. 575.

19. Soave, G. Equilibrium Constants From a Modified Redlich-Kwong Equation of State. *Chemical Engineering Science*, v. 27, 1972, p. 1197.
20. Graboski, M. S., and T. E. Daubert. A Modified Soave Equation of State for Phase Equilibrium Calculations. 1. Hydrocarbon Systems. 2. Systems Containing CO₂, H₂S, N₂, and CO. *Ind. and Eng. Chemistry Process Design and Dev.*, v. 17, No. 4, 1978, p. 448.
21. Peng, D. Y., and D. B. Robinson. A New Two-Constant Equation of State. *Ind. and Eng. Chemistry Fundamentals*, v. 15, No. 1, 1976, p. 59.
22. Oellrich, L., U. Plocker, J. M. Prausnitz, and H. Knapp. Equation-of-State Methods for Computing Phase Equilibria and Enthalpies. *Int. Chem. Eng.*, v. 21, No. 1, January 1981, p. 1.
23. Whitson, C. H. Characterizing Hydrocarbon Plus Fractions. *SPE J.*, August 1983, p. 683.
24. Li, Y. K., L. X. Nghiem, and A. Siu. Phase Behavior Computations for Reservoir Fluids: Effect of Pseudo-Components on Phase Diagrams and Simulation Results. *J. of Canadian Pet. Technology*, November-December 1985, p. 29.
25. Gonzalez, E., P. Colonos, and I. Rusinel. A New Approach for Characterizing Oil Fractions, and for Selecting Pseudo-Components of Hydrocarbons. *J. of Canadian Pet. Technology*, March-April 1986, p. 78.
26. Twu, C. H. An Internally Consistent Correlation for Predicting the Critical Properties and Molecular Weights of Petroleum and Coal-Tar Liquids. *Fluid Phase Equilibria*, v. 16, 1984, p. 137.

TABLE 1. - Measured liquid equilibrium compositions of nitrogen-
hydrocarbon binary systems

Nitrogen - n-Heptane

Pressure, psia	Mole fraction n-heptane in liquid
T = 90° F	
925.0	0.910
1802.0	0.845
2800.0	0.801
3875.0	0.726
4600.0	0.704
5068.0	0.684
T = 124° F	
797.0	0.944
1510.0	0.881
2812.0	0.797
3668.0	0.748
4308.0	0.711
4965.0	0.665
T = 175° F	
998.0	0.916
1995.0	0.823
3027.0	0.761
3945.0	0.696
4980.0	0.628
T = 200° F	
866.0	0.909
1877.0	0.824
2784.0	0.747
3984.0	0.661
4925.0	0.603

TABLE 1. - Measured liquid equilibrium compositions of nitrogen-hydrocarbon binary systems (continued)

Nitrogen - n-Octane

Pressure, psia	Mole fraction n-octane in liquid
T = 120° F	
615.0	0.940
1306.0	0.897
2162.0	0.839
3086.0	0.781
4112.0	0.727
T = 160° F	
468.0	0.957
614.0	0.945
1033.0	0.917
1519.0	0.874
2542.0	0.799
3581.0	0.735
5082.0	0.653

Nitrogen - n-Nonane

Pressure, psia	Mole fraction n-nonane in liquid
T = 120° F	
568.0	0.952
1086.0	0.914
2110.0	0.840
3043.0	0.790
4070.0	0.738
5025.0	0.698
T = 160° F	
540.0	0.950
1065.0	0.908
2033.0	0.832
3020.0	0.777
4016.0	0.718
5038.0	0.668

TABLE 1. - Measured liquid equilibrium compositions of nitrogen-
hydrocarbon binary systems (continued)

Nitrogen - n-Decane

Pressure, psia	Mole fraction n-decane in liquid
T = 160° F	
583.0	0.931
1083.0	0.884
2003.0	0.804
3065.0	0.727
3972.0	0.675
5024.0	0.620

Nitrogen - n-Dodecane

Pressure, psia	Mole fraction n-decane in liquid
T = 130° F	
712.0	0.942
1667.0	0.864
2599.0	0.804
3505.0	0.752
4260.0	0.720
4900.0	0.684
T = 160° F	
512.0	0.945
1476.0	0.862
2209.0	0.788
3147.0	0.742
4038.0	0.693
5031.0	0.651
T = 200° F	
450.0	0.952
1364.0	0.878
2363.0	0.824
3330.0	0.762

TABLE 1. - Measured liquid equilibrium compositions of nitrogen-hydrocarbon binary systems (continued)

Nitrogen - Benzene

Pressure, psia	Mole fraction benzene in liquid
T = 86° F	
982.0	0.969
1908.0	0.943
2900.0	0.919
4230.0	0.892
5060.0	0.878
T = 167° F	
1065.0	0.961
2021.0	0.925
2952.0	0.894
3967.0	0.862
5170.0	0.827
T = 212° F	
977.0	0.959
2105.0	0.910
3060.0	0.872
3967.0	0.838
5036.0	0.799

TABLE 1. - Measured liquid equilibrium compositions of nitrogen-
hydrocarbon binary systems (continued)
Nitrogen - Toluene

Pressure, psia	Mole fraction toluene in liquid
T = 122° F	
528.0	0.982
1021.0	0.968
2055.0	0.938
3070.0	0.912
4025.0	0.891
5127.0	0.861
T = 167° F	
602.0	0.973
945.0	0.966
2033.0	0.929
3375.0	0.889
4003.0	0.870
5044.0	0.841

TABLE 2. - Experimental results of ternary vapor-liquid equilibria
Methane+n-Butane+n-Decane
T = 175° F and 4,000 psia

Mole fraction of methane in		Mole fraction of n-butane in	
vapor	liquid	vapor	liquid
0.8801	0.7299	0.0817	0.1309
0.8987	0.7171	0.0644	0.1121
0.9466	0.6995	0.0152	0.0417
0.9621	0.6793	0.0000	0.0000

Nitrogen+n-Butane+n-Decane
T = 175° F and 4,000 psia

Mole fraction of nitrogen in		Mole fraction of n-butane in	
vapor	liquid	vapor	liquid
0.9763	0.3194	0.0159	0.0951
0.9680	0.3354	0.0253	0.1455
0.9602	0.3186	0.0332	0.1635
0.9579	0.3159	0.0348	0.1772
0.9483	0.3115	0.0439	0.1883
0.9437	0.3158	0.0491	0.2308
0.9000	0.3300	0.0899	0.3127
0.8877	0.3514	0.1023	0.3261
0.8868	0.3542	0.1225	0.3636
0.8559	0.3586	0.1329	0.3761
0.8525	0.3682	0.1355	0.3779
0.8423	0.3720	0.1454	0.3803
0.8377	0.3803	0.1498	0.3905
0.8275	0.3919	0.1595	0.3953
0.8270	0.3885	0.1594	0.3995
0.8139	0.4243	0.1733	0.4115
0.7781	0.4401	0.2053	0.4104

TABLE 3. - Experimental results of quaternary vapor-liquid equilibria
 Nitrogen+Methane+n-Butane+n-Decane
 T = 175° F and 4,000 psia

Mole fraction of nitrogen in		Mole fraction of methane in		Mole fraction of n-butane in	
vapor	liquid	vapor	liquid	vapor	liquid
0.5063	0.1627	0.4864	0.3080	0.0000	0.0000
0.4934	0.1653	0.4861	0.3093	0.0111	0.0434
0.4921	0.1857	0.4444	0.2923	0.0506	0.1630
0.4888	0.2305	0.3768	0.2652	0.1173	0.2826
0.4848	0.1722	0.4813	0.3102	0.0240	0.0887
0.4567	0.2480	0.3717	0.2788	0.1461	0.2966
0.4495	0.2216	0.4034	0.2919	0.1216	0.2710
0.4340	0.2248	0.3944	0.2947	0.1255	0.2562
¹ 0.2737		¹ 0.2837		¹ 0.3201	

¹Single phase region.

TABLE 4. - Lake Barre recombined oil compositions

Component	Stock-tank Oil mol fr.	Solution gas mol fr.	Recombined oil composition		
			GOR = 83.5 scf/bbl mol %	GOR = 247.0 SCF/bbl, mol %	GOR = 563.6 scf/bbl mol %
N ₂	0.00000	0.00000	0.0000	0.0000	0.0000
C ₁	0.00000	0.86032	9.3690	22.6885	38.6197
C ₂	0.00000	0.07220	0.7863	1.9041	3.2411
C ₃	0.00000	0.04770	0.5195	1.2580	2.1413
C ₄	0.00050	0.01480	0.2057	0.4271	0.6919
C ₅	0.02420	0.00498	2.2107	1.9131	1.5572
C ₆	0.09240	0.00000	8.2337	6.8032	5.0922
C ₇	0.16100	0.00000	14.3467	11.8541	8.8727
C ₈	0.1930	0.00000	17.1982	14.2102	10.6362
C ₉	0.15640	0.00000	13.9368	11.5154	8.6192
C ₁₀	0.11910	0.00000	10.6130	8.7691	6.5636
C ₁₁	0.05420	0.00000	4.8298	3.9906	2.9870
C ₁₂	0.04400	0.00000	3.9208	3.2396	2.4248
C ₁₃	0.04470	0.00000	3.9832	3.2912	2.4634
C ₁₄	0.03780	0.00000	3.3684	2.7831	2.0832
C ₁₅₊	0.07270	0.00000	6.4783	5.3527	4.0065
Total	1.00000	1.00000	100.0000	100.0000	100.0000

	N ₂	0.0000	0.0000
	C ₁ -C ₆	21.3249	34.9940
	C ₇₊	78.6751	65.0060
		0.0000	0.0000
		51.3434	48.6566

TABLE 5. - Alaskan crude recombined oil compositions

Component	Stock-tank oil composition, mol fr.	Solution gas composition, mol fr.	Recombined oil composition, GOR = 250.0 scf/bbl mol %
N ₂	0.00000	0.00000	0.00000
C ₁	0.00000	0.86032	27.5845
C ₂	0.00000	0.07220	2.3150
C ₃	0.00020	0.04770	1.5430
C ₄	0.00750	0.01480	0.9841
C ₅	0.03650	0.00498	2.6394
C ₆	0.07220	0.00000	4.9050
C ₇	0.11580	0.00000	7.8671
C ₈	0.14010	0.00000	9.5180
C ₉	0.10700	0.00000	7.2693
C ₁₀	0.09620	0.00000	6.5355
C ₁₁	0.04510	0.00000	3.0640
C ₁₂	0.03600	0.00000	2.4457
C ₁₃	0.05020	0.00000	3.4104
C ₁₄	0.06230	0.00000	4.2325
C ₁₅	0.03760	0.00000	2.5544
C ₁₇₊	0.19330	0.00000	13.1322
Total	1.00000	1.00000	100.0000

N ₂	0.0000
C ₁ -C ₆	39.9709
C ₇₊	60.0291

TABLE 6. - Alaskan crude recombined oil compositions

Component	Stock-tank oil composition, mol fr.	Solution gas composition mol. fr.	Recombined oil composition GOR = 250.0 scf/bbl, mol %
N ₂	0.00000	0.00910	0.3078
CO ₂	0.00000	0.05640	1.7511
C ₁	0.00000	0.77830	24.2541
C ₂	0.00000	0.07960	2.4774
C ₃	0.00020	0.04260	1.3679
C ₄	0.00750	0.02010	1.1468
C ₅	0.03650	0.00770	2.7529
C ₆	0.07220	0.00300	5.0607
C ₇	0.11580	0.00200	8.0288
C ₈	0.14010	0.00090	9.6654
C ₉	0.10700	0.00020	7.3665
C ₁₀	0.09620	0.00010	6.6202
C ₁₁	0.04510	0.00000	3.1023
C ₁₂	0.03600	0.00000	2.4764
C ₁₃	0.05020	0.00000	3.4531
C ₁₄	0.06230	0.00000	4.2855
C ₁₅	0.03760	0.00000	2.5864
C ₁₇₊	0.19330	0.00000	13.2967
Total	1.00000	1.00000	0.09130
100.0000			

N ₂	0.3078
CO ₂	1.7511
C ₁ -C ₆	37.0598
C ₇₊	60.8813

TABLE 7. - Binary interaction parameter

Binary pair	Interaction parameter ¹ k_{ij}
$N_2 - CH_4$	0.031
$N_2 - n-C_4H_{10}$	0.007
$N_2 - n-C_{10}H_{22}$	0.127
$CH_4 - n-C_4H_{10}$	0.027
$CH_4 - n-C_{10}H_{22}$	0.042
$n-C_4H_{10} - n-C_{10}H_{22}$	0.008

¹For Peng-Robinson equation of state.

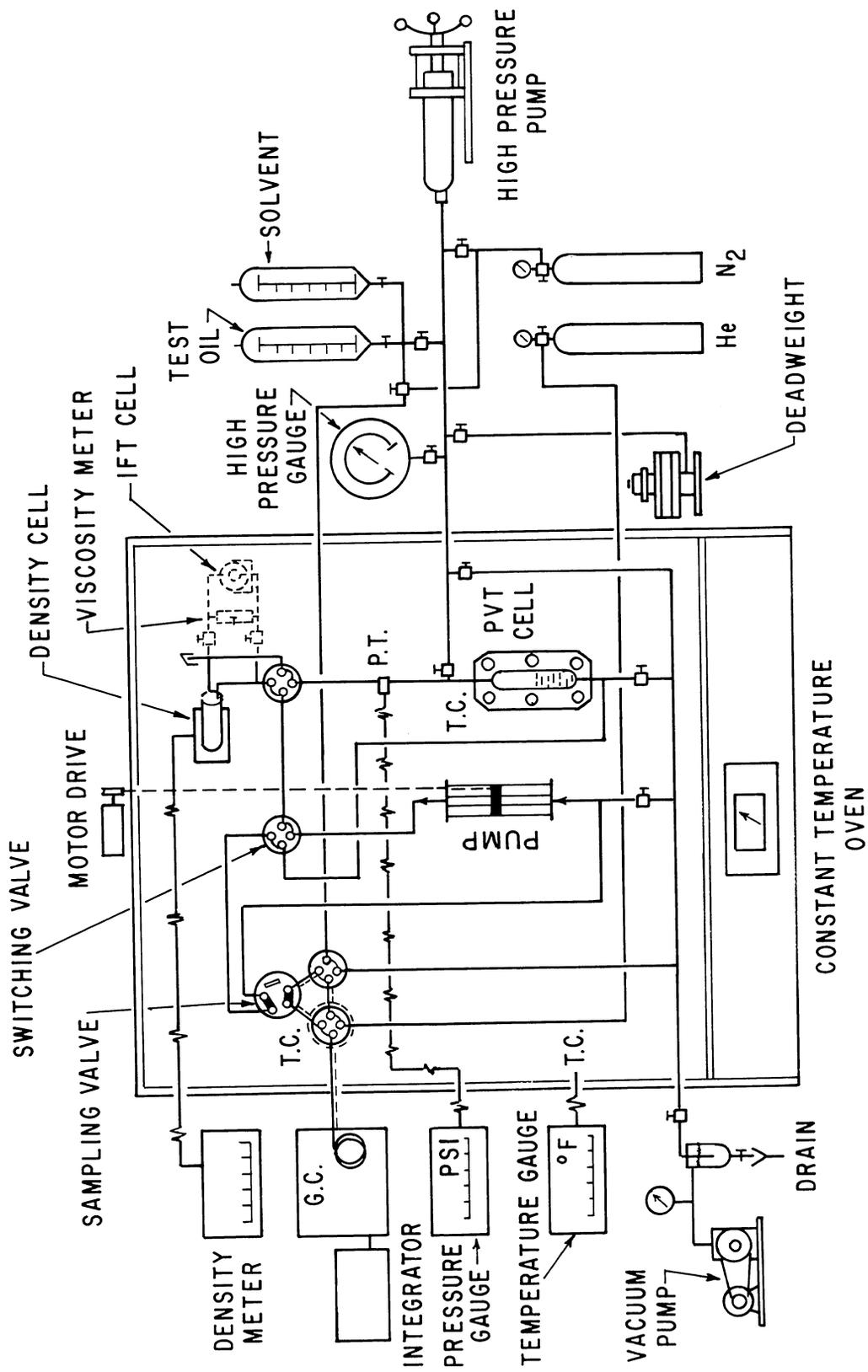


FIGURE 1. - Flow diagram for volumetric and VLE measurement apparatus.

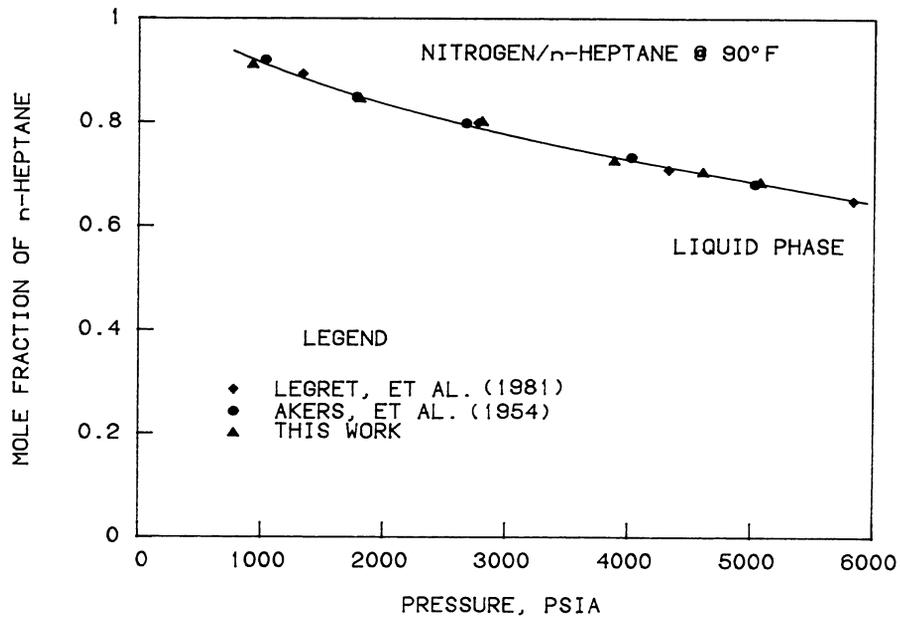


FIGURE 2. - Liquid phase composition of N₂-nC₇ binary system.

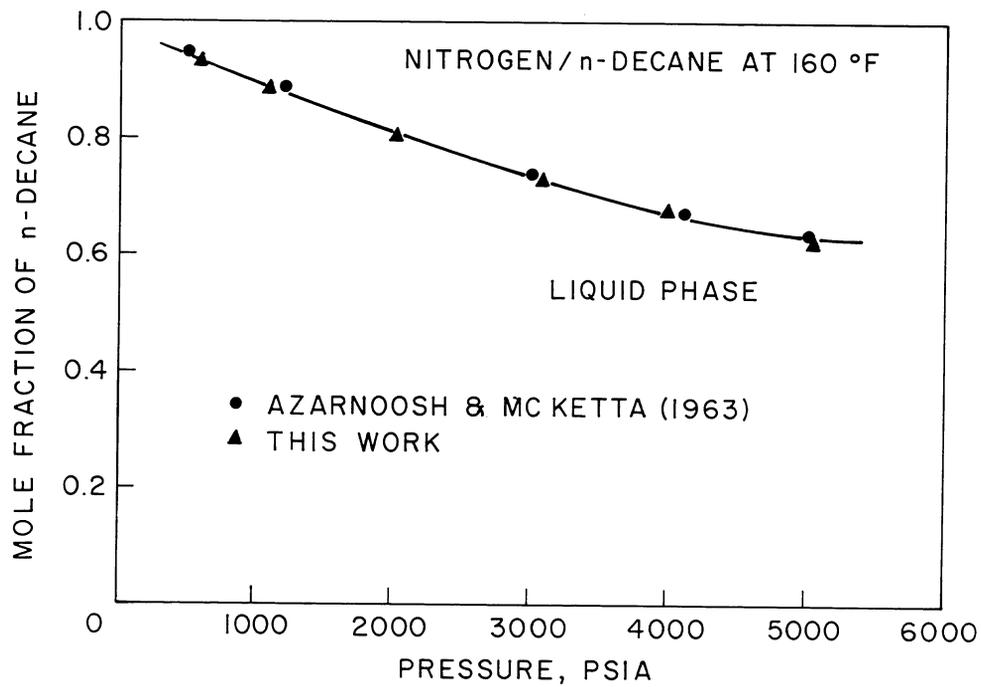
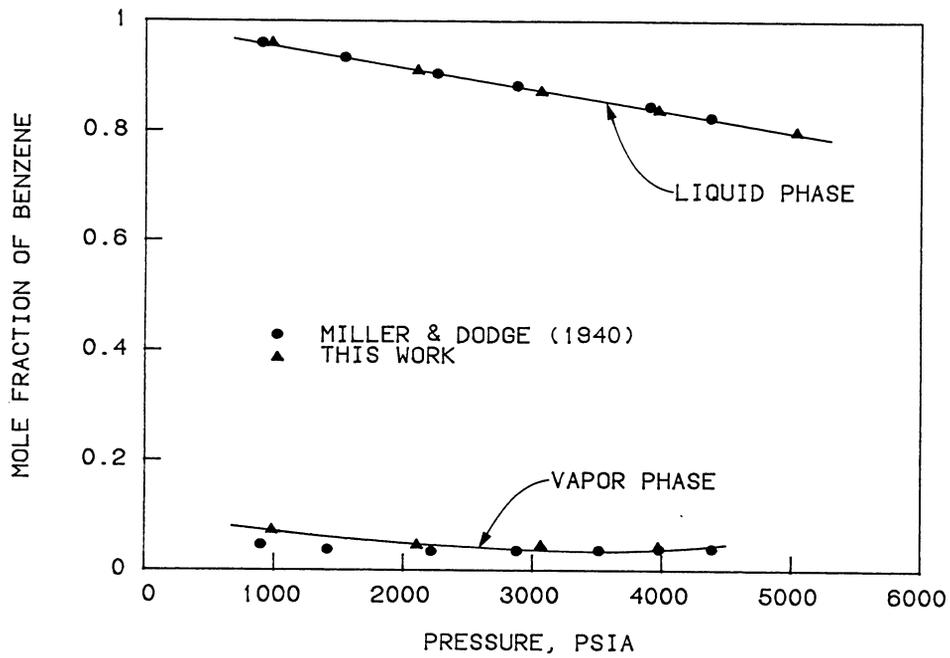


FIGURE 3. - Liquid phase composition for N₂-normal decane system.



COMPARISON OF RESULTS
NITROGEN/BENZENE AT 212° F

FIGURE 4. - Equilibrium phase composition for N₂-benzene binary system.

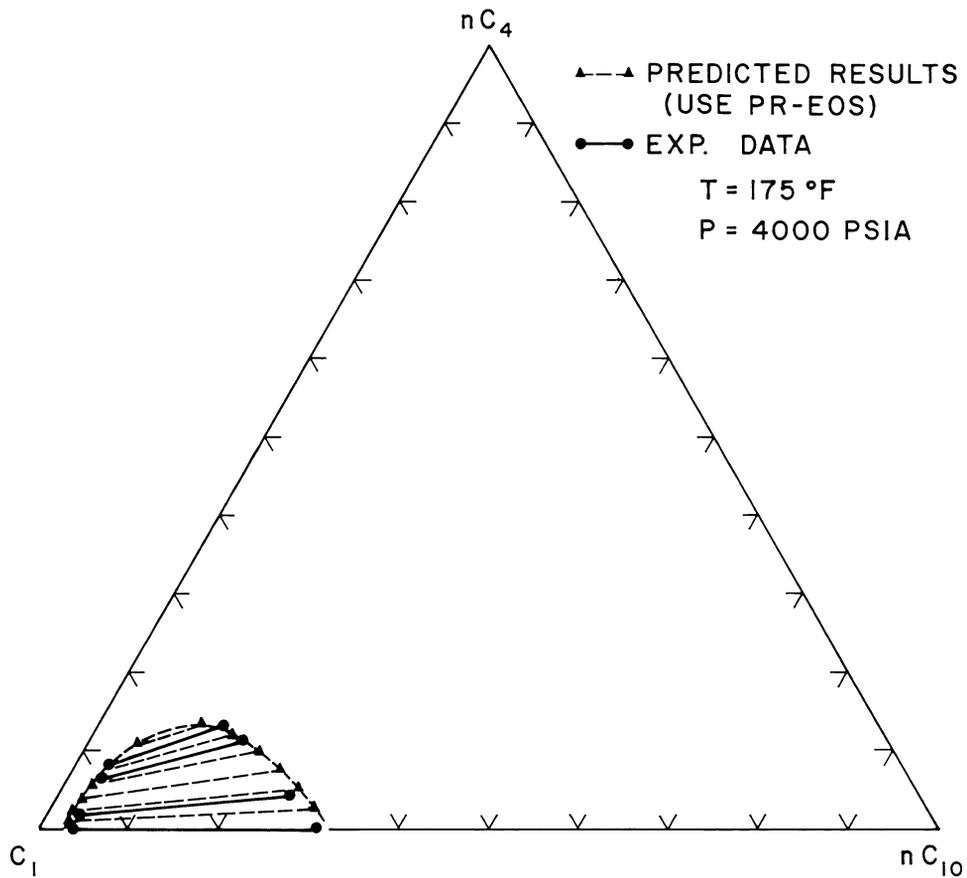


FIGURE 5. - Ternary C₁-nC₄-nC₁₀ phase diagram.

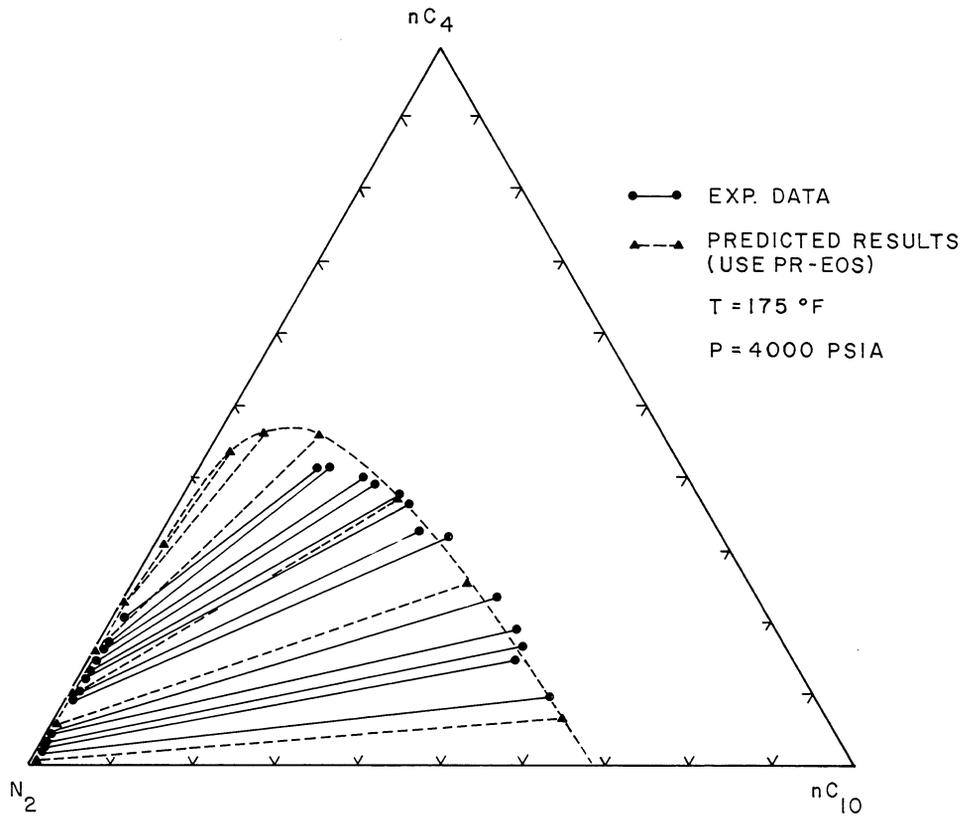


FIGURE 6. - Ternary N_2 - nC_4 - nC_{10} phase diagram.

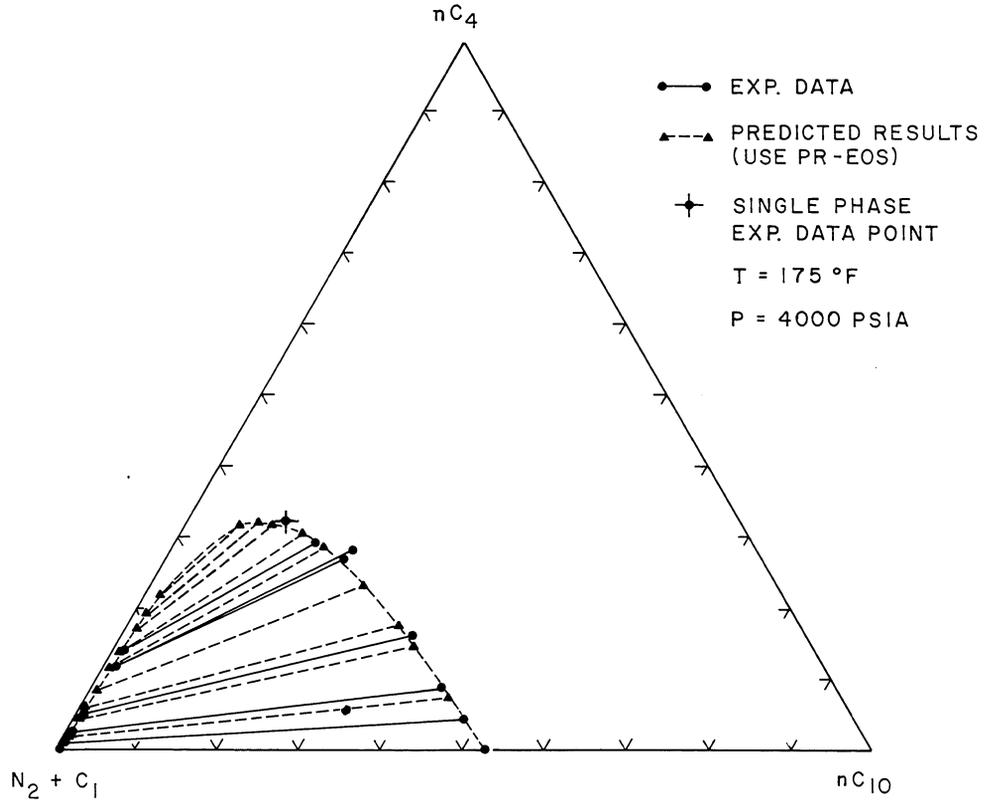


FIGURE 7. - Pseudoternary phase diagram of N_2 - C_1 - nC_4 - nC_{10} system.

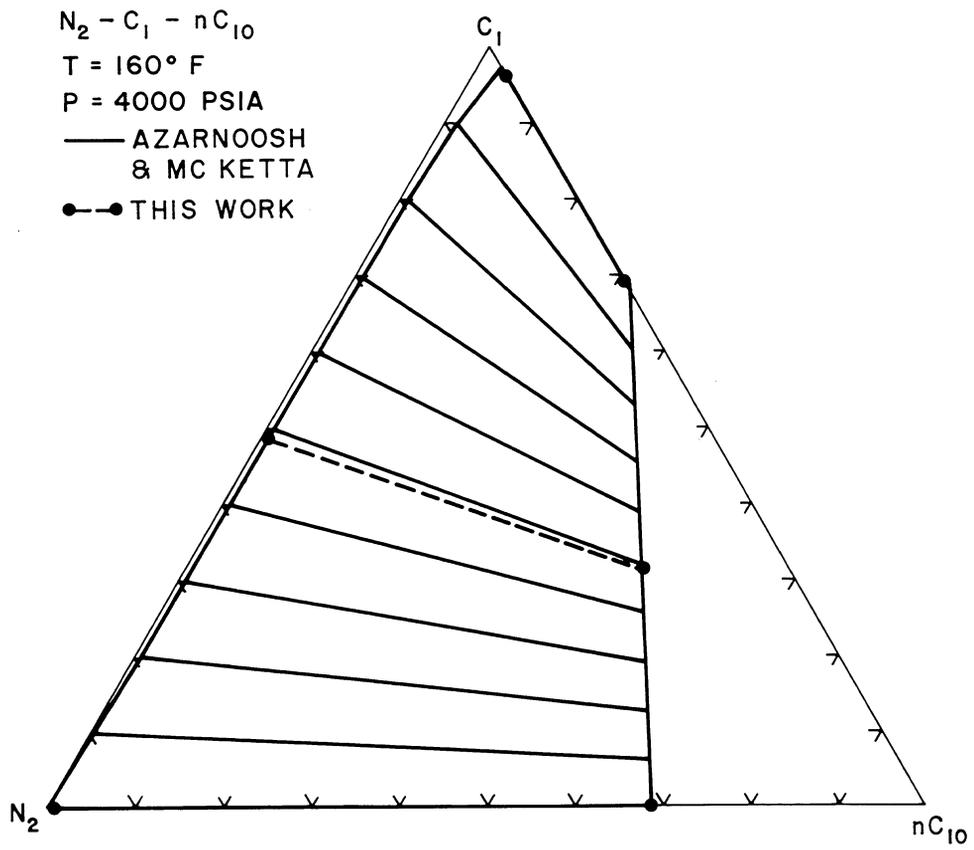


FIGURE 8. - Ternary phase diagram for $N_2-C_1-nC_{10}$.

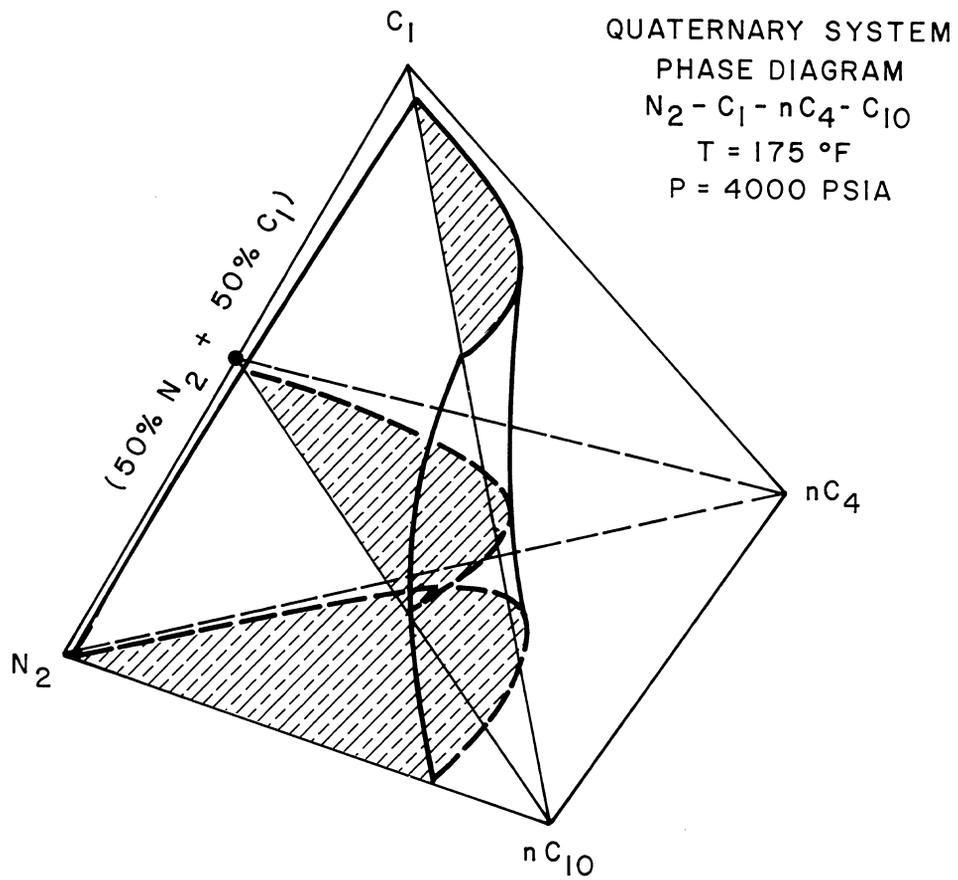
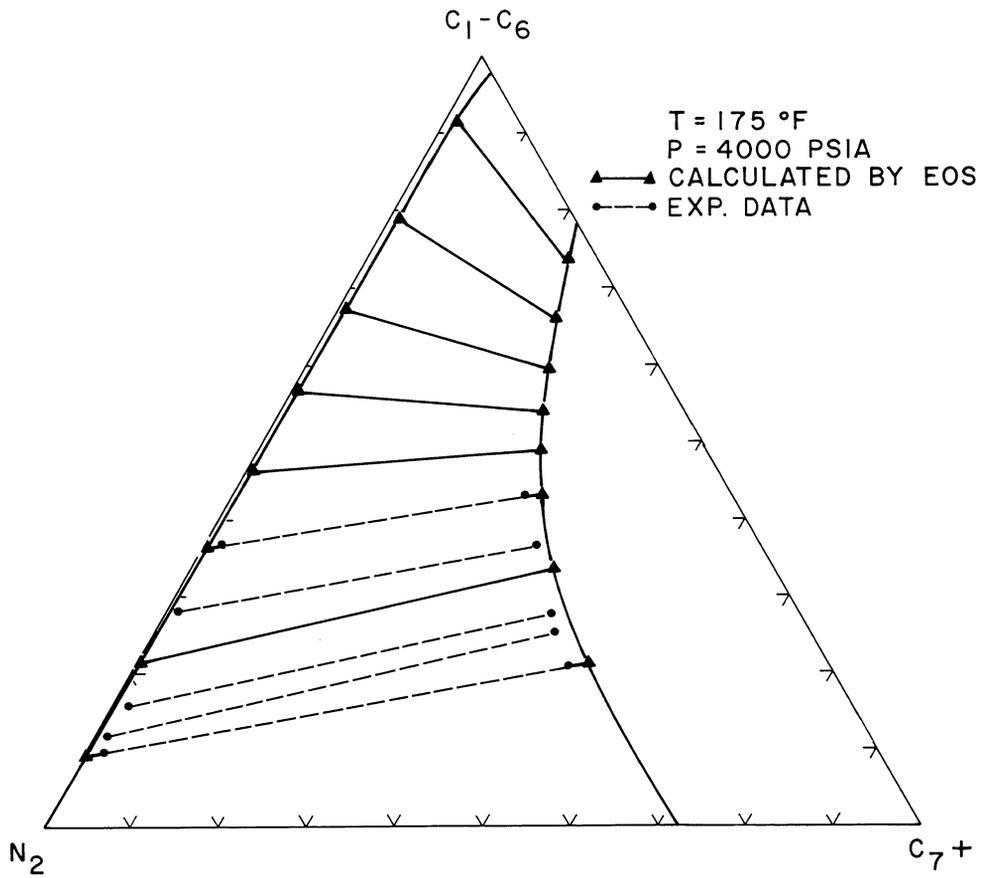


FIGURE 9. - Quaternary phase diagram for $N_2 - C_1 - nC_4 - nC_{10}$.



COMPARISON OF EXPERIMENTAL VS CALCULATED
 N_2 - RECOMBINED OIL PHASE DIAGRAM

FIGURE 10. - Pseudoternary phase diagram of N_2 -crude oil system.

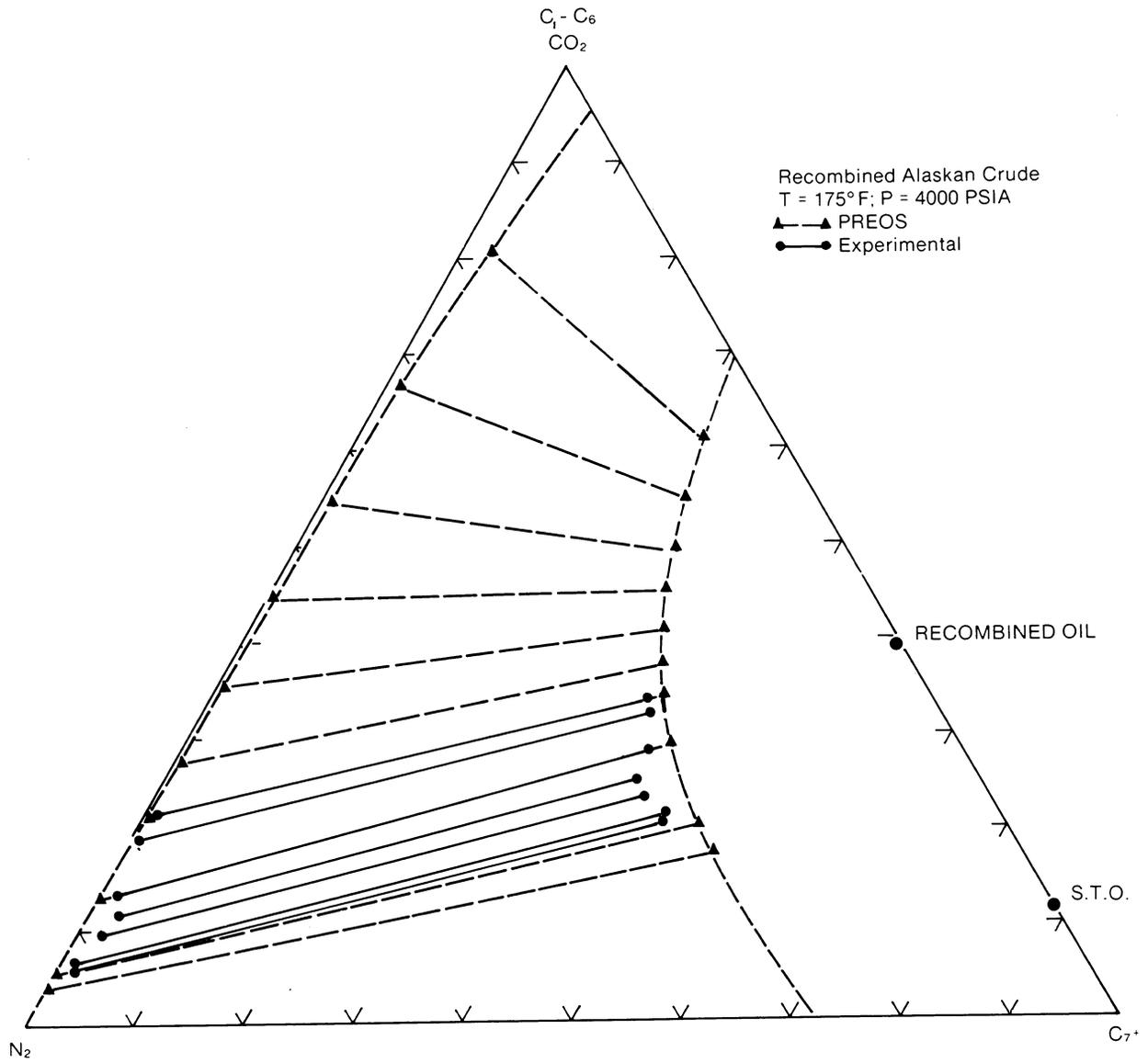


FIGURE 11. - Pseudoternary phase diagram of N₂-crude oil system.

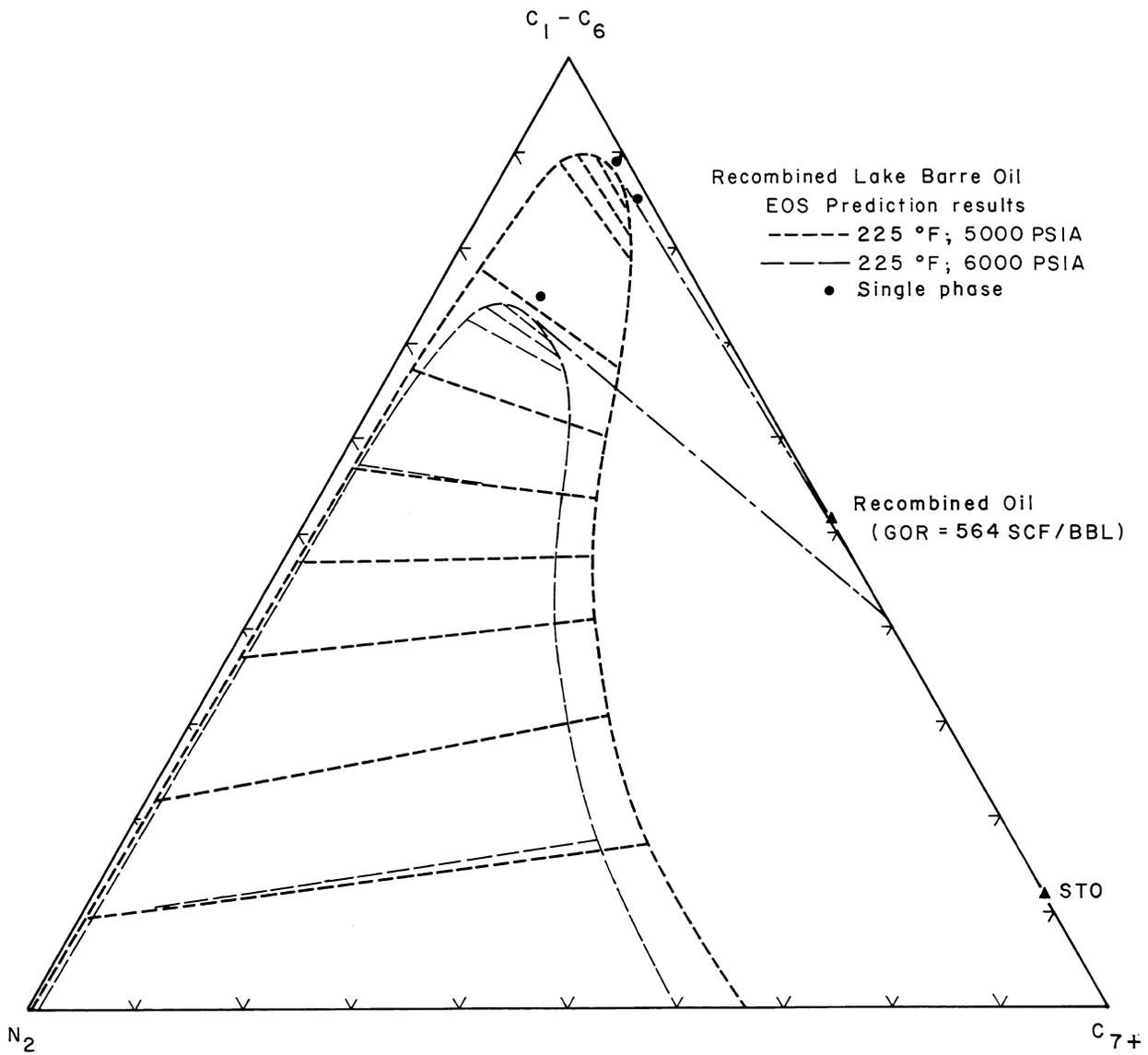


FIGURE 12. - Predicted pseudoternary phase diagram of N_2 -crude oil system.

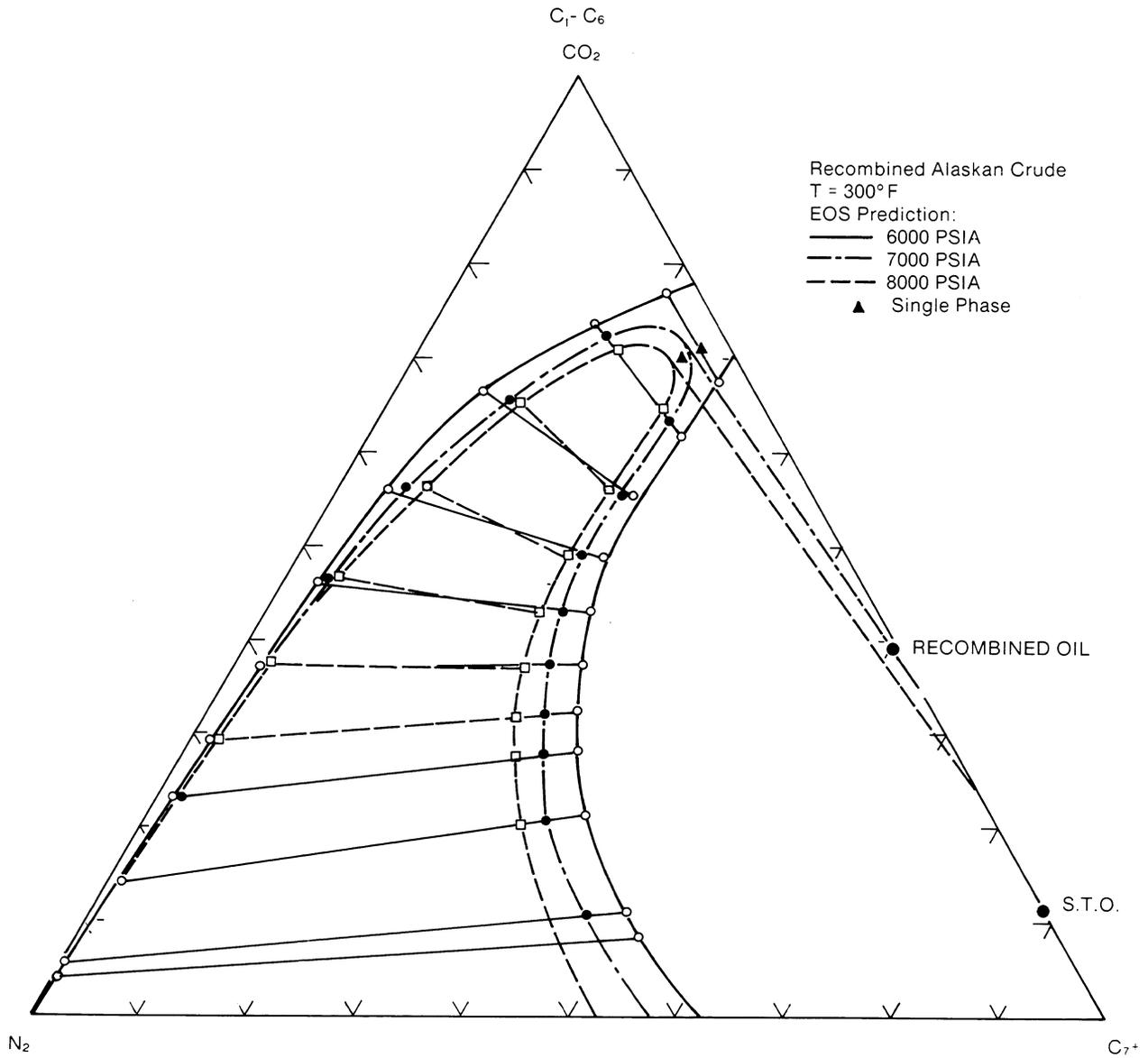


FIGURE 13. - Predicted pseudoternary phase diagram of N₂-crude oil system.

SLIM TUBE MISCIBILITY APPARATUS

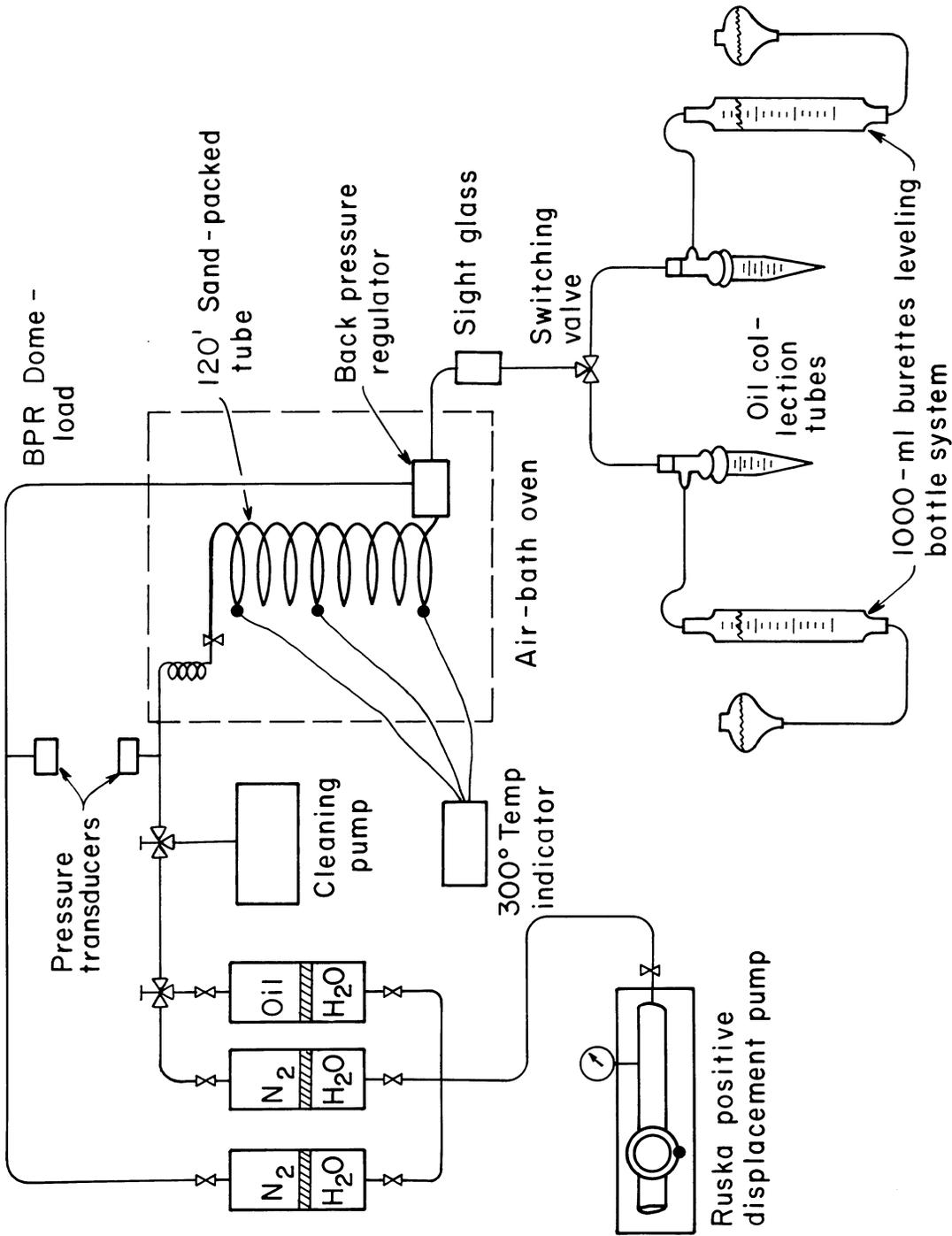


FIGURE 14. - Slim tube miscibility apparatus.

Recombined Lake Barre Crude Slim Tube Tests

Percent Recovery vs HCPV

GOR = 247 SCF/bbl

Temperature = 279°F Pressure = 8000 psia

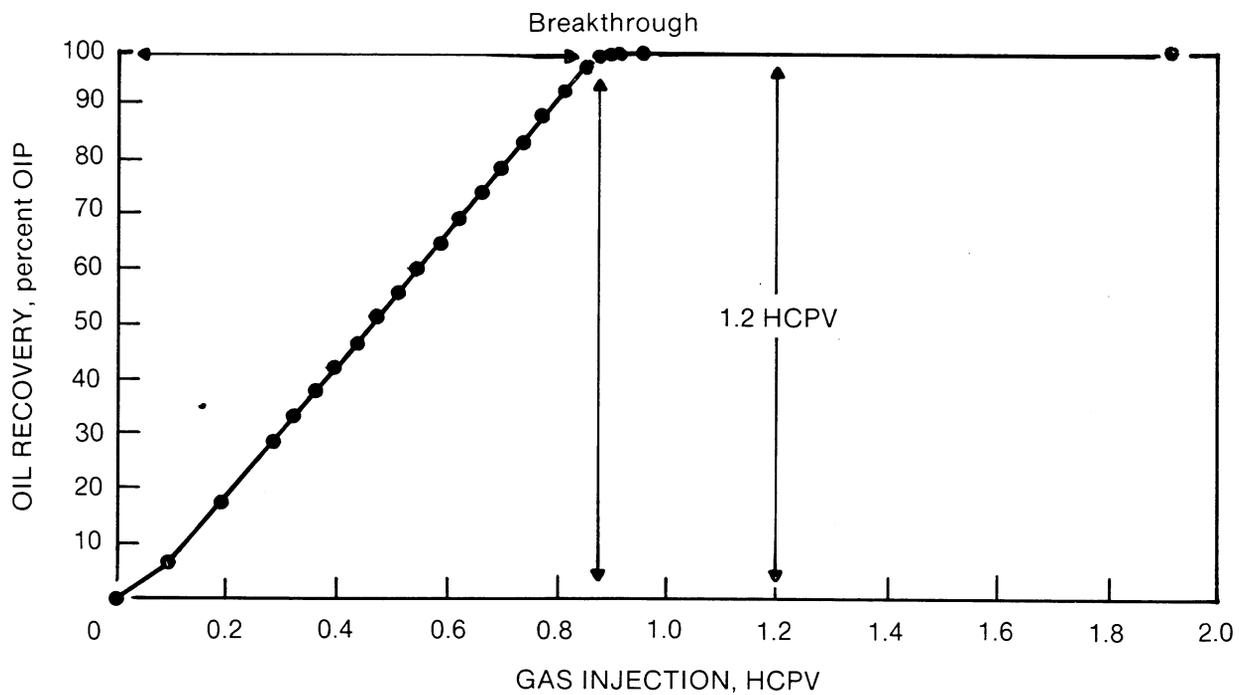


FIGURE 15. - Slim tube displacement test result.

Recombined Lake Barre Crude Slim Tube Tests

Percent Recovery vs Pressure

GOR = 83.45 SCF/bbl

Temperature = 279°F

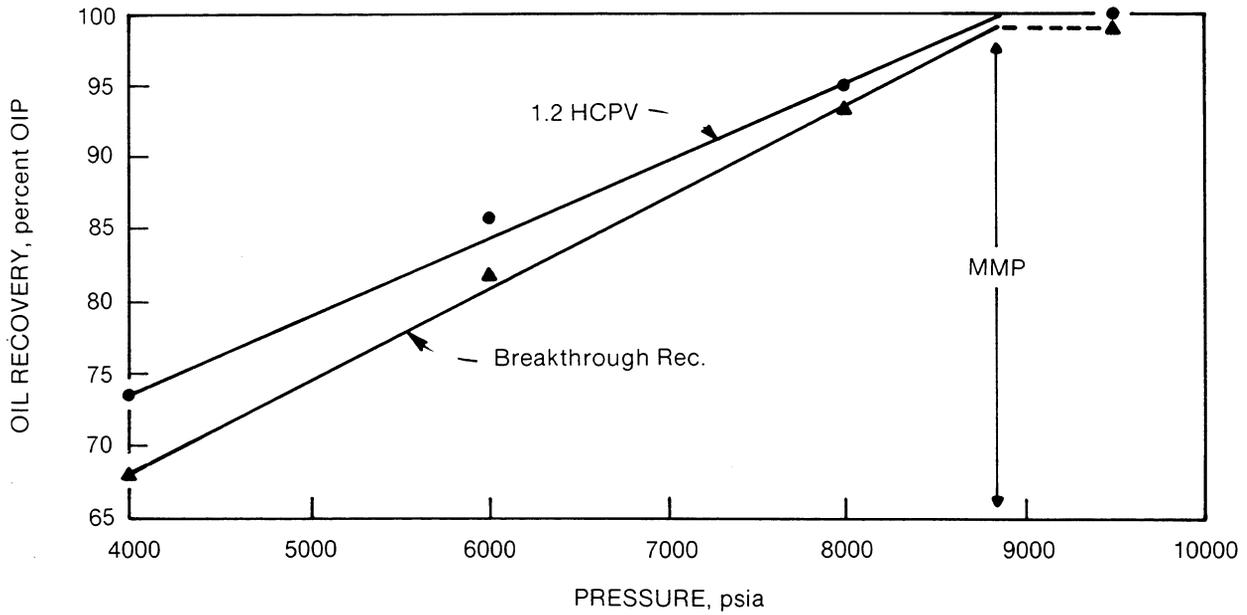


FIGURE 16. - Oil recovery versus pressure.

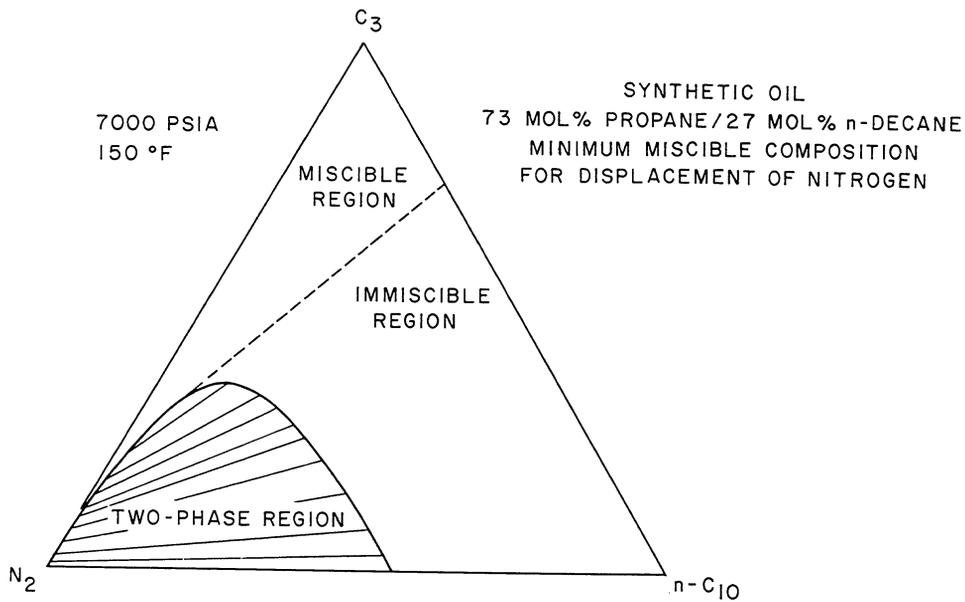


FIGURE 17. - Ternary phase diagram of N_2 - C_3 - nC_{10} system (calculated by PR equation of state).

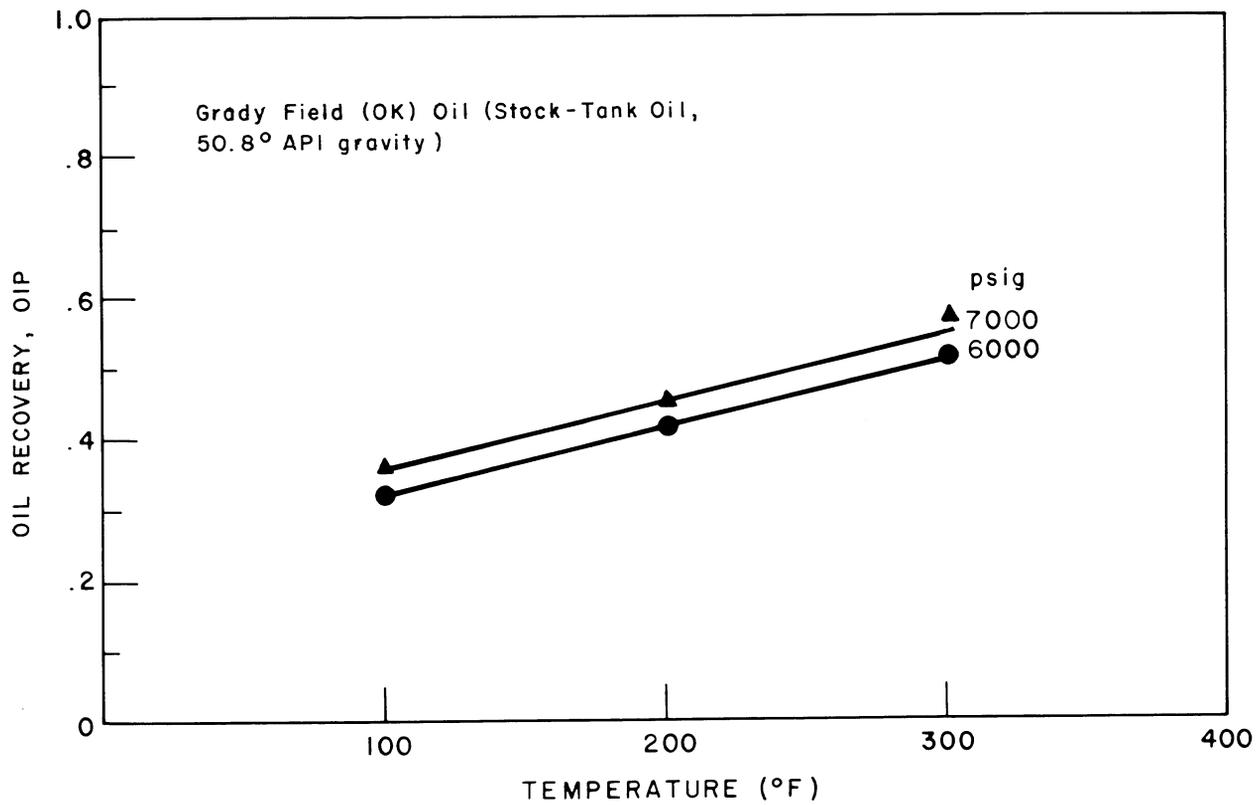


FIGURE 18. - Oil recovery of nitrogen displacement in slim tube.

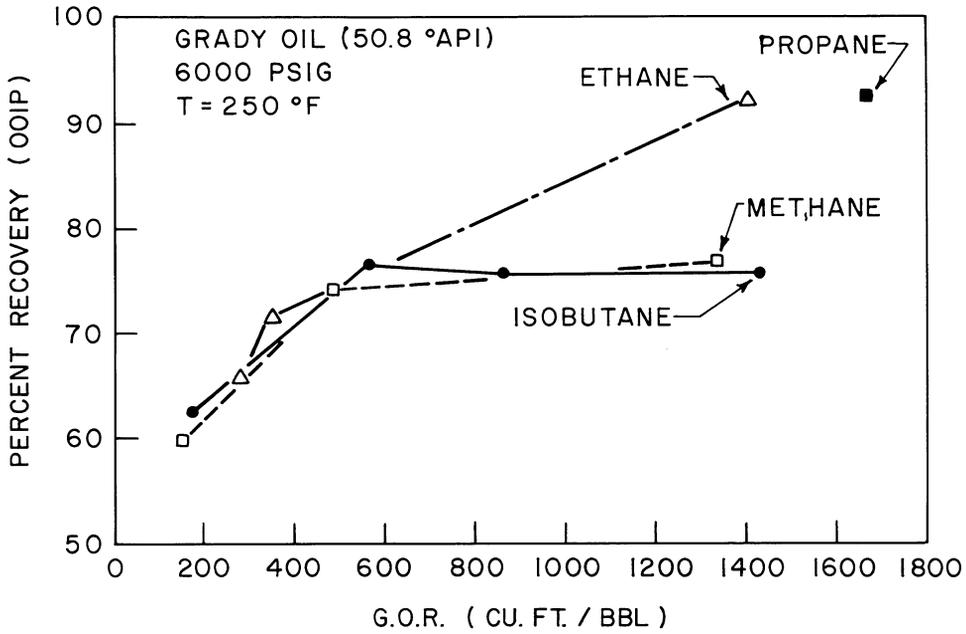


FIGURE 19. - Effect of light components on oil recovery.

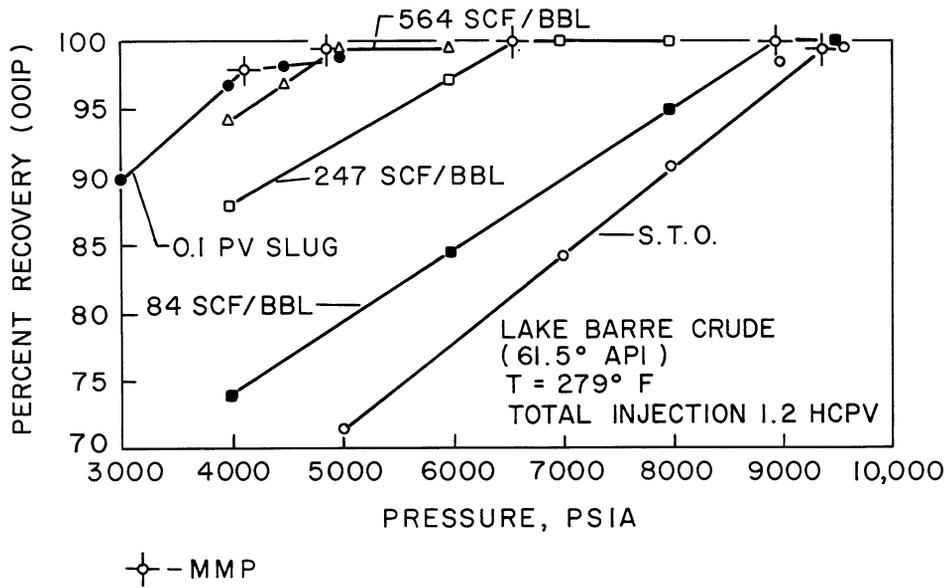


FIGURE 20. - Effect of pressure and GOR on recovery.

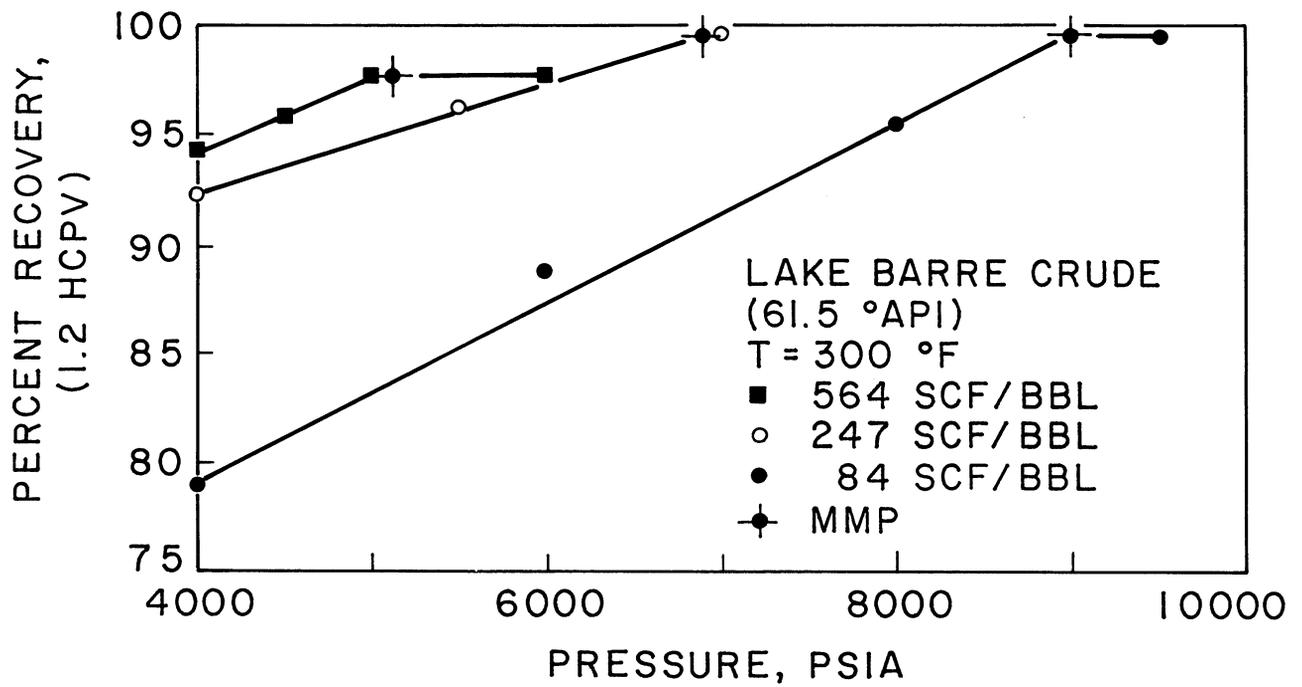


FIGURE 21. - Reconstituted Lake Barre crude oil - percent oil recovery versus pressure at 300° F.

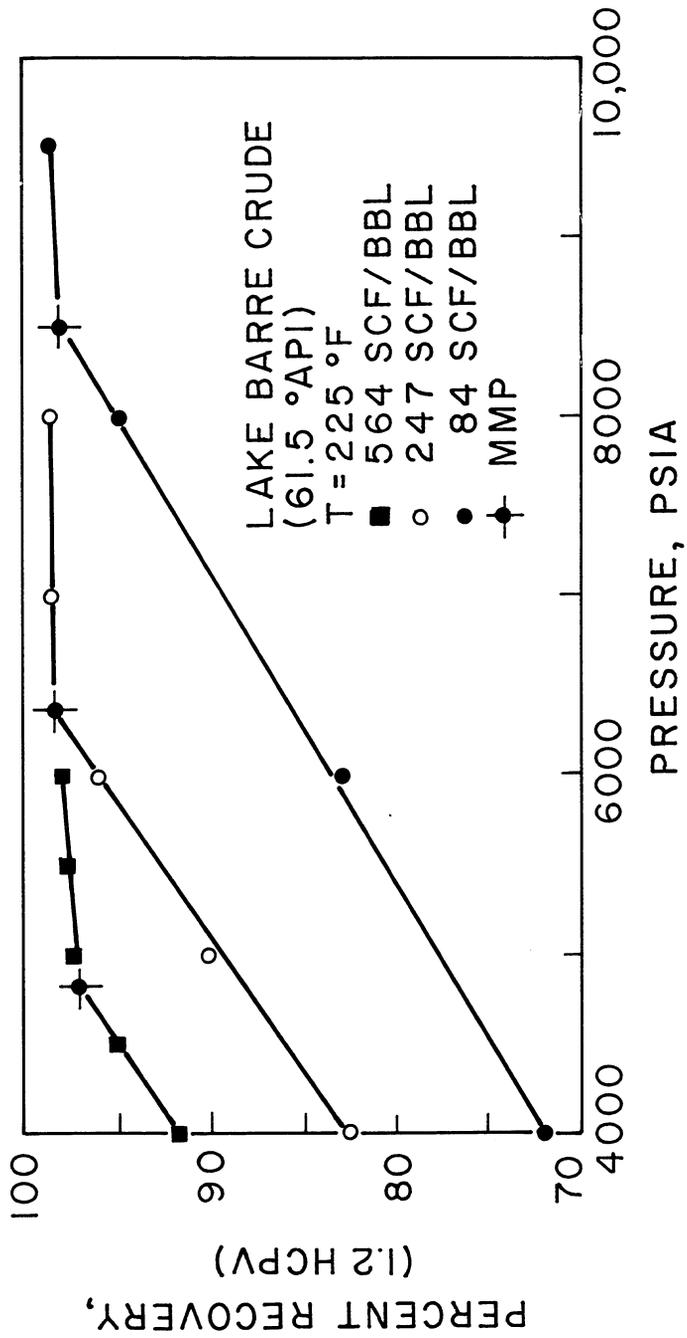


FIGURE 22. - Oil recovery vs. pressure.

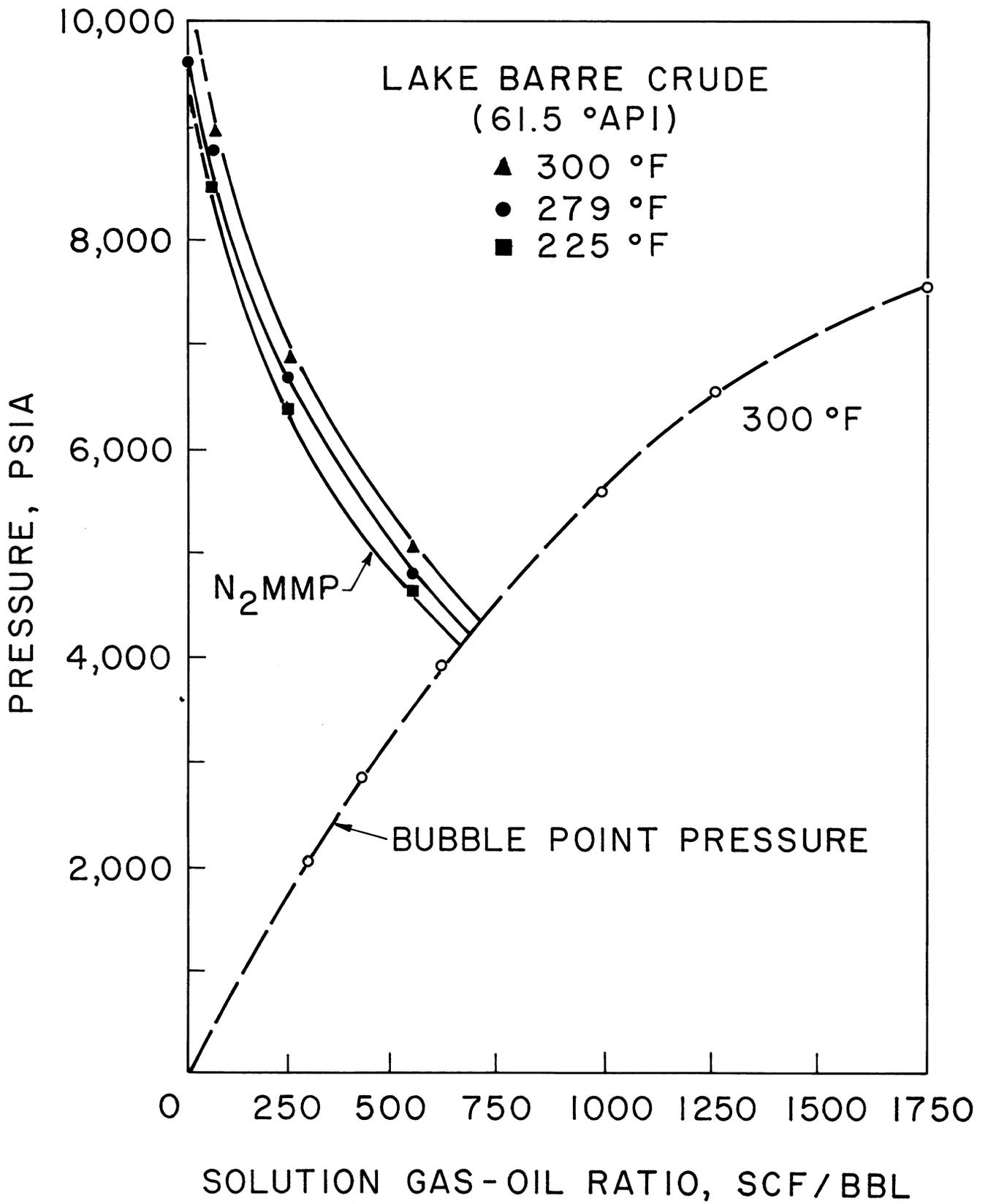


FIGURE 23. - MMP and bubble point pressure vs. GOR.

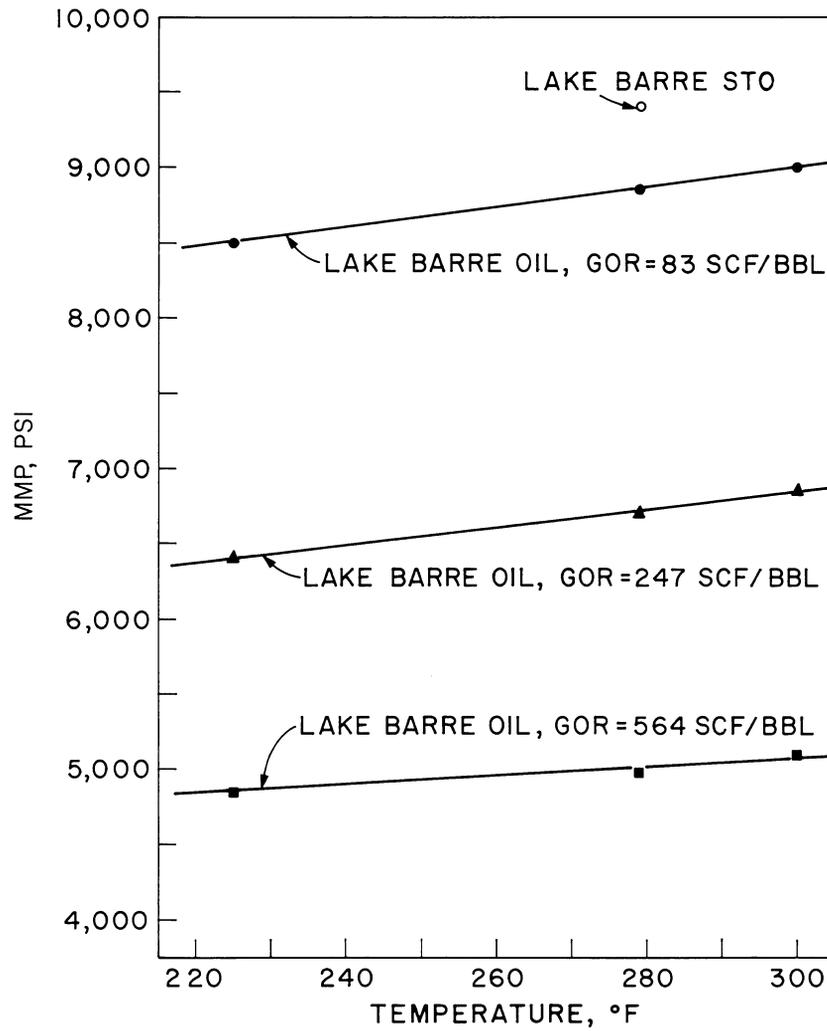


FIGURE 24. - Effect of temperature on MMP.

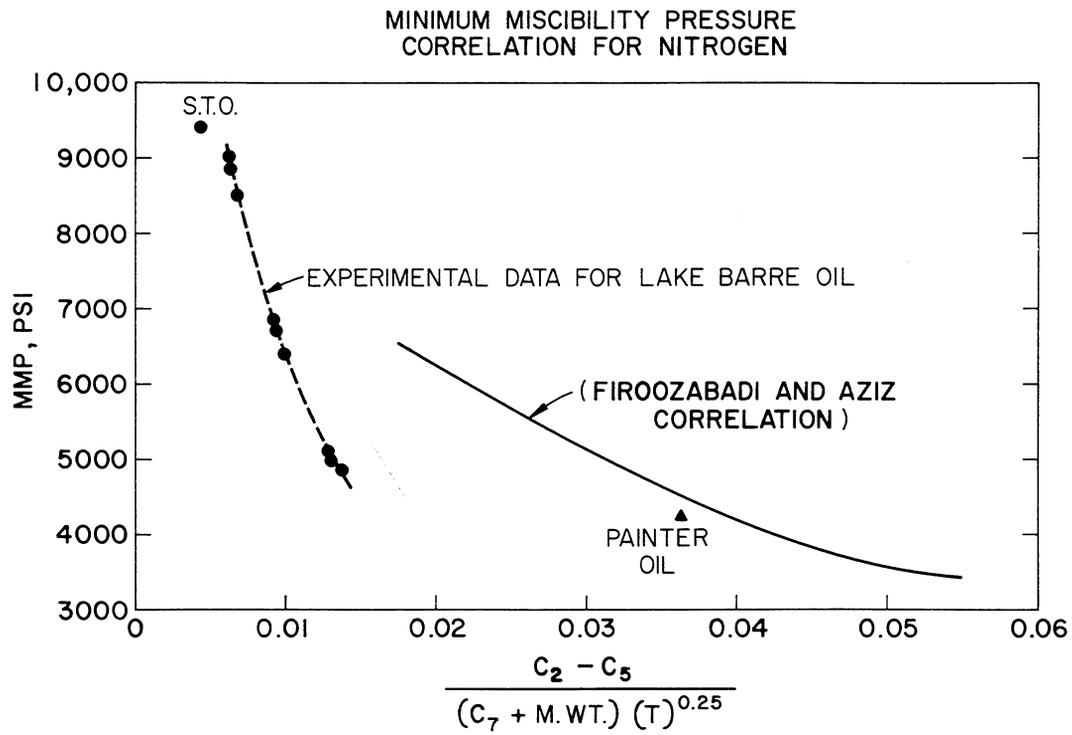


FIGURE 25. - MMP correlations.

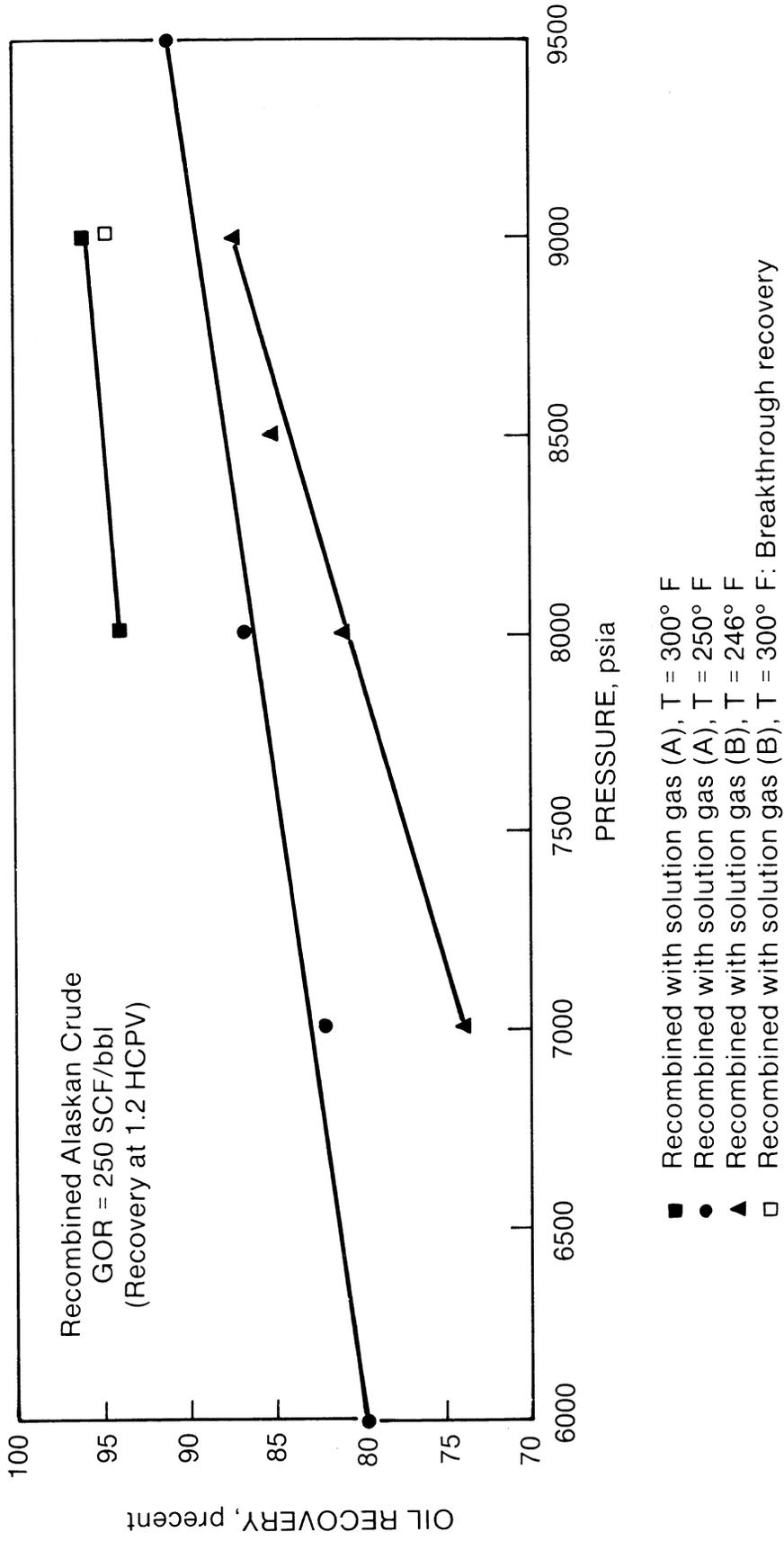


FIGURE 26. Recombined Alaskan crude oil - percent oil recovered versus pressure.

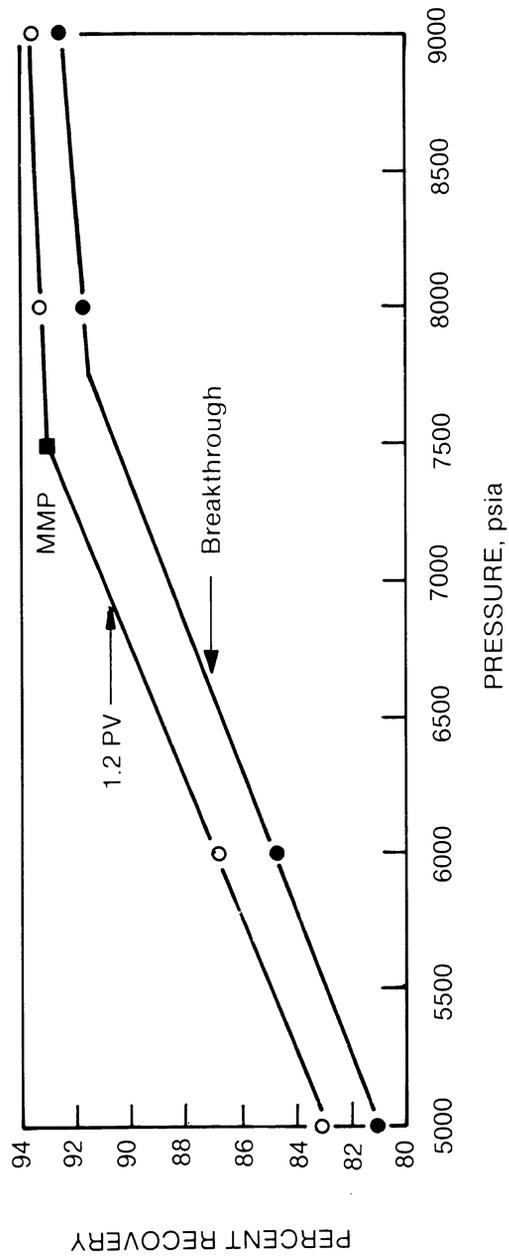


FIGURE 27. - Synthetic oil - percent oil recovered versus pressure at 275° F.

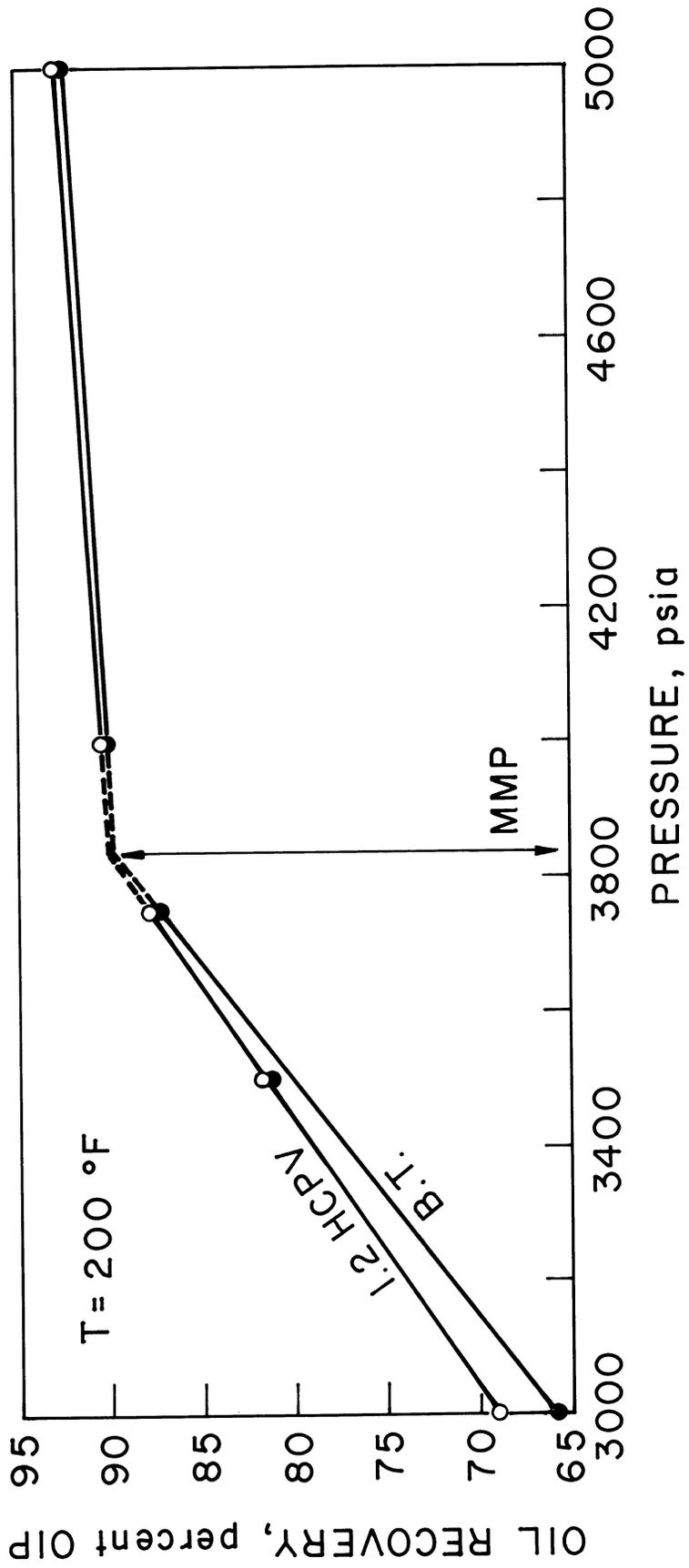


FIGURE 28. - Synthetic oil #2 - percent oil recovered versus pressure at 200° F.

