A THERMODYNAMIC CORRELATION FOR THE MINIMUM MISCEIBILITY PRESSURE
OF CARBON DIOXIDE FLOODING OF PETROLEUM RESERVOIRS

by

Robert Michael Enick
B.S. in Ch.E, University of Pittsburgh
M.S. in Ch.E., University of Pittsburgh
M.S. in Pet.E., University of Pittsburgh

Submitted to the Graduate Faculty
of the School of Engineering
in partial fulfillment of
the requirements for the degree of
Doctor
of
Philosophy

University of Pittsburgh
1985

The author grants permission
to reproduce single copies

Signed
ACKNOWLEDGMENTS

I would like to thank my co-advisors, Prof. G. Holder and Prof. B. Morsi for their assistance over the past three years. I would also like to thank the remaining members of my committee, Prof. A. Reznik, Dr. P. Raimondi, Prof. J. Chen and Dr. A. Yingling, for their time and interest in this project.

The generosity of Exxon and SPE Region IX have been greatly appreciated by myself and my family; the teaching fellowships enabled the bulk of my time to be concentrated on this work and the financial assistance enabled my wife to concentrate her time on our daughter, Liz.

Larry Herman must be commended for his direction, suggestions and assistance during the nine months required to construct the "blue box." He deserves a raise.

I must thank all of those who shared an office with me; R. Mohamed, J. Grenko, D. Mangone, R. Foster, D. Dempsey and S. Klara, for preventing boredom from ever setting in.

I would also like to thank Jocie Glasser for typing this, thereby saving me endless hours of two finger keyboard punching. She and the other secretaries also deserve a raise.

This work and all related publications are dedicated to my wife, Kathy, who constantly encouraged me throughout this whole project.
ABSTRACT

Robert Michael Enick, Ph.D.
University of Pittsburgh

A thermodynamic correlation for the minimum miscibility pressure of carbon dioxide flooding is introduced in which the minimum miscibility pressure is estimated as the cricondenbar of a pseudo-binary system at reservoir temperature. The two components of this system are: (1) the displacing fluid and (2) the displaced crude, where the pentane and heavier fraction is modeled by a single alkane of equivalent average molecular weight. The effects of reservoir temperature, $C_5^+$ average molecular weight, the type and amount of CO$_2$ impurities and any light or intermediate gases present in the oil are all accounted for. The oil molecular weight distribution is not, however.

The correlation is generated using the Peng-Robinson equation of state and is presented in a graphical form in which the contribution of each factor is individually evaluated. With the exception of a low temperature, high molecular weight correction, the correlation is independent of a CO$_2$/crude oil minimum
miscibility pressure database.

Exact agreement between the cricondenbar and the minimum miscibility pressure is achieved for a model binary system, CO$_2$/nC$_{13}$H$_{28}$, over the range of reservoir temperature. The Peng-Robinson equation of state can be used to predict the values exactly only if a temperature dependent interaction parameter is incorporated. Very good agreement of ± 3% is obtained between the minimum miscibility pressures and cricondenbars when CO$_2$ impurities of 5% methane, 10% methane and 5% nitrogen are introduced. The equation of state predictions for the cricondenbars are as much as 30% low, however. When tested against 157 minimum miscibility pressure values for systems containing crude oil, the ratio of the predicted MMP to the actual MMP is 1.09, with a standard deviation of 19%. These results are comparable to many of the purely empirical correlations developed from a MMP data base of CO$_2$/crude oil systems.

Unlike other correlations, a decrease in MMP with temperature is predicted at elevated temperature. This may have a favorable influence on very deep reservoir projects or CO$_2$/steam flooding of reservoirs containing viscous oils.

**DESCRIPTORS**

- Enriching impurity
- First contact miscibility
- Lean impurity
- Minimum miscibility pressure
- Reservoir
- Equation of state
- High pressure volumetric behavior
- Live oil
- Multiple contact miscibility
- Slim tube displacement
# TABLE OF CONTENTS

ACKNOWLEDGMENTS

ABSTRACT

LIST OF FIGURES

LIST OF TABLES

NOMENCLATURE

1.0 INTRODUCTION

   1.1 Overview of Primary, Secondary and Tertiary Recovery
   1.2 CO₂ Flooding
   1.3 Review of MMP Correlations

2.0 STATEMENT OF THE PROBLEM

   2.1 Proposed MMP Correlation
   2.2 Thermodynamic Considerations

3.0 EXPERIMENTAL

   3.1 Experimental Apparatus
      3.1.1 PVT Equipment
      3.1.2 STD Equipment
   3.2 Parameter Specifications
   3.3 Experimental Procedure
      3.3.1 PVT
      3.3.2 STD
   3.4 Proposed Goals
      3.4.1 Experimental Goals
      3.4.2 Equation of State Predictions

4.0 ANALYSIS OF RAW DATA
4.1 PVT Data
   4.1.1 CO₂/nC₁₃H₂₈
   4.1.2 (.95 CO₂ + .05 N₂)/n C₁₃ H₂₈
   4.1.3 (.95 CO₂ + .05 CH₄)/n C₁₃ H₂₈

4.2 STD Data

5.0 DEVELOPMENT OF CORRELATION
   5.1 Equation of State
   5.2 Low Temperature, High Molecular Weight Correction
   5.3 Temperature Dependence of CO₂/Alkane Binary Interaction Parameter
   5.4 Graphical Correlation
      5.4.1 Pure CO₂/Stock Tank Oil Correlation
      5.4.2 Accounting for CO₂ Impurities
      5.4.3 Accounting for Live Oil Gases

6.0 RESULTS AND DISCUSSION
   6.1 Comparison of STD, PVT and PR EOS for Model Systems
   6.2 Comparison of Literature MMP Values with Graphical Correlations

7.0 CONCLUSIONS
   7.1 General Conclusions
   7.2 Evaluation of the Proposed Correlation
   7.3 Extensions to High Temperature Conditions
   7.4 Extensions to Other Miscible Displacement Processes
LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure No.</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Effect of CO₂ Impurities Predicted by Proposed Correlation</td>
</tr>
<tr>
<td>2</td>
<td>Effect of Volatile and Intermediate Gases in Oil Predicted by Proposed Correlation</td>
</tr>
<tr>
<td>3</td>
<td>Schematic Diagram of the Experimental Setup</td>
</tr>
<tr>
<td>4</td>
<td>Two Phase Volumetric Data, CO₂/nC₁₃ H₂₈, 314.1 K, 309.7 K, 307.4 K and 300.8 K</td>
</tr>
<tr>
<td>5</td>
<td>Two Phase Volumetric Data, 377.6 K and 338.7 K</td>
</tr>
<tr>
<td>6</td>
<td>Pressure-Composition Diagram, CO₂/nC₁₃ H₂₈, 310.8 K</td>
</tr>
<tr>
<td>7</td>
<td>Pressure-Composition Diagram, CO₂/nC₁₃ H₂₈, 311.9 K</td>
</tr>
<tr>
<td>8</td>
<td>Pressure-Composition Diagram, CO₂/nC₁₃ H₂₈, 313.0 K</td>
</tr>
<tr>
<td>9</td>
<td>Pressure-Temperature Diagram, CO₂/nC₁₃-H₂₈</td>
</tr>
<tr>
<td>10</td>
<td>Pressure-Temperature-Composition Diagram, CO₂/nC₁₃ H₂₈, LCEP and K Point Region</td>
</tr>
<tr>
<td>11</td>
<td>Three Phase Volumetric Behavior, 310.8 K</td>
</tr>
<tr>
<td>12</td>
<td>Three Phase Volumetric Behavior, 311.9 K</td>
</tr>
<tr>
<td>13</td>
<td>Three Phase Volumetric Behavior, 313.0 K</td>
</tr>
<tr>
<td>14</td>
<td>Three Phase Densities between LCEP and K Point</td>
</tr>
<tr>
<td>15</td>
<td>Two Phase Volumetric Behavior, (.05 N₂ + .95 CO₂)/nC₁₃ H₂₈, 377.6 K, 338.7 K, 310.9 K</td>
</tr>
<tr>
<td>16</td>
<td>Two Phase Volumetric Behavior, (.05 CH₄ + .95 CO₂)/nC₁₃ H₂₈, 377.6 K, 338.7 K, 310.9 K</td>
</tr>
<tr>
<td>17</td>
<td>Two Phase Volumetric Behavior, (.105 CH₄ + .895 CO₂)/nC₁₃ H₂₈, 377.6 K, 310.9 K</td>
</tr>
</tbody>
</table>
LIST OF FIGURES
(Continued)

18 Definition of MMP
19 Results of Displacement Experiments
20 Critical Loci of CO₂/nAlkane Binaries and MMP Correction
21 Temperature Dependency of Binary Interaction Parameter
22 The Effect of Lean Impurities on the CO₂/nC₁₃ H₂₈ Cricondenbar Locus Over the Range of Reservoir Temperature
23 The Effect of Enriching Impurities on the CO₂/nC₁₃ H₂₈ Cricondenbar Locus Over the Range of Reservoir Temperature
24 The Effect of Light Oil Components on the CO₂/nC₁₃ H₂₈ Cricondenbar Locus Over the Range of Reservoir Temperature
25 The Effect of Intermediate Oil Components on the CO₂/nC₁₃ H₂₈ Critical Locus Over the Range of Reservoir Temperature
26 MMP Correlation-Pure CO₂/STO Basis
27 MMP Correlation-Effect of Lean CO₂ Impurities
28 MMP Correlation-Effect of Enriching CO₂ Impurities
29 MMP Correlation-Effect of Enriching CO₂ Impurities
30 MMP Correlation-Effect of Light Gases in Oil
31 MMP Correlation-Effect of Intermediate Gases in Oil
32 Temperature Correction Factor for CO₂ Impurities and Live Oil Gases
33 Comparison of Cricondenbars, MMP's and Peng-Robinson Equation of State
LIST OF FIGURES
(Continued)

34 Comparison of Predicted and Actual MMP Values

35 Comparison of Predicted and Actual MMP Values, with Temperature Correction for CO₂ Impurities and Live Oil Gases

36 Temperature Above which MMP Predicted to Decrease
<table>
<thead>
<tr>
<th>Table No.</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MMP Correlations</td>
</tr>
<tr>
<td>2</td>
<td>Functional Dependency of MMP Correlations</td>
</tr>
<tr>
<td>3</td>
<td>Peng-Robinson and Soave-Redlich-Kwong Equations of State</td>
</tr>
<tr>
<td>4</td>
<td>Volumetric Data for the CO$<em>2$/nC$</em>{13}$H$_{28}$ System at 310.8 K, 338.7 K and 377.6 K</td>
</tr>
<tr>
<td>5</td>
<td>Critical Pressures and Compositions of the CO$<em>2$/nC$</em>{13}$H$_{28}$ System at 310.8 K, 338.7 K and 377.6 K</td>
</tr>
<tr>
<td>6</td>
<td>Volumetric Data for the (.95 CO$<em>2$ + .05 N$<em>2$)/nC$</em>{13}$H$</em>{28}$ System at 310.8 K, 338.7 K and 377.6 K</td>
</tr>
<tr>
<td>7</td>
<td>Change in Cricondenbar Due to CO$<em>2$ Impurities in (CO$<em>2$ + Impurity)/nC$</em>{13}$H$</em>{28}$ Systems</td>
</tr>
<tr>
<td>8</td>
<td>Volumetric Data for the (.95 CO$<em>2$ + .05 CH$<em>4$)/nC$</em>{13}$H$</em>{28}$ System at 310.8 K, 338.7 K and 377.6 K</td>
</tr>
<tr>
<td>9</td>
<td>Volumetric Data for the (.90 CO$<em>2$ + .10 CH$<em>4$)/nC$</em>{13}$H$</em>{28}$ by Pure and Impure CO$_2$ at 310.8 K, 338.7 K and 377.6 K</td>
</tr>
<tr>
<td>10</td>
<td>Slim Tube Displacement Recovery of nC$<em>{13}$H$</em>{28}$ by Pure and Impure CO$_2$ at 310.8 K, 338.7 K and 377.6 K</td>
</tr>
<tr>
<td>11</td>
<td>Range and Ranking of Parameter Variations, PR EOS Prediction of Effects on MMP</td>
</tr>
<tr>
<td>12</td>
<td>Pure Component Data</td>
</tr>
<tr>
<td>13</td>
<td>Binary Interaction Parameters</td>
</tr>
<tr>
<td>14</td>
<td>Prediction and Actual MMP Values for 57 Systems</td>
</tr>
</tbody>
</table>
NOMENCLATURE

A, a  equation of state coefficients
B, b  equation of state coefficients
bbl   barrel
BPP   bubble point pressure
BT    breakthrough
C$_5^+$ pentane and heavier fraction
CP    critical point
DDP   dew point pressure
EOS   equation of state
EVP   extrapolated vapor pressure
f     fugacity
FCM   first contact miscibility
GOR   gas-oil ratio
INT   intermediate mole fraction
K     degrees Kelvin
L     liquid
L$_1$ liquid-hydrocarbon rich
L$_2$ liquid-CO$_2$ rich
LL    lower liquid, 3 phase equilibria
LLV   liquid-liquid-vapor equilibria
MCM   multiple contact miscibility
MDMP  minimum dynamic miscibility pressure
MMP   minimum miscibility pressure
MPa   pascals x 10$^6$
**NOMENCLATURE**

(Continued)

- **MW**  molecular weight
- **MW**  average MW
- **OIP** oil in place
- **P**  pressure
- **PNA** paraffin, napthenic, aromatic
- **Psia** pounds per square inch, absolute
- **PV** pore volume
- **PVT** pressure-volume-temperature
- **PR** Peng–Robinson
- **R** universal gas constant
- **SCF** standard cubic feet
- **STD** slim tube displacement
- **T** temperature
- **UL** upper liquid
- **V** vapor
- **v** molar volume
- **VOL** volatile mole fraction
- **VLE** vapor liquid equilibria
- **w** weight
- **x** mole fraction, liquid phase
- **y** mole fraction, vapor phase
- **Z** compressibility factor
- **z** overall mole fraction
- **δ** binary interaction parameter
NOMENCLATURE
(Continued)

ψ fugacity coefficient
ω acentric factor

Subscripts

c critical
i component i
m mixture
1.0 INTRODUCTION

1.1 Overview of Primary, Secondary and Tertiary Recovery

The initial production from most newly discovered petroleum reservoirs is attributable to several primary mechanisms associated with the energy of the reservoir itself. When a well is placed in a reservoir, liquid expansion and rock compaction force fluids toward the well as the reservoir pressure declines. When the pressure drops far enough, gas comes out of solution, expands and flows toward the well, displacing oil as it proceeds. If the geometry of the reservoir is such that the gas is trapped above the oil, the expanding gas cap can push the oil downslope toward the production well. Water encroachment from adjoining aquifers can serve a similar function and sustain oil production by pressure maintenance and oil displacement.

As the reservoir’s energy is depleted, external energy must be supplied in order to maintain or increase oil production. Fluid injection directly into the reservoir both maintains reservoir pressure and displaces oil in a manner similar to natural gas cap expansion or water encroachment from aquifers. Water and natural gas have been extensively used for this injection procedure, commonly known as secondary recovery. Eventually, these processes become ineffective due to several factors. Water and gas are immiscible with the displaced oil, so a significant residual oil saturation is usually left behind in pores as the water flows past the oil to the production well. In addition, these injection fluids usually flow more easily in the reservoir than the oil, and when this effect is coupled with the effects of gravity segregation and reservoir heterogeneities, only a fraction of the reservoir volume is actually contacted by the displacing fluid. Furthermore, some of the oil
that is displaced may not flow into the production wells, but instead, resaturates unswept pores that have been partially depleted by primary recovery.

Although significant oil recovery may be achieved by primary and secondary mechanisms, substantial amounts of oil may remain in the reservoir. Several more exotic processes, termed tertiary recovery processes, have been developed which are targeted at this residual oil. Thermal techniques, such as steamflooding and fireflooding, are employed in reservoirs containing thick, immobile oil. These processes reduce oil viscosity, enabling it to flow to production wells. Polymer floods improve volumetric sweep since the viscous displacing fluid is less likely to channel to the production wells. Caustic and surfactant floods are characterized by low or ultra-low interfacial tensions which promote effective oil displacement. Miscible flooding techniques, such as first contact miscible, lean gas, rich gas and carbon dioxide floods are also quite effective in mobilizing residual oil since the displaced and displacing fluids become miscible in all proportions, reducing the oil saturation in swept out zones to minimum values.

Each of these tertiary processes, however, have significant difficulties associated with them. Not only are they fairly expensive, but they are also plagued by operational and phenomenological problems, such as corrosion, shear degradation, heat loss, adsorption, poor mobility control, loss of oil bank integrity, asphaltene deposition, etc. Therefore, although these processes have tremendous potential, careful planning, design and operation are required in their risky application.
1.2 CO₂ Flooding

Carbon dioxide flooding has been studied since the 1950's(1-4) and is currently the miscible flooding technique of most interest to the petroleum industry.(5) Much like other miscible flooding techniques, this recovery process may be considered a supercritical extraction process. The critical temperature of CO₂ is at the lower end of a relatively narrow range of reservoir temperatures (30-120 C).(6) Therefore, the high densities and strong solvent properties which are characteristic of fluids just above their critical point may be obtained at relatively low pressures within the reservoir. As the flood proceeds, the dense CO₂ mixes with the oil, often resulting in zones of complete miscibility. When the CO₂-oil mixture is brought to the surface, separation is easily achieved by flashing the mixture to low pressures at ambient temperature. The oil may then be stored or shipped for refining while the CO₂ may be cleaned, compressed and reinjected into the reservoir. Furthermore, CO₂ is safe, available in large quantities and not prohibitive in cost.

In the evaluation of whether a field is appropriate for miscible flooding, several general types of experiments are performed on the oil from that field.(7) These include slim tube displacements (STD) by CO₂, high pressure volumetric (PVT) and vapor-liquid equilibrium (VLE) studies on CO₂-oil systems, core displacements and continuous multiple contact experiments. The displacement of recombined reservoir fluid or stock tank oil from a slim tube packed with sand or glass beads has become a standard experiment performed early in the evaluation of required flooding pressures, and this STD procedure is of primary concern to this study.

*Parenthetical references placed superior to the line of text refer to the bibliography.*
The sand packed coil is used because it provides a medium for the mixing of CO₂ and oil in a flowing multiple contact process which approaches a highly ideal displacement; it is not, however, intended to simulate the reservoir rock. The uniform porous medium and small tube diameter combine to yield a nearly one dimensional, well mixed displacement. Since viscous finger growth of CO₂ flowing past the oil is inhibited by both the tube wall and the transition zone, the experiment isolates the effects of phase behavior at various pressures during the multiple contacts of CO₂ with oil.

The vast differences exhibited in experimental methodology in STD experiments are the result of early research on truly miscible displacements which indicated rate insensitivity of oil recovery in such tests. More recent studies, however, have shown oil recovery to be a function not only of phase behavior, but also (to a lesser degree) of the displacement rate and the level of dispersion which is related to the particle diameter and the rate of displacement. These displacements are also somewhat unstable, so differences in tube diameters, windings and length would be expected to affect the magnitude of fingering and thereby the oil recovery. However, since no industry wide concensus exists on the STD experiment, each investigator must not only choose an apparatus whose design parameters fall within the range of values reported in previous studies, but also maintain experimental consistency throughout his work.

Many methods of evaluating the data obtained from STD experiments have also been proposed in order to determine the pressure requirement for miscible displacement. This minimum miscibility, MMP, or minimum dynamic miscibility pressure, MDMP, has been defined as: the pressure above which no appreciable change in oil recovery occurs, the pressure at which 80% of the oil in place, OIP, is recovered when the gas-oil ratio, GOR, reached 40,000 standard
cubic feet of CO₂ per barrel of oil, SCF/bbl, the lowest pressure at which recovery after the injection of 1.2 pore volumes, PV, of CO₂ yields nearly maximum recovery while exhibiting transition zone fluids which appear to be the result of multiple contact miscibility, MCM, the pressure at which the recovery vs. pressure curve experiences a sharp change in slope and levels off, the pressure at which 85% recovery of OIP is recovered at CO₂ breakthrough and 95-98% recovered at 1.2 PV injected with no two phase flow occurring at the outlet and the pressure at which 90% of the OIP is recovered at CO₂ BT, with no prior two phase flow at the outlet being observed. Although it is certain that the MMP of any single system would depend on which of these definitions is chosen, it is not clear how significant the differences would be.

Despite these variant techniques and MMP definitions, STD remains a commonly used, simple method of obtaining useful information relating pressure and displacement efficiency, the effects of CO₂ contamination on pressure requirements, and the overburden pressure which must exist in the candidate reservoir. The published results of many STD studies, as well as those performed in this work, will serve as a basis of information which will either substantiate or repudiate the proposed correlation detailed in Section 2.

1.3 Review of MMP Correlations

In order to facilitate screening procedures and to gain insight into this miscible displacement process, many MMP correlations have been proposed and they are presented in Table 1. Ideally, such a correlation should not only account for each parameter known to affect the MMP, but it should also be based upon a thermodynamic or physical concept inherent to the mechanisms of CO₂ miscible
TABLE 1

MMP Correlations

<table>
<thead>
<tr>
<th>Author</th>
<th>Gravity NPI(17)</th>
<th>MMP OAPI</th>
<th>Reservoir Temperature Correction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Gravity</td>
<td>MMP psi</td>
<td>Temperature Correction</td>
</tr>
<tr>
<td></td>
<td>Gravity (API)</td>
<td>MMP (psi)</td>
<td>Reservoir Temperature Correction</td>
</tr>
<tr>
<td>&lt; 27</td>
<td>4000</td>
<td>120</td>
<td>0</td>
</tr>
<tr>
<td>27-30</td>
<td>3000</td>
<td>120-150</td>
<td>+200</td>
</tr>
<tr>
<td>&gt; 30</td>
<td>1200</td>
<td>150-200</td>
<td>+350</td>
</tr>
<tr>
<td></td>
<td></td>
<td>200-250</td>
<td>+500</td>
</tr>
</tbody>
</table>

2. Holm and Josendal(11)

F11. Correlation for predicting pressure required for miscible displacement in CO2 flooding (after Benham et al. for a 59 percent methane-41 percent propane displacing fluid).

3. Mungan(14)

FIGURE 3. Pressure required for miscible displacement in carbon dioxide flooding (Holm and Josendal).
4. Glaso(28)

\[ \text{MMP}_{\text{psig}} = 971.8 - 3.950 \times 10^{-9} M_{V_{C7^+}} + (1.700 \times 10^{-9} M_{V_{C7^+}})^{3.73} (7.598 M_{V_{C7^+}}^{-1.058}) T \]

\[ \text{MMP}_{\text{psig}} = 2947.9 - 3.404 \times 10^{-9} M_{V_{C7^+}} + (1.700 \times 10^{-9} M_{V_{C7^+}})^{3.73} (7.368 M_{V_{C7^+}}^{-1.058}) T - 121.2 \]

\[ M_{V_{C7^+}} = \text{molecular weight of C7^+,STO} \]

\[ T = \text{Temperature, } ^\circ\text{F} \]

5. Johnson and Pollin(13)

\[ P_{\text{MMP}} - P_{c,\text{inj}} = \alpha_{\text{inj}} (T_{\text{res}} - T_{c,\text{inj}}) + I (\delta M - M_{\text{inj}})^{2} \]

when \( \gamma_2 < 0.2 \) and \( 300 \text{ K} < T_{\text{res}} < 410 \text{ K} \)

for CO2

\[ \alpha_{\text{inj}} = 18.9 \text{ PSIA/K} \]

for CO2/N2

\[ \alpha_{\text{inj}} = 10.5 (1.8 + 10^{3} \gamma_2 / (T_{\text{res}} - T_{c,\text{inj}})) \]

for CO2/CH4

\[ \alpha_{\text{inj}} = 10.5 (1.8 + 10^{2} \gamma_2 / (T_{\text{res}} - T_{c,\text{inj}})) \]

\[ I = C_{11} + C_{21} M + C_{31} M^2 + C_{41} M^3 + (C_{12} + C_{22} M) \rho + C_{13} \rho^2 \]

\[ C_{11} = -11.73 \]

\[ C_{21} = 6.313 \times 10^{2} \]

\[ C_{31} = 1.954 \times 10^{-4} \]

\[ C_{41} = 2.502 \times 10^{-7} \]

\[ I = 2.22 K - 25.84 + 0.86 K^{-2} \]

\[ K = \text{Watson } K \text{ - factor} \]

\[ P_{c,\text{inj}} = \text{injection gas critical pressure, psia} \]

\[ M = \text{number average molecular weight of oil} \]

\[ \beta = 0.285 \]

\[ T_{c,\text{inj}} = \text{injection gas critical temperature, K} \]

\[ M_{\text{inj}} = \text{molecular weight injection gas} \]

\[ \rho = \text{API gravity} \]

\[ \gamma_2 = \text{mole fraction CO}_2 \text{ impurity} \]
6. Yellig and Metcalfe(12)

7. GURC(21):
8. Dunyushkin and Namiot (23)

9. PRI (24)

If \( T < T_c \) of CO\(_2\), \( \text{MMP} = \text{VP}_{\text{CO}_2} \)

If \( T > T_c \) of CO\(_2\), \( \text{MMP} = \text{EVP}_{\text{CO}_2} = 7.39 \times 10^6 \)

Where \( P : \text{MPa} \quad T : ^\circ \text{R} \)

\[ b = (2.772 - 1519/T) \]

10. PRI (24)

\[ \text{MMP} = -4.8913 + 0.04150 T - 0.0015974 T^2 \]

\( \text{MMP} = \text{BPP} \) if \( \text{MMP} < \text{BPP} \)

Where \( P : \text{MPa} \quad T : ^\circ \text{C} \)
11. Holm and Josendal(19)


\[
\text{MMP}_{\text{impure-pure}} = 8.78 \times 10^{-4}(T)^{0.06}(MW\ C_5^+)^{1.78} \\
\times (VOL/INT)^{0.136} (87.8/T_{cm} = \sum_{i=1}^{n} T_{C_i} - 459.7, \\
\text{weight fraction})
\]

\[
\text{VOL/INT: moles volatile/intermediate in oil}
\]

\[
\text{MMP = BPP if BPP > MMP}
\]

13. Sebastian et al.(27)

\[
\frac{\text{MMP}}{\text{MMP}_{\text{pure}}} = 1.0 - 2.13 \times 10^{-2} (T_{CM-304.2}) \\
+ 2.51 \times 10^{-4} (T_{CM-304.2})^2 \\
- 2.35 \times 10^{-7} (T_{CM-304.2})^3
\]

\[
\text{where } T_{CM} = \sum x_i T_{C_i}, x_i: \text{mole fraction, } T: \text{K}
\]

14. Orr and Taber(26)

(1) Determine the CO\textsubscript{2} density at the MMP at some temperature from a correlation or by slim tube experiment.

(2) Use an equation of state to calculate the pressure required to produce the same density when contaminants are added to the CO\textsubscript{2} or the temperature is changed. That pressure is an estimate of the new MMP.
15. Silva, Taber and Orr(29)

(1) \[ \rho_{\text{MMP}} = -0.524 F + 1.189 \]
\[ \rho_{\text{MMP}} = 0.42 \]
\[ F < 1.1467 \]
\[ F \geq 1.1467 \]

(2) \[ F = \frac{37}{\sum k_i w_i} \]

(3) \[ \log k_i = a_1 + b = \frac{(u_i/1-U_{CO_2})/(v_i/1-v_{CO_2})}{(u_i/1-U_{CO_2})/(v_i/1-v_{CO_2})} \]
\[ a = -0.041 \]
\[ b = 0.761 \]
\[ u_i = \text{wgh. fr. in upper phase of } C_i \]
\[ v_i = \text{wgh. fr. in lower phase of } C_i \]

(4) correct for CO₂ impurities via correlation 14.

16. Enick, Holder, Morsi

Refer to text
flooding. The parameters which have been found to influence the MMP are temperature, oil composition and the contaminants present in the CO₂ (displacing fluid composition). The governing concepts or principles of STD in particular and this process generally include supercritical extraction, miscibility, solvency, solubility, phase behavior, and the drive mechanisms attributed to this process, primarily vaporizing gas drive.

Although the following correlations, summarized in Tables 1 and 2, have contributed toward an improved understanding of CO₂ flooding, none has satisfied all of the aforementioned goals. The National Petroleum Institute's\(^{17}\) empirical correlation of MMP with API gravity and temperature provides only very rough estimates of MMP. Holm and Josendal\(^{11}\) correlated MMP with temperature and the average molecular weight of the C₅ \(^+\) fraction of the crude based on the Benham, et al.\(^{18}\) rich gas correlation. Mungun\(^{14}\) extended Holm and Josendal's work to higher molecular weights. Glaso\(^{28}\) has presented numerical expressions for the Benham et al. correlation. Johnson and Pollin\(^{13}\) empirically correlated MMP with the critical temperature, critical pressure, composition and molecular weight of the injection gas, reservoir temperature, and the API gravity, density and number average molecular weight of oil. This correlation, may be used when the injection gas is a binary mixture of CO₂ and N₂ or CO₂ and CH₄. Yellig and Metcalfe\(^{12}\) correlated MMP with temperature alone, making corrections only if the bubble point pressure exceeds the predicted MMP. This correlation has been soundly critiqued for its neglect of oil composition.\(^{19,20}\) The Gulf Universities Research Consortium research of Conquist\(^{21}\) and subsequent investigations\(^{22}\) yielded empirical correlations of MMP with reservoir temperature and several oil characterization parameters. Dunyushkin and Namiot\(^{23}\) predicted the MMP to be the critical pressure at reservoir temperature of a CO₂-normal alkane binary
<table>
<thead>
<tr>
<th>Correlation</th>
<th>Principle</th>
<th>Form</th>
<th>Independent of CO$_2$/Crude NMR Data Base</th>
<th>Temperature</th>
<th>CO$_2$ Oil Fraction</th>
<th>Light and Intermediate Oil Fraction</th>
<th>CO$_2$ Impurities</th>
</tr>
</thead>
<tbody>
<tr>
<td>NPC</td>
<td>Statistics</td>
<td>Numerical</td>
<td>no</td>
<td>yes</td>
<td>yes</td>
<td>no</td>
<td>no</td>
</tr>
<tr>
<td>Holm and Josendal</td>
<td>Benham, et al.</td>
<td>Graphical</td>
<td>no</td>
<td>yes</td>
<td>yes</td>
<td>no</td>
<td>no</td>
</tr>
<tr>
<td>Mungan</td>
<td>Benham, et al.</td>
<td>Graphical</td>
<td>no</td>
<td>yes</td>
<td>yes</td>
<td>no</td>
<td>no</td>
</tr>
<tr>
<td>Glasso</td>
<td>Benham, et al.</td>
<td>Numerical</td>
<td>no</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>no</td>
</tr>
<tr>
<td>Johnson and Pollin</td>
<td>Statistics</td>
<td>Numerical</td>
<td>no</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>Yellig and Metcalfe</td>
<td>Statistics</td>
<td>Graphical</td>
<td>no</td>
<td>yes</td>
<td>yes</td>
<td>no</td>
<td>no</td>
</tr>
<tr>
<td>CURC</td>
<td>Statistics</td>
<td>Numerical</td>
<td>no</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>no</td>
</tr>
<tr>
<td>Danyushkin and Hamlot</td>
<td>CO$_2$-oil miscibility</td>
<td>Graphical</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>no</td>
</tr>
<tr>
<td>PRI, I</td>
<td>Extrapolated vapor pressure</td>
<td>Numerical</td>
<td>yes</td>
<td>yes</td>
<td>no</td>
<td>no</td>
<td>no</td>
</tr>
<tr>
<td>PRI, II</td>
<td>Statistics</td>
<td>Numerical</td>
<td>no</td>
<td>yes</td>
<td>no</td>
<td>no</td>
<td>no</td>
</tr>
<tr>
<td>Holm and Josendal</td>
<td>CO$_2$ Density</td>
<td>Graphical</td>
<td>no</td>
<td>yes</td>
<td>yes</td>
<td>no</td>
<td>no</td>
</tr>
<tr>
<td>Alston, et al.</td>
<td>Statistics</td>
<td>Numerical</td>
<td>no</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>Sebastian, et al.</td>
<td>Statistics</td>
<td>Numerical</td>
<td>no</td>
<td>yes</td>
<td>–</td>
<td>–</td>
<td>yes</td>
</tr>
<tr>
<td>Orr and Tabor</td>
<td>CO$_2$ Density</td>
<td>Graphical + EOS</td>
<td>no</td>
<td>yes</td>
<td>–</td>
<td>–</td>
<td>yes</td>
</tr>
<tr>
<td>Silva, Tabor and Orr</td>
<td>CO$_2$ Density</td>
<td>Numerical</td>
<td>no</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>Enick, et al. (This Work)</td>
<td>CO$_2$-oil miscibility</td>
<td>EOS or Graphical</td>
<td>yes**</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
</tr>
</tbody>
</table>

*Hubble point correction used.

**Low temperature, high molecular weight correction used.
system where the alkane represented the crude oil's average molecular weight of
the pentane and heavier hydrocarbon, MW C₅⁺, fraction. The Petroleum Recovery
Institute(24) proposed two correlations, one equating the MMP with the
extrapolated vapor pressures of CO₂, also suggested by Orr and Jensen,(25) the
second being an empirical correlation of MMP with reservoir temperature, making
the previously described bubble point correction if necessary. Both of these
correlations, however, ignore oil composition. Holm and Josendal presented a
second correlation(19) in which the required CO₂ density is empirically correlated
to the extractable portion of the crude, (C₅⁻C₃₀)/C₅⁺. The MMP is then found by
determining the pressure required at reservoir temperature to obtain that density.
Orr and Taber(26) modified this correlation to account for CO₂ impurities by using
an equation of state to determine the change in pressure required in the presence
of an impurity to obtain the CO₂ density specified by the Holm and Josendal
correlation.(19) Silva, Taber and Orr(29) also introduced a modification of Holm
and Josendal's density correlation. A weighted composition parameter based on
partition coefficients was used to account for the distribution of the C₂⁺
molecules. This function was then related to the density required for miscible
displacement. Two empirical correlations have been presented which attempt to
account for CO₂ impurities. Alston, et al.(15) empirically correlated MMP with
reservoir temperature, 'live' oil composition and CO₂ impurities. Sebastian et
al.(27) presented a correction factor for MMP of an impure CO₂ system based on
the weight average critical temperature of the CO₂-impurities mixtures. This
factor is then multiplied by the MMP of the same system, only with pure CO₂ as
the displacing fluid.

All of the correlations account for temperature. Most incorporate oil
composition, while only several consider the effects of CO₂ impurities. The
majority of the correlations are highly empirical and only two are based on concepts or principles characteristic of CO₂ flooding. Holm and Jøsendal's second correlation, and modifications thereof, considered the CO₂'s solvency as a function of its density. Dunyushkin and Namiot's correlation incorporated the miscibility limits of CO₂ and alkanes. None of the current correlations are capable of consistently accounting for temperature, oil composition and CO₂ impurities based entirely on thermodynamic principles rather than numerical regression of an extensive data base.
2.0 STATEMENT OF THE PROBLEM

2.1 Proposed MMP Correlation

The goal of this study was to gain an understanding of the effects of temperature, oil composition and CO$_2$ impurities on the MMP. Rather than performing a regression analysis of a large data based to develop a correlation, a fundamental approach was followed which explained these effects on a consistent thermodynamic principle inherent to CO$_2$ flooding.

Specifically, the proposed thesis is that the MMP may be directly correlated to the cricondenbar (maximum possible two phase pressure) of a pseudo-binary system at reservoir temperature. The two components of this system are the impure CO$_2$ and a model crude oil in which the C$_5^+$ hydrocarbons are replaced by a normal alkanne of equivalent molecular weight.

This correlation has been evaluated using experimental data as well as published MMP data. An equation of state was then used to generate the correlation, enhancing its ability to account for parameter variations.

2.2 Thermodynamic Considerations

The foremost consideration of this work is the selection of an appropriate thermodynamic concept which can account for all of the parameters which influence the MMP.

As described in the Introduction, only a few of the previous correlations are based upon such fundamental principles, those of Holm and Josendal$^{19}$ and Dunyushkin and Namiot.$^{23}$ Orr and Taber$^{26}$ modified the Holm and Josendal correlation to account for CO$_2$ impurities. The Dunyushkin and Namiot correlation
may be modified to account for both impurities and light and intermediate gases in the oil, offering strong potential as a comprehensive miscible flooding MMP correlation. Consider the following attributes of such an approach:

(1) The displacement of oil by CO₂ occurs due to many factors and mechanisms, most of which involve the miscibility of the two fluids;

(2) The Dunyushkin and Namiot correlation is defined by the miscibility limit of CO₂ n-alkane systems at reservoir temperature, where the alkanes represent crudes of equivalent MW C₅⁺;

(3) The results of Johnson and Pollin indicate that thermodynamic criticality is a necessary and sufficient condition for first contact miscible displacement of an alkane by CO₂ since the effect of porous media on VLE during STD is small;

(4) The effect of temperature on MMP is clearly defined by the L-V critical locus of these binary systems over the range of reservoir temperatures; the MMP increases with temperature. This is in agreement with all correlations;

(5) The effect of the oil composition as measured by MW C₅⁺ on MMP is also readily defined by comparing the critical branches of the CO₂ n-alkane series; the MMP increases as the MW C₅⁺ increases. This trend is consistent with all correlations which consider the oil composition in terms of MW C₅⁺;

(6) This correlation may be modified to account for CO₂ impurities by determining the miscibility limit, or cricondenbar, of impure CO₂/n-alkane mixtures at reservoir temperature. Note that unlike the binary CO₂/n-alkane systems, the cricondenbar is not necessarily the critical pressure;

(7) Volatile oil components may also be accounted for by simply considering the cricondenbar of pseudo-binary systems at reservoir temperature in which the pure or impure CO₂ would be mixed with the proper normal alkane
combined with the volatile gas components of the actual crude;

(8) As illustrated qualitatively in Figure 1, the modification suggested for CO₂ impurities would result in a decrease in MMP if the critical temperature of the impurity was greater than that of CO₂ and less than that of pentane. Conversely, the MMP would increase if the critical temperature of the impurity was less than that of CO₂. Both of these trends would be enhanced by increasing the concentration of the impurity. These expected results are entirely consistent with observations in literature and the empirical MMP correlations which account for impurities. N₂ and CH₄ increase the MMP(10,13,15,27,30-35) while SO₂, H₂S, C₂H₆ and C₃H₈(10,15,27,32,36) decrease the MMP. In fact, LPG, C₃H₈ and C₄H₁₀ have been added to CO₂ slugs to reduce miscibility pressure requirements.(10,29,34,37,38) Similar results have been observed in rich gas displacements.(18,37,49,40)

(9) As illustrated qualitatively in Figure 2, the modification for 'live oil' components would result in a decrease in MMP if the critical temperature of the component was greater than that of CO₂. Conversely, the MMP would increase if the impurity's critical temperature was less than that of CO₂. These trends are enhanced by an increase of the component's concentration. Again, the expected results are consistent with published observations and empirical MMP correlations. Volatile gases, CH₄ and N₂, in the oil increase the MMP(15,21) or decrease recovery while intermediate gases C₂H₆, C₃H₈, C₄H₁₀, H₂S and CO₂ decrease the MMP.(15) Although CO₂ alone would be expected to have no effect on the MMP, it is usually considered an intermediate gas since it offsets the effects of the volatile components.

(10) Crude oil contains many hydrocarbons, but is modeled as a single normal alkane, thereby not accounting for either molecular distribution or
FIGURE 2: Effect of Volatile and Intermediate Gases in Oil Predicted by Proposed Correlation
paraffinic, naphthenic, and aromatic content. Both of these have recently been shown to influence the MMP, with some disagreement as to the degree of each.\textsuperscript{(19,29,41,42)} Recent studies\textsuperscript{(43,44)} have indicated, however, the PNA characterization of the oil has insignificant effects on the MMP;

(2) Miscible displacement of crude oils is achieved by multiple contact miscibility, MCM, in which the injected CO\textsubscript{2} is initially immiscible with the crude, but develops miscibility as the CO\textsubscript{2} extracts more and more of the C\textsubscript{5}–C\textsubscript{30} hydrocarbons as it passes through the tube. Miscible displacement of pure n-alkanes is achieved by first contact miscibility, FCM, in which the CO\textsubscript{2} and oil are miscible in all proportions, no analogous extraction occurs;

(3) Complete recovery is possible in FCM displacements, however, only 90–98% recovery is achieved in MCM due to multiple phase transition zones.

(4) Due to the heavy components in crude oils, the cricordenbars of CO\textsubscript{2}–crude oil Px diagrams at reservoir temperature are so high (>35 MPa) that they often cannot be measured, and are not related at all to the MMP. The cricordenbar of the CO\textsubscript{2}–alkane mixtures, however, will be used to determine the MMP;

(5) The MW C\textsubscript{5}\textsuperscript{+} of crude oils falls in the 170–240 range. The MW of n-alkanes is fixed at discrete values in increments of 14, so pseudo-alkanes whose critical properties and interaction parameters are interpolated between n-alkanes must be introduced;

(6) The Holm and Josendal correlation\textsuperscript{(19)} indicates that crudes of equivalent MW C\textsubscript{5}\textsuperscript{+} will not have equivalent MP's if the extractable portions of the crude, (C\textsubscript{5}–C\textsubscript{30})/C\textsubscript{5}\textsuperscript{+}, are different. A higher presssure is required for crude oils with lower extractable portions. The proposed MMP correlation would not predict such effects. Conversely, however, this MMP correlation would predict that crudes
of equivalent extractable portions but different MW C$_5$+ would have different MMP's while the Holm and Josendal correlation would predict the same MMP for each crude. If one considers crudes of high extractable portions, it is clear that the Holm and Josendal correlation would not yield correct trends. It is evident, therefore, that neither (C$_5$–C$_{30}$/C$_5$+) nor MW C$_5$+ is a complete oil characterization parameter, however, each is sufficient in MMP correlations. Perhaps a more advanced correlation would incorporate both parameters;

(7) The proposed correlation will not work well, if at all, for some low temperature reservoirs since liquid-liquid immiscibility in this region prohibits the existence of a cricondenbar for high MW alkanes.$^{(38,39)}$ The proposed correlation, therefore, would predict that miscible displacement cannot occur. Experimental MMP values of 6-9 MPa have been reported, however, in these low temperature systems.

Whether these weaknesses are severe enough to render the proposed MMP correlation inaccurate or ineffective is established by the data and results in this investigation.

In summary, this work may provide a comprehensive MMP correlation which: (1) is based on miscibility principles; (2) is independent of experimental CO$_2$-crude oil MMP values; (3) can account for temperature, oil composition; and CO$_2$ impurities and (4) can be generated by an equation of state.
3.0 EXPERIMENTAL

3.1 Experimental Apparatus

The apparatus used in the PVT and STD experiments is shown in Figure 3. The major components of this experiment, the visual cell and slim tube, are contained within a constant temperature air bath. This oven consists of 3 mm aluminum walls insulated with 3 cm of Fiberfrax, a ceramic material. Expanded aluminum sheets hold the insulation against the walls and also secure five heating tapes against the insulation facing the oven's interior. The oven floor is also insulated and is covered by a 3 mm steel sheet to which hardware is firmly attached. The entire front of the oven is hinged along the 2.5 cm x 2.5 cm x 3 mm angle iron supporting structure to allow access to the inside of the oven. A 6 mm tempered glass panel is attached to this door to allow visual observation. A mirror is mounted on a 45° angle along the center of the glass to enable the high pressure cell to be observed indirectly. Four high temperature lights and sockets are found on the sides of the box's interior which illuminate the equipment. A constant temperature within the oven is maintained by a Thermoelectric temperature controller.

A uniform temperature distribution is achieved in this 1.25 m x 1.25 m x 1 m volume by a .25 m fan at the top of the box which rotates at 1750 RPM and forces the lighter, warmer and towards the bottom of the oven. Temperatures at the top and bottom of the oven are monitored with iron-constantum thermocouples. The outputs of these and all other thermocouples are then converted into a digital temperature reading by an Omega Model 400 temperature indicator. This display, along with all on-off switches, the temperature controller and pressure gauges are mounted on two 3 mm aluminum side panels which flank the oven.
Schematic Diagram of the Experimental Set-Up

1. Huska Pump
2. Mercury Reservoir
3. Pressure Gauge
4. Pressure Gauge (20,000 psig)
5. Oil Cell
6. Alcohol Cell
7. Cylinder of Either Pure CO$_2$ or CO$_2$ Containing Gaseous Impurities
8. Pressure Regulators
9. Heater
10. Displacing Fluid Cell
11. Pressure Gauge
12. Thermocouples
13. Slim Tube
14. Huska Pressure Regulator
15. Pressure Transducer
16. Flash Chamber
17. Wet Test Meter
18. Huska Volatile Oil Cell
19. Trap
20. Vacuum Pump
21. Vacuum Gauge
22. Solvent Cell
23. Nitrogen Cylinder
24. Lapp Pump
25. Constant Temperature Bath
26. Valve

FIGURE 3: Experimental Apparatus
3.1.1 PVT Equipment

The oil and CO₂ were charged into a 400 cm³ Ruska windowed, volatile oil cell, which is rated to 150°C and 70 MPa. The entire volume of the cell may be viewed, allowing visual determination of bubble points. This cell is supported by a 3 cm x 3 cm x .5 cm angle iron frame upon which two pillow blocks are bolted. The pillow blocks hold a 2.5 cm 304 SS rod which is welded to a 304 SS plate which in turn is bolted to the cell. The rod passes through the back wall and is bolted into a 8 cm x 2.5 cm x 10 cm 304 SS bar. This bar may be rotated manually in order to invert the cell in the event that an interface is hidden by the two steel supports in front of the windows. The levels of all interfaces are measured with an Eberbach 40 cm cathetometer. The cell is designed such that if an interface is hidden, it must be visible when the cell is inverted. The cell may be rocked in order to mix the components by a Scotch yoke assembly powered by a variable speed D.C. motor. All tubing which leads to the cell is coiled about the supporting rod to permit rotation without removal of any fittings or connections.

Thermocouples are inserted into the cell's thermowells to accurately monitor the temperature in the cell's walls.

All Hg displacement is achieved with a Ruska double cylinder proportioning pump.

In order to charge the Ruska cell with CO₂ with a known amount of CO₂, both the Ruska cell and the CO₂ sample cylinders were evaluated with a Cence Hyvac 14 vacuum pump. After heating the over to 32.2°C ± .2°C, the large CO₂ supply cylinder was opened, charging both the Ruska cell and the sample cylinder to the vapor pressure of CO₂ (since the supply cylinder was at room temperature). The supply cylinder was then closed and Hg forced into the CO₂ sample cylinder,
compressing the supercritical CO\textsubscript{2} in not only the sample cylinder, but also the Ruska cell. When the pressure reached 6.895 MPa, the top valve of the Ruska cell was closed. Hg was then displaced into the Ruska cell, and a series of volume-pressure measurements at constant temperature obtained which can be used to determine the density of the supercritical CO\textsubscript{2} with density charts. Coupling the density with volume led to determination of the mass of CO\textsubscript{2} in the Ruska cell.

Oil was then charged into the Ruska cell from the 500 cm\textsuperscript{3} high pressure oil storage cell by Hg displacement. Since the volume injected and oil density were both known, the mass of oil injected was calculated. Hg was then displaced into the Ruska cell, decreasing the total volume, and thereby increasing the pressure, of a system of known overall composition at constant temperature. Interface levels were then measured and phase volumes calculated. These flash equilibrium experiments yielded the required PVT information for this study.

Upon completion of the experiment, the fluids in the cell were discharged in the hood. In order to clean the visual cell, a 300 cm\textsuperscript{3} sample cylinder was charged with solvent using a Lapp pump. Nitrogen from an Air Products A cylinder, regulated to low pressure, forced solvent from the cylinder into the Ruska cell, removing all residual oil. The N\textsubscript{2} then followed the solvent, drying the interior of the cell.

3.1.2 STD Equipment

The slim tube used in these experiments was .64 cm OD 304 SS seamless tubing packed with No. 60 sea sand from Crystal Silica Co. The permeability and porosity of the packed tube 20 darcies and 38\%, respectively. This 6.4 m tube is coiled into a 30 cm diameter winding. Inlet and outlet temperatures were monitored with two in line thermocouples.
Oil saturation was achieved by Hg displacement of the alkane from the oil storage cell into the coil. CO₂ displacement was also achieved by a constant rate displacement of CO₂ from the Ruska cell into the coil. A 0–42 MPa back pressure regulator maintained a constant outlet pressure. This outlet pressure was monitored by a Viatran 700A 0–70 MPa psia pressure transmitter mounted outside of the box to protect its components from heat damage. The produced fluids entered an equilibrium flash chamber equipped with a scale to measure the produced oil. The produced amount of CO₂ was measured with a Precision Scientific wet test meter.

After completing a run, the tube was cleaned using the same procedure as in the PVT study or simply resaturated by injecting several PV of oil at high pressure.

3.2 Parameter Specifications

(1) Most temperature-carbon dioxide floods have been performed in fields whose temperatures fall in the 30°C to 115°C interval and the correlation has already been shown to break down in the low temperature range, PVT and STD studies were performed at 37.8, 65.6 and 104.4°C;

(2) (a) CO₂ - Coleman grade CO₂, 99.99% pure, purchased from Air Products was used in this work;

(b) Impurities - Cylinders of gas phase mixtures of 5% CH₄, 10% CH₄ and 10% N₂ were also purchased from Air Products. Methane and nitrogen are the most common CO₂ impurities and these three mixtures of impure CO₂ will permit trends of both concentration and type of impurity to be established.
(3) Normal Alkane - The MW $C_5^+$ of crude oils considered for CO$_2$ flooding ranges from 170 to 260. Normal tridecane of 99+% purity was purchased from Aldrich and used in this study. This alkane's MW of 184 falls within the crude oil range and its PT diagram with CO$_2$ represents a transition in the CO$_2$/n-alkane system, therefore, not only provides the information required to analyze the proposed correlation, but also lends insight into CO$_2$/n-alkane PT behavior where conflicting and incomplete results have been published.\(^{45-47}\)

3.3 Experimental Procedure

3.3.1 PVT

In order to determine the cricondenbar, as well as to observe two and three phase volumetric behavior of these systems, isothermal compressions of mixtures of known overall composition were performed. When liquid phase volume was plotted against pressure, for each overall composition, a series of curves resulted. As pressure increased, the liquid phase volume of mixtures characterized by a dew point reached a maximum value and then terminated at 0 liquid. The liquid phase volume of mixtures characterized by a bubble point saturation pressure increased steadily to a value of 100% liquid. The cricondenbar was then defined as the limiting pressure above which no multiphase equilibrium can occur. In binary systems, this corresponded to the critical pressure.

3.3.2 STD

STD experiments were performed to determine this MMP, with at least two above and two below the MMP. Since complete recovery is possible in these model systems, the MMP is defined as the lowest pressure in which 100% recovery
of OIP is achieved. Due to the pressure drop across the tube, an uncertainty of ± .14 MPa existed for the MMP. High displacement rates of 250-500 cm/hr were used in these systems since only two or three components are present and quick equilibration in the mixing zone should result.

3.4 Proposed Goals

3.4.1 Experimental Goals

Both PVT and STD experiments were performed in order to establish the validity of the proposed correlation. Specific goals, in sequential order, included the following:

(1) PVT study of a CO₂/n-alkane system at several temperatures which spanned the range of reservoir temperatures. This led to the determination of the cricondenbar (critical pressure for binary systems) at each temperature;

(2) STD of the n-alkane by CO₂ at the same temperatures, the MMP was then compared to the critical pressures obtained in the PVT experiments. Good agreement was expected between these results, indicating that

(a) thermodynamic criticality is a necessary and sufficient condition for FCM displacement,

(b) the proposed correlation is exact for pure alkane systems, which, as the simplest model of crude oil systems, must be accurately predicted to establish confidence in this correlation's capabilities.
(3) PVT study at the same temperatures and using the same alkane, but with impure CO₂. This established the change effected by the impurity on the cricondenbar, and thereby the predicted MMP.

(4) STD of the alkane by the impure CO₂ at the three temperatures. The MMP of these tests was then compared to the previously determined cricondenbars.

(5) Repeat of steps 3 and 4 for systems containing the same CO₂ impurity at different concentrations to establish the effects of concentration on the predicted MMP.

(6) Repeat of steps 3 and 4 for systems containing a different CO₂ impurity in order to establish the effects of the type of impurity.

Crude oils were not used in the experimental study since MMP data for over 150 systems, 10 MMP correlations based on pure CO₂/crude oil systems and 5 MMP correlations which also consider the effects of impurities were available in the literature.

3.4.2 Equation of State Predictions

A method of predicting the experimental results has been developed which allows greater versatility in dealing with a wide range of alkanes, impurities and temperatures and rapid estimation of MMP. An equation of state multicomponent program, capable of implementing the Peng-Robinson or Soave-Redlich-Kwong(49) equations, listed in Table 3, was available which performs flash calculations which are convergent even in the critical region. This was used since the experimental PVT studies consists of flash equilibrations where the temperature, pressure and overall composition are known and phase volumes and compositions must be calculated. From these computed results, a graphical correlation of MMP was
Table 3: SRK and PR Equations of State

Soave-Redlich-Kwong

\[ P = \frac{RT}{v-b} - \frac{a}{v(v+b)} \]  
\[ b = 0.08664 \frac{RT}{P_c} \]  
\[ a(T) = 0.42747 \frac{RT}{P_c}^2 \]  
\[ \alpha^{0.5} = 1 + m(1 - \alpha^{0.5}) \]  
\[ m = 0.480 - 1.574\omega - 0.176\omega^2 \]
(1a) \hspace{1cm} \hspace{1cm} \hspace{1cm} \hspace{1cm} (2a) \hspace{1cm} \hspace{1cm} \hspace{1cm} \hspace{1cm} \hspace{1cm} \hspace{1cm} (3a) \hspace{1cm} \hspace{1cm} \hspace{1cm} \hspace{1cm} \hspace{1cm} (4a) \hspace{1cm} \hspace{1cm} \hspace{1cm} \hspace{1cm} (5a)

Peng-Robinson

\[ P = \frac{RT}{v-b} - \frac{a}{v(v+b) + b(v-b)} \]  
\[ b = 0.07780 \frac{RT}{P_c} \]  
\[ a(T) = 0.45724 \frac{RT}{P_c}^2 \]  
\[ \alpha^{0.5} = 1 + m(1 - \alpha^{0.5}) \]  
\[ m = 0.37464 + 1.54226\omega - 0.26992\omega^2 \]
(1b) \hspace{1cm} \hspace{1cm} \hspace{1cm} \hspace{1cm} (2b) \hspace{1cm} \hspace{1cm} \hspace{1cm} \hspace{1cm} \hspace{1cm} \hspace{1cm} (3b) \hspace{1cm} \hspace{1cm} \hspace{1cm} \hspace{1cm} (4b) \hspace{1cm} \hspace{1cm} \hspace{1cm} \hspace{1cm} (5b)

Compressibility Factor

\[ Z^3 - Z^2 + (A - B - B^2)Z - AB = 0 \]  
\[ Z^3 - (1 - B)Z^2 + (A - 3B^2 - 2B^3)Z - (AB - B^2 - B^3) = 0 \]
(6a) \hspace{1cm} \hspace{1cm} \hspace{1cm} \hspace{1cm} (6b)

where

\[ Z = \frac{Pv}{RT} \]  
\[ A = \frac{aP}{RT^2} \]  
\[ B = \frac{bP}{RT} \]
(7a) \hspace{1cm} \hspace{1cm} \hspace{1cm} (8a) \hspace{1cm} \hspace{1cm} \hspace{1cm} \hspace{1cm} (9a)

Fugacity Coefficient

\[ \ln \frac{\psi}{k} = \frac{b}{k} (Z-1) - \ln (Z-B) - \frac{A}{B} \left( \frac{2x_i a_{ik}}{a} - \frac{b}{b} \right) \ln \left( 1 + \frac{B}{Z} \right) \]
(10a)
\[ \ln \frac{\psi}{k} = \frac{b}{k} (Z-1) - \ln (Z-B) - \frac{A}{2\sqrt{2B}} \left( \frac{2x_i a_{ik}}{a} - \frac{b}{b} \right) \ln \left( \frac{Z + (\sqrt{2}+1)B}{Z - (\sqrt{2}-1)B} \right) \]
(10b)

Mixing rules for both equations, where \( \sigma_{ij} \) are binary interaction coefficients

\[ b = \sum_{i} x_i b_i \]
(11)
\[ a = \sum_{ij} x_i x_j a_{ij} \]
(12)
\[ a_{ij} = (1 - f_{ij}) a_i^{0.5} a_j^{0.5} \]
(13)
developed which accounts for temperature, oil composition and CO₂ impurities. The 157 crude oil systems were then analyzed by modeling the crude's C₅⁺ portion by a single alkane and determining the cricondenbar at reservoir temperature of the alkane with the pure or impure CO₂ used to displace the actual crude. An error analysis was then used to compare the predicted and actual MMP values for all of the systems.
4.0 ANALYSIS OF RAW DATA

In this section, the experimental data obtained following the previously detailed procedures will be presented.

4.1 PVT data

4.1.1 CO$_2$/nC$_{13}$H$_{28}$

A comprehensive study of this binary system has been completed which not only details the unique, transitional PT diagram of this particular system in the CO$_2$/n-alkane series,$^{(50)}$ but also introduces methods of describing three phase, two component volumetric behavior. These results have been verified in simultaneous independent study.$^{(51)}$ Although all of the data obtained for this system have been presented in Figures 4 through 15, only the information pertinent to this MMP study will be discussed, Figures 5 and 6 and Table 4.

Two phase volumetric behavior is evidenced at 377.6 K and 338.7 K, Figure 5 and Table 4. From the plots of liquid phase volume fraction vs. pressure at constant temperature for specified overall composition, both the critical pressure and critical composition can be determined, Table 5. In Figure 6, the Px diagram at 310.8 K is presented. Since this temperature lies between the LCEP and K point$^{(48,49)}$ which are critical endpoints of the L$_2$-V and L$_1$-L$_2$ critical loci, respectively, three phase behavior is evidenced at approximately 8.2 MPa and two distinct critical points exist. The cricondenbar of such a system corresponds to the greater of the two critical pressures, which in this instance, is the liquid-liquid-critical point. The critical composition and pressure of this region are listed in Table 4.
FIGURE 4: Two Phase Volumetric Data, CO$_2$/nC$_{13}$H$_{28}$, 314.1 K, 309.7 K, 307.4 K and 300.8 K
FIGURE 5: Two Phase Volumetric Data, 377.6 K and 338.7 K
FIGURE 6: Pressure-Composition Diagram, CO$_2$/nC$_{13}$H$_{28}$, 310.8 K
FIGURE 7: Pressure-Composition Diagram, CO$_2$/nC$_{13}$H$_{28}$, 311.9 K
FIGURE 8: Pressure-Composition Diagram, CO₂/nC₁₃H₂₈, 313.0 K
FIGURE 9: Pressure-Temperature Diagram, CO$_2$/nC$_{13}$H$_{28}$
FIGURE 10: Pressure-Temperature-Composition Diagram, CO$_2$/nC$_{13}$H$_{28}$, LCEP and K Point Region
FIGURE 11: Three Phase Volumetric Behavior, 310.8 K
FIGURE 12: Three Phase Volumetric Behavior, 311.9 K
FIGURE 13: Three Phase Volumetric Behavior, 313.0 K
FIGURE 14: Three Phase Densities between LCEP and K Point
TABLE 4
Volumetric Data for the CO$_2$/nC$_{13}$H$_{28}$ System at 310.8 K, 338.7 K and 377.6 K

<table>
<thead>
<tr>
<th></th>
<th>310.8 K</th>
<th>338.7 K</th>
<th>377.6 K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.01 nC$<em>{13}$H$</em>{28}$</td>
<td>0.01 nC$<em>{13}$H$</em>{28}$</td>
<td>0.01 nC$<em>{13}$H$</em>{28}$</td>
</tr>
<tr>
<td>P</td>
<td>L$_1$</td>
<td>L$_2$</td>
<td>P</td>
</tr>
<tr>
<td>MPa</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.454</td>
<td>0.9394</td>
<td>0.9999</td>
<td></td>
</tr>
<tr>
<td>7.791</td>
<td>0.0379</td>
<td>0.0000</td>
<td></td>
</tr>
<tr>
<td>7.991</td>
<td>0.0444</td>
<td>0.0000</td>
<td></td>
</tr>
<tr>
<td>8.088</td>
<td>0.0545</td>
<td>0.0000</td>
<td></td>
</tr>
<tr>
<td>8.095</td>
<td>0.0489</td>
<td>0.0000</td>
<td></td>
</tr>
<tr>
<td>8.191</td>
<td>0.0586</td>
<td>0.0000</td>
<td></td>
</tr>
<tr>
<td>8.178</td>
<td>0.0636</td>
<td>0.0000</td>
<td></td>
</tr>
<tr>
<td>8.219</td>
<td>0.0479</td>
<td>0.0511</td>
<td></td>
</tr>
<tr>
<td>8.198</td>
<td>0.0369</td>
<td>0.0759</td>
<td></td>
</tr>
<tr>
<td>8.191</td>
<td>0.0306</td>
<td>0.0983</td>
<td></td>
</tr>
<tr>
<td>8.191</td>
<td>0.0202</td>
<td>0.1241</td>
<td></td>
</tr>
<tr>
<td>8.178</td>
<td>0.0000</td>
<td>0.1638</td>
<td></td>
</tr>
<tr>
<td>8.170</td>
<td>0.0000</td>
<td>0.2479</td>
<td></td>
</tr>
<tr>
<td>8.198</td>
<td>0.0000</td>
<td>0.3485</td>
<td></td>
</tr>
<tr>
<td>8.226</td>
<td>0.0000</td>
<td>0.5143</td>
<td></td>
</tr>
<tr>
<td>8.233</td>
<td>0.0000</td>
<td>0.8505</td>
<td></td>
</tr>
<tr>
<td>8.260</td>
<td>0.0000</td>
<td>0.9239</td>
<td></td>
</tr>
<tr>
<td>8.260</td>
<td>0.0000</td>
<td>1.0000</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>0.02 nC$<em>{13}$H$</em>{28}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>L$_1$</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>7.143</td>
<td>0.0474</td>
</tr>
<tr>
<td>7.495</td>
<td>0.0550</td>
</tr>
<tr>
<td>7.750</td>
<td>0.0666</td>
</tr>
<tr>
<td>8.026</td>
<td>0.0837</td>
</tr>
<tr>
<td>8.116</td>
<td>0.0893</td>
</tr>
<tr>
<td>8.191</td>
<td>0.0968</td>
</tr>
<tr>
<td>8.129</td>
<td>0.1052</td>
</tr>
<tr>
<td>8.178</td>
<td>0.1148</td>
</tr>
<tr>
<td>8.185</td>
<td>0.1068</td>
</tr>
<tr>
<td>8.205</td>
<td>0.0904</td>
</tr>
<tr>
<td>8.212</td>
<td>0.0742</td>
</tr>
<tr>
<td>8.191</td>
<td>0.0640</td>
</tr>
<tr>
<td>8.150</td>
<td>0.0436</td>
</tr>
<tr>
<td>8.157</td>
<td>0.0249</td>
</tr>
<tr>
<td>D MPa</td>
<td>L₁</td>
</tr>
<tr>
<td>-------</td>
<td>------</td>
</tr>
<tr>
<td>8.198</td>
<td>.0000</td>
</tr>
<tr>
<td>8.205</td>
<td>.0000</td>
</tr>
<tr>
<td>8.205</td>
<td>.0000</td>
</tr>
<tr>
<td>8.287</td>
<td>.0000</td>
</tr>
<tr>
<td>8.164</td>
<td>.0000</td>
</tr>
<tr>
<td>8.260</td>
<td>.0000</td>
</tr>
</tbody>
</table>

**TABLE 4**  
(Continued)

<table>
<thead>
<tr>
<th>310.8 K</th>
<th>338.7 K</th>
<th>377.6 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>P MPa</td>
<td>L₁</td>
<td>L₂</td>
</tr>
<tr>
<td>---------</td>
<td>---------</td>
<td>---------</td>
</tr>
<tr>
<td>7.326</td>
<td>.1309</td>
<td>.0000</td>
</tr>
<tr>
<td>8.102</td>
<td>.1595</td>
<td>.0000</td>
</tr>
<tr>
<td>8.150</td>
<td>.1671</td>
<td>.0000</td>
</tr>
<tr>
<td>8.205</td>
<td>.1762</td>
<td>.0000</td>
</tr>
<tr>
<td>8.219</td>
<td>.1856</td>
<td>.0000</td>
</tr>
<tr>
<td>8.274</td>
<td>.2148</td>
<td>.0541</td>
</tr>
<tr>
<td>8.185</td>
<td>.1865</td>
<td>.1046</td>
</tr>
<tr>
<td>8.288</td>
<td>.1720</td>
<td>.1647</td>
</tr>
<tr>
<td>8.178</td>
<td>.1504</td>
<td>.2409</td>
</tr>
<tr>
<td>8.178</td>
<td>.1201</td>
<td>.3764</td>
</tr>
<tr>
<td>8.267</td>
<td>.0841</td>
<td>.5303</td>
</tr>
<tr>
<td>8.302</td>
<td>.0360</td>
<td>.7072</td>
</tr>
<tr>
<td>8.357</td>
<td>.0000</td>
<td>.9572</td>
</tr>
<tr>
<td>8.316</td>
<td>.0000</td>
<td>1.0000</td>
</tr>
</tbody>
</table>

**.03 nC₁₃H₂₈**

<p>| 0.04 nC₁₃H₂₈ |</p>
<table>
<thead>
<tr>
<th>MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.998</td>
</tr>
<tr>
<td>8.205</td>
</tr>
<tr>
<td>8.226</td>
</tr>
<tr>
<td>8.219</td>
</tr>
<tr>
<td>8.219</td>
</tr>
<tr>
<td>8.274</td>
</tr>
</tbody>
</table>
TABLE 4
(Continued)

<table>
<thead>
<tr>
<th>P (MPa)</th>
<th>L₁</th>
<th>L₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.274</td>
<td>.2611</td>
<td>.1195</td>
</tr>
<tr>
<td>8.226</td>
<td>.2387</td>
<td>.2272</td>
</tr>
<tr>
<td>8.185</td>
<td>.1946</td>
<td>.3974</td>
</tr>
<tr>
<td>8.157</td>
<td>.1529</td>
<td>.5880</td>
</tr>
<tr>
<td>8.122</td>
<td>.0816</td>
<td>.7491</td>
</tr>
<tr>
<td>8.136</td>
<td>.0753</td>
<td>.8575</td>
</tr>
<tr>
<td>8.150</td>
<td>.0741</td>
<td>.9147</td>
</tr>
<tr>
<td>8.164</td>
<td>.0548</td>
<td>.9452</td>
</tr>
<tr>
<td>8.205</td>
<td>.0000</td>
<td>1.000</td>
</tr>
</tbody>
</table>

310.8 K

<table>
<thead>
<tr>
<th>P (MPa)</th>
<th>L₁</th>
<th>L₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.943</td>
<td>.1995</td>
<td>.0000</td>
</tr>
<tr>
<td>8.136</td>
<td>.2200</td>
<td>.0000</td>
</tr>
<tr>
<td>8.178</td>
<td>.2372</td>
<td>.0000</td>
</tr>
<tr>
<td>8.178</td>
<td>.2483</td>
<td>.0000</td>
</tr>
<tr>
<td>8.247</td>
<td>.2645</td>
<td>.0000</td>
</tr>
<tr>
<td>8.240</td>
<td>.2849</td>
<td>.0000</td>
</tr>
<tr>
<td>8.316</td>
<td>.3010</td>
<td>.0000</td>
</tr>
<tr>
<td>8.302</td>
<td>.3332</td>
<td>.0000</td>
</tr>
<tr>
<td>8.178</td>
<td>.3677</td>
<td>.0000</td>
</tr>
<tr>
<td>8.191</td>
<td>.3592</td>
<td>.0811</td>
</tr>
<tr>
<td>8.191</td>
<td>.3426</td>
<td>.1840</td>
</tr>
<tr>
<td>8.205</td>
<td>.3264</td>
<td>.2898</td>
</tr>
<tr>
<td>8.212</td>
<td>.3133</td>
<td>.4101</td>
</tr>
<tr>
<td>8.205</td>
<td>.2931</td>
<td>.5409</td>
</tr>
<tr>
<td>8.205</td>
<td>.2700</td>
<td>.6732</td>
</tr>
<tr>
<td>8.233</td>
<td>.2354</td>
<td>.7646</td>
</tr>
<tr>
<td>8.309</td>
<td>.1273</td>
<td>.8727</td>
</tr>
<tr>
<td>8.316</td>
<td>.0000</td>
<td>1.000</td>
</tr>
</tbody>
</table>

338.7 K

<table>
<thead>
<tr>
<th>P (MPa)</th>
<th>L₁</th>
<th>L₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.943</td>
<td>.1995</td>
<td>.0000</td>
</tr>
<tr>
<td>8.136</td>
<td>.2200</td>
<td>.0000</td>
</tr>
<tr>
<td>8.178</td>
<td>.2372</td>
<td>.0000</td>
</tr>
<tr>
<td>8.178</td>
<td>.2483</td>
<td>.0000</td>
</tr>
<tr>
<td>8.247</td>
<td>.2645</td>
<td>.0000</td>
</tr>
<tr>
<td>8.240</td>
<td>.2849</td>
<td>.0000</td>
</tr>
<tr>
<td>8.316</td>
<td>.3010</td>
<td>.0000</td>
</tr>
<tr>
<td>8.302</td>
<td>.3332</td>
<td>.0000</td>
</tr>
<tr>
<td>8.178</td>
<td>.3677</td>
<td>.0000</td>
</tr>
<tr>
<td>8.191</td>
<td>.3592</td>
<td>.0811</td>
</tr>
<tr>
<td>8.191</td>
<td>.3426</td>
<td>.1840</td>
</tr>
<tr>
<td>8.205</td>
<td>.3264</td>
<td>.2898</td>
</tr>
<tr>
<td>8.212</td>
<td>.3133</td>
<td>.4101</td>
</tr>
<tr>
<td>8.205</td>
<td>.2931</td>
<td>.5409</td>
</tr>
<tr>
<td>8.205</td>
<td>.2700</td>
<td>.6732</td>
</tr>
<tr>
<td>8.233</td>
<td>.2354</td>
<td>.7646</td>
</tr>
<tr>
<td>8.309</td>
<td>.1273</td>
<td>.8727</td>
</tr>
<tr>
<td>8.316</td>
<td>.0000</td>
<td>1.000</td>
</tr>
</tbody>
</table>

377.6 K

<table>
<thead>
<tr>
<th>P (MPa)</th>
<th>L₁</th>
<th>L₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.943</td>
<td>.1995</td>
<td>.0000</td>
</tr>
<tr>
<td>8.136</td>
<td>.2200</td>
<td>.0000</td>
</tr>
<tr>
<td>8.178</td>
<td>.2372</td>
<td>.0000</td>
</tr>
<tr>
<td>8.178</td>
<td>.2483</td>
<td>.0000</td>
</tr>
<tr>
<td>8.247</td>
<td>.2645</td>
<td>.0000</td>
</tr>
<tr>
<td>8.240</td>
<td>.2849</td>
<td>.0000</td>
</tr>
<tr>
<td>8.316</td>
<td>.3010</td>
<td>.0000</td>
</tr>
<tr>
<td>8.302</td>
<td>.3332</td>
<td>.0000</td>
</tr>
<tr>
<td>8.178</td>
<td>.3677</td>
<td>.0000</td>
</tr>
<tr>
<td>8.191</td>
<td>.3592</td>
<td>.0811</td>
</tr>
<tr>
<td>8.191</td>
<td>.3426</td>
<td>.1840</td>
</tr>
<tr>
<td>8.205</td>
<td>.3264</td>
<td>.2898</td>
</tr>
<tr>
<td>8.212</td>
<td>.3133</td>
<td>.4101</td>
</tr>
<tr>
<td>8.205</td>
<td>.2931</td>
<td>.5409</td>
</tr>
<tr>
<td>8.205</td>
<td>.2700</td>
<td>.6732</td>
</tr>
<tr>
<td>8.233</td>
<td>.2354</td>
<td>.7646</td>
</tr>
<tr>
<td>8.309</td>
<td>.1273</td>
<td>.8727</td>
</tr>
<tr>
<td>8.316</td>
<td>.0000</td>
<td>1.000</td>
</tr>
</tbody>
</table>

.05 nC₁₃H₂₈

<table>
<thead>
<tr>
<th>P (MPa)</th>
<th>L₁</th>
<th>L₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.825</td>
<td>.1888</td>
<td>.2093</td>
</tr>
<tr>
<td>12.328</td>
<td>.2268</td>
<td>.2378</td>
</tr>
<tr>
<td>12.873</td>
<td>.2361</td>
<td>.2385</td>
</tr>
<tr>
<td>13.321</td>
<td>.199</td>
<td></td>
</tr>
<tr>
<td>13.839</td>
<td>.1693</td>
<td></td>
</tr>
<tr>
<td>14.038</td>
<td>.0567</td>
<td></td>
</tr>
<tr>
<td>14.096</td>
<td>.0398</td>
<td></td>
</tr>
<tr>
<td>14.100</td>
<td>.0199</td>
<td></td>
</tr>
<tr>
<td>14.135</td>
<td>.0000</td>
<td></td>
</tr>
</tbody>
</table>

.06 nC₁₃H₂₈

<table>
<thead>
<tr>
<th>P (MPa)</th>
<th>L₁</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.998</td>
<td>.2674</td>
</tr>
<tr>
<td>8.219</td>
<td>.3144</td>
</tr>
<tr>
<td>8.205</td>
<td>.3234</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>P (MPa)</th>
<th>L₁</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.756</td>
<td>.2313</td>
</tr>
<tr>
<td>12.584</td>
<td>.2697</td>
</tr>
<tr>
<td>13.700</td>
<td>.2982</td>
</tr>
<tr>
<td>P (MPa)</td>
<td>L₁</td>
</tr>
<tr>
<td>--------</td>
<td>------</td>
</tr>
<tr>
<td>8.239</td>
<td>.3459</td>
</tr>
<tr>
<td>0.247</td>
<td>.3707</td>
</tr>
<tr>
<td>6.198</td>
<td>.4006</td>
</tr>
<tr>
<td>8.219</td>
<td>.4342</td>
</tr>
<tr>
<td>8.219</td>
<td>.4790</td>
</tr>
<tr>
<td>8.219</td>
<td>.4572</td>
</tr>
<tr>
<td>8.205</td>
<td>.4496</td>
</tr>
<tr>
<td>8.205</td>
<td>.4400</td>
</tr>
<tr>
<td>8.205</td>
<td>.4345</td>
</tr>
<tr>
<td>8.219</td>
<td>.4224</td>
</tr>
<tr>
<td>8.205</td>
<td>.4145</td>
</tr>
<tr>
<td>8.274</td>
<td>.3864</td>
</tr>
<tr>
<td>8.364</td>
<td>.0000</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>P (MPa)</th>
<th>L₁</th>
<th>L₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>310.8 K</td>
<td>.065 nC₁₃H₂₈</td>
<td></td>
</tr>
<tr>
<td>7.571</td>
<td>.1424</td>
<td>.0000</td>
</tr>
<tr>
<td>8.171</td>
<td>.3580</td>
<td>.0000</td>
</tr>
<tr>
<td>8.205</td>
<td>.4378</td>
<td>.0098</td>
</tr>
<tr>
<td>8.274</td>
<td>.5058</td>
<td>.0000</td>
</tr>
<tr>
<td>8.274</td>
<td>.5120</td>
<td>.0435</td>
</tr>
<tr>
<td>8.219</td>
<td>.5097</td>
<td>.1182</td>
</tr>
<tr>
<td>8.274</td>
<td>.4984</td>
<td>.2207</td>
</tr>
<tr>
<td>8.205</td>
<td>.4901</td>
<td>.3265</td>
</tr>
<tr>
<td>8.205</td>
<td>.4821</td>
<td>.4544</td>
</tr>
<tr>
<td>8.205</td>
<td>.4707</td>
<td>.5293</td>
</tr>
<tr>
<td>8.384</td>
<td>.8613</td>
<td>.1387</td>
</tr>
<tr>
<td>8.384</td>
<td>1.000</td>
<td>.0000</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>P (MPa)</th>
<th>L₁</th>
<th>L₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>338.7 K</td>
<td>.07 nC₁₃H₂₈</td>
<td></td>
</tr>
<tr>
<td>7.860</td>
<td>.2498</td>
<td>.0000</td>
</tr>
<tr>
<td>8.171</td>
<td>.4589</td>
<td>.0000</td>
</tr>
<tr>
<td>8.171</td>
<td>.5391</td>
<td>.0000</td>
</tr>
<tr>
<td>8.178</td>
<td>.5581</td>
<td>.1873</td>
</tr>
<tr>
<td>8.191</td>
<td>.5559</td>
<td>.2215</td>
</tr>
<tr>
<td>8.205</td>
<td>.5773</td>
<td>.0185</td>
</tr>
<tr>
<td>8.115</td>
<td>.5733</td>
<td>.0522</td>
</tr>
<tr>
<td>8.219</td>
<td>.5574</td>
<td>.1878</td>
</tr>
<tr>
<td>8.178</td>
<td>.5507</td>
<td>.2665</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>P (MPa)</th>
<th>L₁</th>
</tr>
</thead>
<tbody>
<tr>
<td>377.6 K</td>
<td>.07 nC₁₃H₂₈</td>
</tr>
<tr>
<td>7.860</td>
<td>.2498</td>
</tr>
<tr>
<td>8.171</td>
<td>.4589</td>
</tr>
<tr>
<td>8.171</td>
<td>.5391</td>
</tr>
<tr>
<td>8.178</td>
<td>.5581</td>
</tr>
<tr>
<td>8.191</td>
<td>.5559</td>
</tr>
<tr>
<td>8.205</td>
<td>.5773</td>
</tr>
<tr>
<td>8.115</td>
<td>.5733</td>
</tr>
<tr>
<td>8.219</td>
<td>.5574</td>
</tr>
<tr>
<td>8.178</td>
<td>.5507</td>
</tr>
</tbody>
</table>
TABLE 4  
(Continued)

<p>| | | | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>F</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>F</td>
<td></td>
</tr>
<tr>
<td>8.171</td>
<td>.5474</td>
<td>.3199</td>
<td>14.176</td>
<td>.5649</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.171</td>
<td>.5494</td>
<td>.32580</td>
<td>14.169</td>
<td>.5908</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.171</td>
<td>.5510</td>
<td>.3290</td>
<td>14.183</td>
<td>.8190</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.171</td>
<td>.5476</td>
<td>.4335</td>
<td>14.183</td>
<td>.9794</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.171</td>
<td>.5433</td>
<td>.4467</td>
<td>14.190</td>
<td>1.0000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.205</td>
<td>.5533</td>
<td>.4467</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.185</td>
<td>.5617</td>
<td>.4383</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.232</td>
<td>.5665</td>
<td>.4335</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.198</td>
<td>.5703</td>
<td>.4297</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.233</td>
<td>.5849</td>
<td>.4151</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.239</td>
<td>.6409</td>
<td>.3591</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.246</td>
<td>.6914</td>
<td>.3006</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.253</td>
<td>.9901</td>
<td>.0099</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.295</td>
<td>1.0000</td>
<td>.0000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>310.8 K</th>
<th></th>
<th>338.7 K</th>
<th></th>
<th>377.6 K</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>.08 nC_{13}H_{28}</td>
<td></td>
<td>.08 nC_{13}H_{28}</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>P (MPa)</th>
<th>L_1</th>
<th>L_2</th>
<th>P (MPa)</th>
<th>L_1</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.964</td>
<td>.3705</td>
<td>.0000</td>
<td>15.549</td>
<td>.2579</td>
</tr>
<tr>
<td>8.101</td>
<td>.4148</td>
<td>.0000</td>
<td>16.934</td>
<td>.3075</td>
</tr>
<tr>
<td>8.150</td>
<td>.4664</td>
<td>.0000</td>
<td>18.741</td>
<td>.3763</td>
</tr>
<tr>
<td>8.274</td>
<td>.5806</td>
<td>.0000</td>
<td>19.665</td>
<td>.4287</td>
</tr>
<tr>
<td>8.171</td>
<td>.6859</td>
<td>.0645</td>
<td>19.386</td>
<td>.9937</td>
</tr>
<tr>
<td>8.136</td>
<td>.6833</td>
<td>.0240</td>
<td>19.392</td>
<td>1.0000</td>
</tr>
<tr>
<td>8.171</td>
<td>.6859</td>
<td>.0645</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.17</td>
<td>.6821</td>
<td>.1137</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.17</td>
<td>.6815</td>
<td>.1672</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.184</td>
<td>.6761</td>
<td>.2325</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.205</td>
<td>.6748</td>
<td>.2860</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.171</td>
<td>.6732</td>
<td>.3249</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.302</td>
<td>.9950</td>
<td>.0050</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.302</td>
<td>1.0000</td>
<td>.0000</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>.09 nC_{13}H_{28}</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>P (MPa)</td>
<td>L_1</td>
<td>L_2</td>
</tr>
<tr>
<td>---------</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>8.033</td>
<td>.5255</td>
<td>.0000</td>
</tr>
<tr>
<td>8.226</td>
<td>.7768</td>
<td>.0000</td>
</tr>
<tr>
<td>8.205</td>
<td>.7878</td>
<td>.0408</td>
</tr>
<tr>
<td>8.205</td>
<td>.7925</td>
<td>.0888</td>
</tr>
<tr>
<td>8.218</td>
<td>.7927</td>
<td>.1907</td>
</tr>
<tr>
<td>P (MPa)</td>
<td>L₁</td>
<td>L₂</td>
</tr>
<tr>
<td>--------</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>8.060</td>
<td>.6294</td>
<td>.3706</td>
</tr>
<tr>
<td>8.247</td>
<td>.9375</td>
<td>.0393</td>
</tr>
<tr>
<td>8.239</td>
<td>.9692</td>
<td>.0308</td>
</tr>
<tr>
<td>8.185</td>
<td>.9462</td>
<td>.0448</td>
</tr>
<tr>
<td>8.295</td>
<td>.9437</td>
<td>.0563</td>
</tr>
<tr>
<td>8.343</td>
<td>1.0000</td>
<td>.0000</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**.10 nC₁₃H₂₈**

<table>
<thead>
<tr>
<th>P (MPa)</th>
<th>L₁</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.861</td>
<td>.2068</td>
</tr>
<tr>
<td>7.585</td>
<td>.3350</td>
</tr>
<tr>
<td>7.991</td>
<td>.4452</td>
</tr>
<tr>
<td>8.205</td>
<td>.7629</td>
</tr>
<tr>
<td>8.239</td>
<td>.9928</td>
</tr>
<tr>
<td>8.136</td>
<td>.9048</td>
</tr>
<tr>
<td>8.240</td>
<td>1.0000</td>
</tr>
</tbody>
</table>

**.20 nC₁₃H₂₈**

<table>
<thead>
<tr>
<th>P (MPa)</th>
<th>L₁</th>
<th>D (MPa)</th>
<th>L₁</th>
<th>P</th>
<th>L₁</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.081</td>
<td>.5144</td>
<td>9.970</td>
<td>.5373</td>
<td>14.286</td>
<td>.6019</td>
</tr>
<tr>
<td>7.378</td>
<td>.6301</td>
<td>10.666</td>
<td>.6300</td>
<td>15.833</td>
<td>.7310</td>
</tr>
<tr>
<td>7.639</td>
<td>.7301</td>
<td>11.549</td>
<td>.7730</td>
<td>17.782</td>
<td>.9564</td>
</tr>
<tr>
<td>7.654</td>
<td>.7785</td>
<td>11.929</td>
<td>.8619</td>
<td>17.789</td>
<td>1.0000</td>
</tr>
<tr>
<td>7.688</td>
<td>.7900</td>
<td>12.439</td>
<td>.9589</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.688</td>
<td>.8174</td>
<td>12.493</td>
<td>.9899</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.757</td>
<td>.8366</td>
<td>12.507</td>
<td>1.0000</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
TABLE 4
(Continued)

| 7.791   | .8705  |
| 7.826   | .8894  |
| 7.819   | .9091  |
| 7.881   | .9997  |
| 7.826   | .9884  |
| 7.791   | .9618  |
| 7.929   | 1.0000 |
TABLE 5

Critical Pressures and Compositions of the
$\text{CO}_2/\text{nC}_{13}\text{H}_{28}$ System at 310.8 K, 338.7 K and 377.6 K

<table>
<thead>
<tr>
<th>T/K</th>
<th>$x_{\text{nC}<em>{13}\text{H}</em>{28}}$</th>
<th>P/MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>310.8</td>
<td>0.0625</td>
<td>8.398</td>
</tr>
<tr>
<td>338.7</td>
<td>0.065</td>
<td>14.204</td>
</tr>
<tr>
<td>377.6</td>
<td>0.75</td>
<td>19.927</td>
</tr>
</tbody>
</table>
The cricondenbar increased with temperature as expected, displaying good agreement with a previous study, (44, 45) Figure 9. The critical composition increased slightly with temperature as shown in Table 4 and this is in agreement with expected behavior.

4.1.2 (.95 CO₂ + .05 N₂)/nC₁₃H₂₈

To provide experimental results of systems containing impure CO₂, two phase volumetric behavior was recorded for the (.95 CO₂ + .05 N₂)/nC₁₃H₂₈ system at the same temperatures as the pure CO₂ system. The results are presented in Table 6 and Figure 15. The addition of N₂ to the CO₂ caused a dramatic increase in the cricondenbar at each temperature, Table 7, due to its low critical temperature relative to CO₂. Note that the cricondenbar corresponds to a bubble point pressure at each of the three temperatures.

4.1.3 (.95 CO₂ + .05 CH₄)/nC₁₃H₂₈

Two phase volumetric behavior was recorded for this system over the same range of temperature, Table 8 and Figure 16. The addition of this lean impurity also raises the cricondenbar at each temperature, Table 7, although not to the extent of the N₂.

4.1.4 (.90 CO₂ + .10 CH₄)/nC₁₃H₂₈

The two phase volumetric behavior of this system is detailed in Table 9 and Figure 17. The change in cricondenbar due to the increased amount of CH₄ is listed in Table 7 for each temperature.
TABLE 6

Volumetric Data for the (.95 CO₂ + .05 N₂)/nC₁₃H₂₈ System
at 310.8 K, 338.6 K and 377.4 K

<table>
<thead>
<tr>
<th></th>
<th>310.8 K</th>
<th></th>
<th>338.6 K</th>
<th></th>
<th>377.4 K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>.01 nC₁₃H₂₈</td>
<td>.01 nC₁₃H₂₈</td>
<td>.01 nC₁₃H₂₈</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P MPa</td>
<td>L₁</td>
<td>P MPa</td>
<td>L₁</td>
<td>P MPa</td>
<td>L₁</td>
</tr>
<tr>
<td>7.660</td>
<td>.0401</td>
<td>11.500</td>
<td>.0514</td>
<td>15.961</td>
<td>.0404</td>
</tr>
<tr>
<td>9.873</td>
<td>.0669</td>
<td>13.886</td>
<td>.0548</td>
<td>17.333</td>
<td>.0220</td>
</tr>
<tr>
<td>10.066</td>
<td>.0464</td>
<td>14.479</td>
<td>.0415</td>
<td>17.375</td>
<td>.0128</td>
</tr>
<tr>
<td>10.190</td>
<td>.0434</td>
<td>14.755</td>
<td>.1230</td>
<td>17.540</td>
<td>.0000</td>
</tr>
<tr>
<td>10.266</td>
<td>.0323</td>
<td>14.755</td>
<td>.0000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.280</td>
<td>.0000</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>.03 nC₁₃H₂₈</td>
<td>.03 nC₁₃H₂₈</td>
<td>.03 nC₁₃H₂₈</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P MPa</td>
<td>L₁</td>
<td>P MPa</td>
<td>L₁</td>
<td>P MPa</td>
<td>L₁</td>
</tr>
<tr>
<td>7.826</td>
<td>.0740</td>
<td>12.631</td>
<td>.1197</td>
<td>17.058</td>
<td>.0992</td>
</tr>
<tr>
<td>9.136</td>
<td>.1329</td>
<td>13.734</td>
<td>.1341</td>
<td>19.112</td>
<td>.0965</td>
</tr>
<tr>
<td>9.228</td>
<td>.1657</td>
<td>15.024</td>
<td>.1369</td>
<td>20.477</td>
<td>.0703</td>
</tr>
<tr>
<td>10.080</td>
<td>.1771</td>
<td>15.548</td>
<td>.1087</td>
<td>21.029</td>
<td>.0304</td>
</tr>
<tr>
<td>10.273</td>
<td>.1682</td>
<td>16.037</td>
<td>.1075</td>
<td>21.070</td>
<td>.0000</td>
</tr>
<tr>
<td>10.452</td>
<td>.1626</td>
<td>16.541</td>
<td>.0616</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.825</td>
<td>.1500</td>
<td>16.692</td>
<td>.0000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11.142</td>
<td>.1199</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11.321</td>
<td>.1013</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11.542</td>
<td>.0944</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11.659</td>
<td>.0578</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11.679</td>
<td>.0000</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>.05 nC₁₃H₂₈</td>
<td>.05 nC₁₃H₂₈</td>
<td>.05 nC₁₃H₂₈</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P MPa</td>
<td>L₁</td>
<td>P MPa</td>
<td>L₁</td>
<td>P MPa</td>
<td>L₁</td>
</tr>
<tr>
<td>7.943</td>
<td>.1188</td>
<td>13.233</td>
<td>.2097</td>
<td>18.374</td>
<td>.1917</td>
</tr>
<tr>
<td>9.680</td>
<td>.2454</td>
<td>15.003</td>
<td>.2626</td>
<td>21.505</td>
<td>.1803</td>
</tr>
<tr>
<td>10.452</td>
<td>.2567</td>
<td>16.099</td>
<td>.2596</td>
<td>22.035</td>
<td>.1052</td>
</tr>
<tr>
<td>11.514</td>
<td>.2745</td>
<td>16.858</td>
<td>.2441</td>
<td>22.077</td>
<td>.0704</td>
</tr>
<tr>
<td>12.328</td>
<td>.2011</td>
<td>17.512</td>
<td>.1095</td>
<td>22.132</td>
<td>.0466</td>
</tr>
<tr>
<td>12.583</td>
<td>.0000</td>
<td>17.526</td>
<td>.0000</td>
<td>22.201</td>
<td>.0000</td>
</tr>
<tr>
<td></td>
<td>.07 nCi$<em>3$H$</em>{28}$</td>
<td>.07 nCi$<em>3$H$</em>{28}$</td>
<td>.07 nCi$<em>3$H$</em>{28}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>------</td>
<td>---------------------</td>
<td>---------------------</td>
<td>---------------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>P</td>
<td>L$_1$</td>
<td>P</td>
<td>L$_1$</td>
<td>P</td>
</tr>
<tr>
<td>MPa</td>
<td></td>
<td></td>
<td>MPa</td>
<td></td>
<td>MPa</td>
</tr>
<tr>
<td>7.943</td>
<td>.1759</td>
<td></td>
<td>13.548</td>
<td>.2995</td>
<td>18.816</td>
</tr>
<tr>
<td>10.562</td>
<td>.3728</td>
<td></td>
<td>15.858</td>
<td>.3758</td>
<td>21.780</td>
</tr>
<tr>
<td>11.280</td>
<td>.4301</td>
<td></td>
<td>16.685</td>
<td>.4234</td>
<td>22.373</td>
</tr>
<tr>
<td>12.169</td>
<td>.4320</td>
<td></td>
<td>17.333</td>
<td>.4479</td>
<td>22.573</td>
</tr>
<tr>
<td>12.769</td>
<td>.4090</td>
<td></td>
<td>17.809</td>
<td>.4444</td>
<td>22.615</td>
</tr>
<tr>
<td>12.893</td>
<td>.3061</td>
<td></td>
<td>17.871</td>
<td>.0000</td>
<td></td>
</tr>
<tr>
<td>12.914</td>
<td>.0000</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>.09 nCi$<em>3$H$</em>{28}$</th>
<th>.09 nCi$<em>3$H$</em>{28}$</th>
<th>.09 nCi$<em>3$H$</em>{28}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>P</td>
<td>L$_1$</td>
<td>P</td>
</tr>
<tr>
<td>MPa</td>
<td></td>
<td></td>
<td>MPa</td>
</tr>
<tr>
<td>9.315</td>
<td>.3602</td>
<td></td>
<td>14.700</td>
</tr>
<tr>
<td>10.493</td>
<td>.4916</td>
<td></td>
<td>16.203</td>
</tr>
<tr>
<td>11.273</td>
<td>.5487</td>
<td></td>
<td>17.402</td>
</tr>
<tr>
<td>12.369</td>
<td>.6059</td>
<td></td>
<td>17.788</td>
</tr>
<tr>
<td>13.066</td>
<td>.7400</td>
<td></td>
<td>18.009</td>
</tr>
<tr>
<td>13.279</td>
<td>.8709</td>
<td></td>
<td>18.037</td>
</tr>
<tr>
<td>13.258</td>
<td>1.0000</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>.II nCi$<em>3$H$</em>{28}$</th>
<th>.II nCi$<em>3$H$</em>{28}$</th>
<th>.II nCi$<em>3$H$</em>{28}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>P</td>
<td>L$_1$</td>
<td>P</td>
</tr>
<tr>
<td>MPa</td>
<td></td>
<td></td>
<td>MPa</td>
</tr>
<tr>
<td>10.308</td>
<td>.5635</td>
<td></td>
<td>15.444</td>
</tr>
<tr>
<td>11.397</td>
<td>.6648</td>
<td></td>
<td>16.996</td>
</tr>
<tr>
<td>12.176</td>
<td>.7281</td>
<td></td>
<td>17.892</td>
</tr>
<tr>
<td>13.135</td>
<td>.8387</td>
<td></td>
<td>18.071</td>
</tr>
<tr>
<td>13.341</td>
<td>.9604</td>
<td></td>
<td>18.098</td>
</tr>
<tr>
<td>13.348</td>
<td>1.0000</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### TABLE 6
(Continued)

<table>
<thead>
<tr>
<th>P MPa</th>
<th>( L_1 )</th>
<th>P MPa</th>
<th>( L_1 )</th>
<th>P MPa</th>
<th>( L_1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.901</td>
<td>.4277</td>
<td>13.893</td>
<td>.5326</td>
<td>18.581</td>
<td>.5232</td>
</tr>
<tr>
<td>10.314</td>
<td>.5680</td>
<td>15.141</td>
<td>.6239</td>
<td>20.422</td>
<td>.6418</td>
</tr>
<tr>
<td>12.307</td>
<td>.8334</td>
<td>17.719</td>
<td>.8929</td>
<td>22.504</td>
<td>9.000</td>
</tr>
<tr>
<td>13.038</td>
<td>.9907</td>
<td>17.892</td>
<td>.9753</td>
<td>27.725</td>
<td>1.0000</td>
</tr>
<tr>
<td>13.128</td>
<td>1.0000</td>
<td>17.961</td>
<td>1.0000</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
FIGURE 15: Two Phase Volumetric Behavior, (0.05 N₂ + 0.95 CO₂)/
nC₁₃H₂₈, 377.6 K, 338.7 K, 310.9 K
<table>
<thead>
<tr>
<th>CO₂</th>
<th>(.95 CO₂+.05 N₂)</th>
<th>(.95 CO₂+.05 CH₄)</th>
<th>(8.95 CO₂+.105 CH₄)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T K</td>
<td>P MPa</td>
<td>P MPa</td>
<td>P MPa</td>
</tr>
<tr>
<td>310.8</td>
<td>8.398</td>
<td>13.376</td>
<td>10.805</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>12.963</td>
</tr>
<tr>
<td>338.7</td>
<td>14.204</td>
<td>18.134</td>
<td>16.204</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>18.031</td>
</tr>
<tr>
<td>377.6</td>
<td>19.927</td>
<td>22.892</td>
<td>21.423</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>22.657</td>
</tr>
<tr>
<td></td>
<td>310.8 K</td>
<td>338.6 K</td>
<td>377.4 K</td>
</tr>
<tr>
<td>----------</td>
<td>------------------</td>
<td>------------------</td>
<td>------------------</td>
</tr>
<tr>
<td><strong>0.01 C_{13}H_{28}</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P (MPa)</td>
<td>L₁</td>
<td>P (MPa)</td>
<td>L₁</td>
</tr>
<tr>
<td>6.381</td>
<td>0.0227</td>
<td>8.422</td>
<td>0.0261</td>
</tr>
<tr>
<td>7.033</td>
<td>0.0224</td>
<td>9.503</td>
<td>0.0258</td>
</tr>
<tr>
<td>7.589</td>
<td>0.0279</td>
<td>10.389</td>
<td>0.0465</td>
</tr>
<tr>
<td>8.237</td>
<td>0.0404</td>
<td>12.367</td>
<td>0.0513</td>
</tr>
<tr>
<td>8.979</td>
<td>0.0519</td>
<td>13.489</td>
<td>0.0400</td>
</tr>
<tr>
<td>9.278</td>
<td>0.0692</td>
<td>13.831</td>
<td>0.0300</td>
</tr>
<tr>
<td>9.555</td>
<td>0.0219</td>
<td>13.842</td>
<td>0.0000</td>
</tr>
<tr>
<td>9.588</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>0.03 C_{13}H_{28}</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P (MPa)</td>
<td>L₁</td>
<td>P (MPa)</td>
<td>L₁</td>
</tr>
<tr>
<td>6.713</td>
<td>0.0516</td>
<td>8.776</td>
<td>0.0595</td>
</tr>
<tr>
<td>7.343</td>
<td>0.0618</td>
<td>10.646</td>
<td>0.0926</td>
</tr>
<tr>
<td>7.953</td>
<td>0.0740</td>
<td>12.346</td>
<td>0.1293</td>
</tr>
<tr>
<td>8.669</td>
<td>0.1200</td>
<td>13.500</td>
<td>0.1444</td>
</tr>
<tr>
<td>9.321</td>
<td>0.1676</td>
<td>14.836</td>
<td>0.1296</td>
</tr>
<tr>
<td>9.919</td>
<td>0.1339</td>
<td>15.456</td>
<td>0.0656</td>
</tr>
<tr>
<td>10.037</td>
<td>0.1336</td>
<td>15.542</td>
<td>0.0196</td>
</tr>
<tr>
<td>10.251</td>
<td>0.0336</td>
<td>15.584</td>
<td>0.0000</td>
</tr>
<tr>
<td>10.272</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>0.05 C_{13}H_{28}</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P (MPa)</td>
<td>L₁</td>
<td>P (MPa)</td>
<td>L₁</td>
</tr>
<tr>
<td>6.531</td>
<td>0.0781</td>
<td>8.618</td>
<td>0.885</td>
</tr>
<tr>
<td>7.685</td>
<td>0.1193</td>
<td>9.700</td>
<td>1.111</td>
</tr>
<tr>
<td>8.412</td>
<td>0.1619</td>
<td>11.597</td>
<td>0.1710</td>
</tr>
<tr>
<td>9.032</td>
<td>0.2399</td>
<td>13.286</td>
<td>0.2307</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

TABLE 8
Volumetric Data for the (.95 CO₂ + .05 CH₄)/nC_{13}H_{28} System
at 310.8 K, 338.6 K and 377.4 K
<table>
<thead>
<tr>
<th>P MPa</th>
<th>L1</th>
<th>P MPa</th>
<th>L1</th>
<th>P MPa</th>
<th>L1</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.860</td>
<td>.1211</td>
<td>8.439</td>
<td>.1198</td>
<td>11.314</td>
<td>.1334</td>
</tr>
<tr>
<td>7.515</td>
<td>.1570</td>
<td>9.515</td>
<td>.1469</td>
<td>13.831</td>
<td>.1856</td>
</tr>
<tr>
<td>8.232</td>
<td>.2160</td>
<td>10.997</td>
<td>.2054</td>
<td>17.788</td>
<td>.2842</td>
</tr>
<tr>
<td>8.977</td>
<td>.3317</td>
<td>12.493</td>
<td>.2839</td>
<td>19.671</td>
<td>.3344</td>
</tr>
<tr>
<td>10.542</td>
<td>.5169</td>
<td>16.010</td>
<td>.4602</td>
<td>21.277</td>
<td>.2265</td>
</tr>
<tr>
<td>10.625</td>
<td>.5425</td>
<td>16.092</td>
<td>1.0000</td>
<td>21.305</td>
<td>.1327</td>
</tr>
<tr>
<td>10.632</td>
<td>.5790</td>
<td></td>
<td></td>
<td>21.394</td>
<td>.0000</td>
</tr>
<tr>
<td>10.694</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>P MPa</th>
<th>L1</th>
<th>P MPa</th>
<th>L1</th>
<th>P MPa</th>
<th>L1</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.860</td>
<td>.1668</td>
<td>8.722</td>
<td>.1663</td>
<td>11.411</td>
<td>.1720</td>
</tr>
<tr>
<td>7.577</td>
<td>.2292</td>
<td>10.204</td>
<td>.2301</td>
<td>13.521</td>
<td>.2311</td>
</tr>
<tr>
<td>8.549</td>
<td>.3274</td>
<td>11.893</td>
<td>.3299</td>
<td>16.306</td>
<td>.3225</td>
</tr>
<tr>
<td>10.314</td>
<td>.6534</td>
<td>15.244</td>
<td>.5706</td>
<td>19.932</td>
<td>.4503</td>
</tr>
<tr>
<td>10.587</td>
<td>.9682</td>
<td>16.092</td>
<td>.9946</td>
<td>20.732</td>
<td>.5180</td>
</tr>
<tr>
<td>10.763</td>
<td>.9953</td>
<td>16.099</td>
<td>1.0000</td>
<td>21.305</td>
<td>.7071</td>
</tr>
<tr>
<td>10.770</td>
<td>1.0000</td>
<td></td>
<td></td>
<td>21.360</td>
<td>.9938</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>21.367</td>
<td>1.0000</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>P MPa</th>
<th>L1</th>
<th>P MPa</th>
<th>L1</th>
<th>P MPa</th>
<th>L1</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.964</td>
<td>.2093</td>
<td>11.721</td>
<td>.3946</td>
<td>15.872</td>
<td>.4018</td>
</tr>
<tr>
<td>7.874</td>
<td>.3043</td>
<td>13.548</td>
<td>.5184</td>
<td>18.767</td>
<td>.5148</td>
</tr>
<tr>
<td>9.411</td>
<td>.6456</td>
<td>15.527</td>
<td>.8135</td>
<td>20.733</td>
<td>.7560</td>
</tr>
<tr>
<td>10.190</td>
<td>.8493</td>
<td>15.927</td>
<td>1.0000</td>
<td>21.229</td>
<td>1.0000</td>
</tr>
<tr>
<td>Value</td>
<td>Number</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>--------</td>
<td>---------</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.321</td>
<td>0.9411</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.446</td>
<td>0.9619</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.521</td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
FIGURE 16: Two Phase Volumetric Behavior (0.05 CH\textsubscript{4} + 0.95 CO\textsubscript{2})/nC\textsubscript{13}H\textsubscript{28}, 377.6 K, 338.7 K, 310.9 K
<table>
<thead>
<tr>
<th>Temperature</th>
<th>.01 nC_{13}H_{28}</th>
<th>.01 nC_{13}H_{28}</th>
<th>.01 nC_{13}H_{28}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>P (MPa)</td>
<td>L _1</td>
<td>P (MPa)</td>
</tr>
<tr>
<td>310.8 K</td>
<td>8.239</td>
<td>.0475</td>
<td>11.114</td>
</tr>
<tr>
<td></td>
<td>10.756</td>
<td>.0375</td>
<td>13.858</td>
</tr>
<tr>
<td></td>
<td>10.927</td>
<td>.0177</td>
<td>14.782</td>
</tr>
<tr>
<td></td>
<td>10.928</td>
<td>.0430</td>
<td>14.996</td>
</tr>
<tr>
<td></td>
<td>11.045</td>
<td>.0000</td>
<td>15.175</td>
</tr>
<tr>
<td>338.6 K</td>
<td>.03 nC_{13}H_{28}</td>
<td>.03 nC_{13}H_{28}</td>
<td>.03 nC_{13}H_{28}</td>
</tr>
<tr>
<td></td>
<td>P (MPa)</td>
<td>L _1</td>
<td>P (MPa)</td>
</tr>
<tr>
<td></td>
<td>9.466</td>
<td>.1305</td>
<td>13.700</td>
</tr>
<tr>
<td></td>
<td>9.832</td>
<td>.1533</td>
<td>14.739</td>
</tr>
<tr>
<td></td>
<td>10.438</td>
<td>.1811</td>
<td>15.817</td>
</tr>
<tr>
<td></td>
<td>11.949</td>
<td>.189</td>
<td>17.099</td>
</tr>
<tr>
<td></td>
<td>12.227</td>
<td>.0968</td>
<td>17.133</td>
</tr>
<tr>
<td></td>
<td>12.286</td>
<td>.0000</td>
<td></td>
</tr>
<tr>
<td>377.4 K</td>
<td>.05 nC_{13}H_{28}</td>
<td>.05 nC_{13}H_{28}</td>
<td>.05 nC_{13}H_{28}</td>
</tr>
<tr>
<td></td>
<td>P (MPa)</td>
<td>L _1</td>
<td>P (MPa)</td>
</tr>
<tr>
<td></td>
<td>8.287</td>
<td>.1330</td>
<td>12.183</td>
</tr>
<tr>
<td></td>
<td>10.618</td>
<td>.2929</td>
<td>15.237</td>
</tr>
<tr>
<td></td>
<td>11.618</td>
<td>.3212</td>
<td>16.168</td>
</tr>
<tr>
<td></td>
<td>12.679</td>
<td>.1963</td>
<td>17.726</td>
</tr>
<tr>
<td></td>
<td>12.803</td>
<td>.081</td>
<td>17.802</td>
</tr>
<tr>
<td></td>
<td>12.803</td>
<td>.0000</td>
<td>17.816</td>
</tr>
<tr>
<td>P (MPa)</td>
<td>L1</td>
<td>P (MPa)</td>
<td>L1</td>
</tr>
<tr>
<td>---------</td>
<td>------</td>
<td>---------</td>
<td>------</td>
</tr>
<tr>
<td>8.205</td>
<td>.1878</td>
<td>11.307</td>
<td>.2022</td>
</tr>
<tr>
<td>9.763</td>
<td>.3153</td>
<td>12.962</td>
<td>.2599</td>
</tr>
<tr>
<td>10.646</td>
<td>.3587</td>
<td>16.719</td>
<td>.4501</td>
</tr>
<tr>
<td>11.480</td>
<td>.4684</td>
<td>17.175</td>
<td>.4781</td>
</tr>
<tr>
<td>11.997</td>
<td>.5028</td>
<td>17.623</td>
<td>.5138</td>
</tr>
<tr>
<td>12.700</td>
<td>.5509</td>
<td>17.892</td>
<td>.6175</td>
</tr>
<tr>
<td>12.858</td>
<td>.6352</td>
<td>17.947</td>
<td>.9598</td>
</tr>
<tr>
<td>12.934</td>
<td>1.0000</td>
<td>17.961</td>
<td>1.0000</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>P (MPa)</th>
<th>L1</th>
<th>P (MPa)</th>
<th>L1</th>
<th>P (MPa)</th>
<th>L1</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.584</td>
<td>.2712</td>
<td>12.597</td>
<td>.3238</td>
<td>17.305</td>
<td>.3391</td>
</tr>
<tr>
<td>11.342</td>
<td>.6035</td>
<td>17.237</td>
<td>.6596</td>
<td>20.919</td>
<td>.4889</td>
</tr>
<tr>
<td>12.339</td>
<td>.7165</td>
<td>17.754</td>
<td>.7641</td>
<td>21.753</td>
<td>.5588</td>
</tr>
<tr>
<td>12.700</td>
<td>.8450</td>
<td>17.995</td>
<td>.9920</td>
<td>22.436</td>
<td>.6238</td>
</tr>
<tr>
<td>12.824</td>
<td>.9538</td>
<td>18.002</td>
<td>1.0000</td>
<td>22.614</td>
<td>.9868</td>
</tr>
<tr>
<td>12.900</td>
<td>1.0006</td>
<td></td>
<td></td>
<td>22.649</td>
<td>1.0000</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>P (MPa)</th>
<th>L1</th>
<th>P (MPa)</th>
<th>L1</th>
<th>P (MPa)</th>
<th>L1</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.473</td>
<td>.3074</td>
<td>14.065</td>
<td>.4974</td>
<td>17.327</td>
<td>.4164</td>
</tr>
<tr>
<td>10.480</td>
<td>.5826</td>
<td>15.444</td>
<td>.6094</td>
<td>19.291</td>
<td>.5238</td>
</tr>
<tr>
<td>11.100</td>
<td>.6820</td>
<td>16.561</td>
<td>.7315</td>
<td>20.546</td>
<td>.5982</td>
</tr>
<tr>
<td>11.597</td>
<td>.7443</td>
<td>17.444</td>
<td>.8815</td>
<td>21.353</td>
<td>.6708</td>
</tr>
<tr>
<td>12.100</td>
<td>.8167</td>
<td>17.699</td>
<td>.9798</td>
<td>22.029</td>
<td>.7752</td>
</tr>
<tr>
<td>12.548</td>
<td>.9199</td>
<td>17.719</td>
<td>1.0000</td>
<td>22.367</td>
<td>.9170</td>
</tr>
<tr>
<td>12.576</td>
<td>1.0000</td>
<td></td>
<td></td>
<td>22.511</td>
<td>.9700</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>22.518</td>
<td>1.0000</td>
</tr>
</tbody>
</table>
FIGURE 17: Two Phase Volumetric Behavior (.105 CH₄ + .895 CO₂)/
nC₁₃H₂₈, 377.6 K, 338.7 K, 310.9 K
4.2 STD Data

Slim tube displacements were performed at the three temperatures of interest, 210.8 K, 338.7 K and 377.6 K. Pure nC_{13}H_{28} was displaced in each experiment. The displacing fluids included the same gas mixtures which were used in the PVT study, CO₂, (.95 CO₂ + 0.5 N₂), (.95 CO₂ + .05 CH₄) and (.90 CO₂ + .10 CH₄). As shown in the system, Figure 18, the MMP can be estimated from such recovery tests by observing where a distinct inflection occurs in the recovery curve. Note that in the displacement of completely miscible systems, such as those in this work, 100% oil recovery is possible, whereas only 95-98% recovery is attainable in crude oil systems.

The data obtained from the 42 slim test displacements are tabulated in Table 10 and illustrated in Figure 19. The MMP's obtained from this data are also listed in Table 10. Increases in MMP occurred with increases in temperature, reduced temperature of the impurity and amount of impurity.
FIGURE 18: Definition of MMP
TABLE 10

Slim Tube Displacement Recovery of nC$_{13}$H$_{28}$ by Pure and Impure CO$_2$ at 310.8 K, 338.7 K and 377.6 K

<table>
<thead>
<tr>
<th>Displacing Fluid</th>
<th>P MPa</th>
<th>Recovery %</th>
<th>P MPa</th>
<th>Recovery %</th>
<th>P MPa</th>
<th>Recovery %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>6.895</td>
<td>57</td>
<td>13.55</td>
<td>81</td>
<td>18.96</td>
<td>70</td>
</tr>
<tr>
<td></td>
<td>7.688</td>
<td>61</td>
<td>13.93</td>
<td>83</td>
<td>19.89</td>
<td>80</td>
</tr>
<tr>
<td></td>
<td>8.102</td>
<td>66</td>
<td>14.03</td>
<td>90</td>
<td>20.68</td>
<td>80</td>
</tr>
<tr>
<td></td>
<td>8.274</td>
<td>77</td>
<td>14.20</td>
<td>100</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>8.412</td>
<td>100</td>
<td>14.55</td>
<td>100</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>8.619</td>
<td>100</td>
<td>14.55</td>
<td>100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>.95 CO$_2$ .05 N$_2$</td>
<td>12.45</td>
<td>87</td>
<td>16.55</td>
<td>72</td>
<td>20.34</td>
<td>68</td>
</tr>
<tr>
<td>.05 CH$_4$</td>
<td>13.10</td>
<td>93</td>
<td>17.24</td>
<td>79</td>
<td>21.37</td>
<td>80</td>
</tr>
<tr>
<td>.95 CO$_2$</td>
<td>13.79</td>
<td>100</td>
<td>19.93</td>
<td>96</td>
<td>22.41</td>
<td>91.5</td>
</tr>
<tr>
<td>.05 CH$_4$</td>
<td>9.136</td>
<td>75</td>
<td>14.55</td>
<td>65</td>
<td>19.31</td>
<td>65</td>
</tr>
<tr>
<td>.895 CO$_2$ .105 CH$_4$</td>
<td>9.826</td>
<td>91.5</td>
<td>15.24</td>
<td>74</td>
<td>20.68</td>
<td>82</td>
</tr>
<tr>
<td></td>
<td>10.51</td>
<td>100</td>
<td>16.07</td>
<td>100</td>
<td>21.37</td>
<td>97</td>
</tr>
<tr>
<td></td>
<td>11.72</td>
<td>100</td>
<td>22.27</td>
<td>100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>.895 CO$_2$ .105 CH$_4$</td>
<td>11.20</td>
<td>78</td>
<td>16.38</td>
<td>72</td>
<td>21.03</td>
<td>77</td>
</tr>
<tr>
<td></td>
<td>11.89</td>
<td>90</td>
<td>17.06</td>
<td>82</td>
<td>21.72</td>
<td>84</td>
</tr>
<tr>
<td></td>
<td>12.58</td>
<td>100</td>
<td>17.75</td>
<td>92</td>
<td>22.41</td>
<td>92</td>
</tr>
</tbody>
</table>
5.0 DEVELOPMENT OF THE CORRELATION

5.1 Equation of State

An efficient and accurate method for describing multicomponent fluid phase equilibria would allow a wide range of all possible parametric variations to be incorporated into the proposed MMP correlation. If such a technique could be shown to predict the cricondenbar of the pseudo-binary mixture used to model the displacing fluid/displaced fluid system, it would provide a numerical means of estimating the MMP.

An equation of state is the most obvious choice for describing CO₂/hydrocarbon phase behavior. The Peng-Robinson equation of state, found in Table 3, is a popular tool in EOR reservoir engineering studies which has been shown to adequately predict liquid and vapor phase compositions and densities. Although this Van der Waals type expression is empirical in nature, its basic form is founded on thermodynamic relationship between pressure, temperature and volume. Furthermore, the pure component and binary interaction data required in the equation of state computations is independent of any crude oil data base, since the C₅+ oil fraction is replaced by a single alkane.

The Peng-Robinson equation of state, PR EOS, is used in all subsequent calculations. The objectives to be achieved using the PR EOS include reproducing the Namiot-Dunyushkin correlation, predicting the experiment cricondenbar data obtained in Section 3 and providing a generalized graphical correlation for the MMP.
5.2 Low Temperature-High Molecular Weight Correction

The Namiot-Dunyushkin correlation, Table 1, contains a fundamental flaw which must be addressed before considering CO$_2$ impurities or live oil components. According to this correlation, as temperature falls below approximately 50°C, the MMP is predicted to increase for crude oils whose C$_5^+$ fraction has a molecular weight of 212 or more. This is due to the low temperature liquid-liquid immiscibility of CO$_2$ with heavier alkanes and is reflected by a steeply rising critical locus in this region. There are no experiment investigations which support this prediction, the MMP is known to steadily diminish with temperature. In order to modify the correlation to correctly account for this phenomena, the critical loci of the heavier alkanes have been extrapolated through the CO$_2$ critical point as shown in Figure 20. This correction is reasonable since the critical loci of the CO$_2$/alkane binaries for alkanes lighter than tetradecane pass through the CO$_2$ critical point and many of the previous correlations, Table 1, pass near the CO$_2$ critical point region. This low temperature-high molecular weight correction is the only aspect of the correlation in which an experimental trend in CO$_2$/crude oil MMP values has been incorporated.

This correlation may also be modified when the critical loci of the CO$_2$/n-alkane binaries for the systems containing C$_{14}$H$_{30}$, C$_{15}$H$_{32}$, C$_{17}$H$_{36}$ and C$_{18}$H$_{38}$ are experimentally determined. In the present form, the C$_{14}$H$_{30}$ and C$_{15}$H$_{32}$ loci are interpolated, whereas the C$_{17}$H$_{36}$ and C$_{18}$H$_{38}$ loci are extrapolated.

5.3 Temperature Dependence of Binary Interaction Parameters

In order to generate the critical loci of the CO$_2$/n-alkane series, using the PR EOS, temperature dependent binary interaction parameters must be introduced.
Figure 20: Critical Loci of CO$_2$/n-Alkane Binaries and MMP Correction
The temperature dependency of the interaction parameter for four separate binaries is illustrated in Figure 21. If conventional values of approximately 0.13 are used, errors of several MPa will result.

The ability of the equations of state to reproduce the critical pressures does not insure that it will correctly give the remaining phase volumes and compositions at the given temperature. Even the critical composition may be in error. In order to provide excellent agreement of the entire PTx space of a binary system using the geometric mixing rule, a temperature and pressure dependent interaction parameter must be used, even for systems of similar, non-polar molecules. Since the cricondenbar is of primary concern to this investigation, the temperature dependency of the parameter is sufficient to model the critical loci and pressure dependent parameters are not used.

5.4 Graphical Correlation

The results of this work show that the MMP of pure CO₂/stock tank oil systems can be estimated by using the PR EOS to calculate the critical pressure of the system at reservoir pressure while the C₅⁺ fraction is replaced by a single alkane. Several factors, however, provided incentive toward representation of these calculations graphically. These include: (1) the low temperature-high molecular weight correction; (2) the temperature dependency of the interaction parameter; (3) the need to introduce pseudo-alkanes whose molecular weight falls between the values of the n-alkanes; and (4) the user preference of such a format in the presentation of such correlations, as indicated in Tables 1 and 2. In light of these considerations, some form of graphical or highly empirical approach to using the PR EOS seemed inevitable, so the development of a very simple PR EOS
FIGURE 21: Temperature Dependency of Binary Interaction Parameter
generated graphical correlation became a goal of this investigation.

In preliminary evaluation of the form of such a graphical correlation, each parameter, such as temperature and composition, known to influence the MMP was varied over the entire range of values encountered in reservoir conditions. These parameters, their ranges of magnitude and a ranking of their effect on MMP are listed in Table II. Pure component data are found in Table I2. A preliminary correlation, which did not incorporate the effects of oil molecular weight, is shown in Figures 22-25.

The final form of the graphical correlation, presented in Figures 26-32, is divided into three convenient categories: (1) pure CO₂/stock tank (no light or intermediate gaseous components) oil MMP prediction; (2) accounting for CO₂ impurities; and (3) accounting for live oil gas components. Such an approach is comprehensive and logical, and will be described in detail in the following discussion. The most convenient way to explain their use is to present an example calculation. Consider a displacing fluid of 95% CO₂, 5% CH₄ and 5% C₃H₈, a displaced fluid of 20% CH₄, 5% C₄H₁₀ and 75% C₅⁺ whose MW is 184. Reservoir temperature is 75°C.

5.4.1 Pure CO₂/Stock Tank Oil Correlation

The first step in the estimation of the MMP is to predict the pure CO₂/STO MMP. All CO₂ impurities and live oil gaseous components, if any, must be ignored at this point. Using Figure 26, the locus corresponding to an average C₅⁺ molecular weight of 184 has a value of 15.6 MPa at 75°C. This is the pure CO₂/STO MMP prediction. Note that MW C₅⁺ values which fall between the n-alkane increments must be interpolated.
### TABLE II

Range and Ranking of Parameter Variations, PR EOS Prediction of Effects on MMP

<table>
<thead>
<tr>
<th>Parameter and Range</th>
<th>Figure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Temperature; 35°C - 115°C</td>
<td>26</td>
</tr>
<tr>
<td>2. Oil Molecular Weight; 156-254</td>
<td>26</td>
</tr>
<tr>
<td>3. CO₂ Impurities; N₂, CH₄, C₂H₆, C₃H₈, C₄H₁₀, H₂S, SO₂</td>
<td>27-29</td>
</tr>
<tr>
<td>4. Live Oil Gases; N₂, CH₄, C₂H₆, C₃H₈, C₄H₁₀</td>
<td>30-31</td>
</tr>
<tr>
<td>5. Effect of Oil Molecular Weight on CO₂ Impurities and Live Oil Gases</td>
<td>27-31</td>
</tr>
<tr>
<td>6. Effect of Temperature on CO₂ Impurities and Live Oil Gases</td>
<td>32</td>
</tr>
<tr>
<td>Component</td>
<td>MW</td>
</tr>
<tr>
<td>-------------</td>
<td>----</td>
</tr>
<tr>
<td>CO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>44</td>
</tr>
<tr>
<td>SO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>64</td>
</tr>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;S</td>
<td>34</td>
</tr>
<tr>
<td>N&lt;sub&gt;2&lt;/sub&gt;</td>
<td>28</td>
</tr>
<tr>
<td>CH&lt;sub&gt;4&lt;/sub&gt;</td>
<td>16</td>
</tr>
<tr>
<td>C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt;</td>
<td>30</td>
</tr>
<tr>
<td>nC&lt;sub&gt;3&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt;</td>
<td>44</td>
</tr>
<tr>
<td>nC&lt;sub&gt;4&lt;/sub&gt;H&lt;sub&gt;10&lt;/sub&gt;</td>
<td>58</td>
</tr>
<tr>
<td>nC&lt;sub&gt;10&lt;/sub&gt;H&lt;sub&gt;22&lt;/sub&gt;</td>
<td>142</td>
</tr>
<tr>
<td>nC&lt;sub&gt;11&lt;/sub&gt;H&lt;sub&gt;24&lt;/sub&gt;</td>
<td>156</td>
</tr>
<tr>
<td>nC&lt;sub&gt;12&lt;/sub&gt;H&lt;sub&gt;26&lt;/sub&gt;</td>
<td>170</td>
</tr>
<tr>
<td>nC&lt;sub&gt;13&lt;/sub&gt;H&lt;sub&gt;28&lt;/sub&gt;</td>
<td>184</td>
</tr>
<tr>
<td>nC&lt;sub&gt;14&lt;/sub&gt;H&lt;sub&gt;30&lt;/sub&gt;</td>
<td>198</td>
</tr>
<tr>
<td>nC&lt;sub&gt;15&lt;/sub&gt;H&lt;sub&gt;32&lt;/sub&gt;</td>
<td>212</td>
</tr>
<tr>
<td>nC&lt;sub&gt;16&lt;/sub&gt;H&lt;sub&gt;34&lt;/sub&gt;</td>
<td>226</td>
</tr>
<tr>
<td>nC&lt;sub&gt;17&lt;/sub&gt;H&lt;sub&gt;36&lt;/sub&gt;</td>
<td>240</td>
</tr>
<tr>
<td>nC&lt;sub&gt;18&lt;/sub&gt;H&lt;sub&gt;38&lt;/sub&gt;</td>
<td>254</td>
</tr>
</tbody>
</table>
FIGURE 22: The Effect of Lean Impurities on the CO$_2$/nC$_{13}$H$_{28}$ Crondonbar Locus over the Range of Reservoir Temperature
FIGURE 23: The Effect of Enriching Impurities on the CO₂/nC₁₃H₂₄ Cricondenbar Locus over the Range of Reservoir Temperature
FIGURE 24: The Effect of Light Oil Components on the CO$_2$/nC$_{13}$H$_{28}$ Critical Locus over the Range of Reservoir Temperature
FIGURE 25: The Effect of Intermediate Oil Components on the CO$_2$/nC$_{13}$H$_{28}$ Critical Locus over the Range of Reservoir Temperature
FIGURE 26: MMP Correlation—Pure CO₂/STO Basis
FIGURE 27: MMP Correlation—Effect of Lean CO$_2$ Impurities
FIGURE 28: MMP Correlation—Effect of Enriching CO₂ Impurities
FIGURE 29: MMP Correlation—Effect of Enriching CO₂ Impurities
FIGURE 30: MMP Correlation-Effect of Light Gases in Oil
FIGURE 31: MMP Correlation-Effect of Intermediates Gases in Oil
FIGURE 32: Temperature Correction Factor for CO₂ Impurities and Live Oil Gases
Before proceeding to the subsequent sections, it must be emphasized that if more than one impurity or oil gas is present, the summation of their individual effects will not be exactly equivalent to their total effect when combined, since interactions between the impurities or oil gases themselves will not be accounted for. It is impossible, however, to address these interactions with the graphical correlation. Such effects were investigated using the PR EOS for ternary mixtures and the errors were small relative to the parameter variations being considered.

5.4.2 Accounting for CO₂ Impurities

CO₂ impurities may be classified as either lean, those which raise the MMP, Figure 27, or enriching, those which lower the MMP, Figures 28 and 29. The changes in the CO₂/n-alkane critical loci induced by the presence of these impurities up to a concentration of 25 mole percent are presented in these illustrations. Note that with the exception of CH₄, the magnitude of the change for any particular impurity increased with the molecular weight of the oil.

Using these figures for the example problem, for a MW C₅⁺, a 5% CH₄ concentration at 75°C raises the MMP 1.5 MPa while a 5% C₃H₈ concentration lowers it by 1.3 MPa. Therefore, the MMP = 15.6 + 1.5 - 1.3 = 15.8 before further corrections.

5.4.3 Accounting for Live Oil Gases

Live oil gases may also be categorized into two distinct classes. Light or volatile gases raise the MMP, as shown in Figure 30, while intermediate gases lower the MMP, as shown in Figure 31. Once again, with the exception of CH₄, the magnitude of the change for any live oil component increases with the molecular weight of the alkane.
The 20% CH₄ concentration in the oil of the example problem results in a .75 MPa increase of the MMP, the 5% C₄H₁₀ lowers the MMP by .2 MPa. The MMP value would therefore be adjusted as follows: 15.8 - .75 + .2 = 15.25 MPa.

Note that the magnitude of the changes in the MMP due to the presence of live oil gases are much smaller than those induced by CO₂ impurities. In fact, MMP values are usually measured within an accuracy of ± .50 MPa. This may be the reason that several investigators have considered these effects insignificant, and have not included them in their MMP correlations (Table 2).

The final adjustment which may be incorporated into the MMP calculation is the temperature correction factor for CO₂ impurities and live oil gases. Figures 27-31 are based on calculations at 150°F (65.6°C). The CO₂ impurities and live oil gases have a weak temperature dependencies, however, which are illustrated in Figure 32 (also Figures 22-25). The effects of CH₄ and N₂ on the MMP, whether they occur in the CO₂ or oil, both decreased to a similar degree with temperature. The effects of the remaining components on the MMP, whether present as enriching impurities on intermediate live oil gases, increase with temperature in a similar manner. If the corrections are used for the example problem in which T = 75°C, the correction factors for lean impurities/light live oil components and enriching impurities/intermediate live oil components are 1.08 and .95, respectively. Therefore, the MMP is calculated as 15.6 + 1.08 (1.5 + .2) - .95 (1.3 + .75) = 15.49 MPa. If one chooses not to include this correction as a matter of convenience (since it is the least sensitive parameter incorporated into the correlation), 15.6 + 1.5 + .2 - 1.3 + .75 = 15.25 MPa.
6.0 RESULTS AND DISCUSSION

6.1 Comparison of STD, PVT and PR EOS

The proposed MMP correlation should be most accurate for the pure component systems in which first contact miscibility is attainable. This serves as a limiting case for crude oil systems as the molecular distribution becomes increasingly narrow. Good agreement is required between the STD and PVT results of these simple aklane/CO$_2$ model systems to justify the use of the correlation for estimating the MMP of multicomponent crude oil/CO$_2$ systems. Furthermore, the PR EOS must be capable of adequately defining the cricondenbar loci to substantiate the validity of the graphical correlation developed in the previous section.

A comparison of the STD, MMP, PVT cricondenbar and the PR EOS is depicted in Figure 33. Excellent agreement was achieved between the STD MMP and experimental PVT. Results for the CO$_2$/nC$_{13}$H$_{28}$ system, verifying that thermodynamic criticality is a necessary and sufficient condition for FCM displacement. Very good agreement was also achieved in the impure CO$_2$ systems. The STD MMP locus fell slightly below the cricondenbar locus. This may be attributed to the multiple contact miscibility which may be established when three or more components are present in a displacement process. This MCM can result in complete recovery at pressures below the cricondenbar. In these cases, however, the difference is small and the cricondenbar locus provides a very good estimate of the MMP.

The PR EOS was forced to match the critical locus of the CO$_2$/nC$_{13}$H$_{28}$ system by adjusting the binary interaction parameter, Figure 21. The shifts due to
FIGURE 33: Comparison of Cricondenbar, MMP's and Peng-Robinson Equation of State
the presence of impurities were consistently underestimated, however, and the loci could be forced to match only by choosing CO₂/impurity and alkane/impurity interaction parameters substantially different from those reported in literature (Table 13). Rather than manipulating this entire table of parameters to match the crencondenbar, the parameters recorded in Table 13 were retained and the following results observed concerning CO₂ impurities:

1. the PR EOS correctly predict the direction of the shifts observed in the crencondenbar locus;

2. the PR EOS underestimates the magnitude of these shifts by up to 30% when interaction parameters available in literature sources are employed;

3. the magnitude of the error decreases as:
   a) the concentration of the impurity decreases and
   b) temperature increases.

Whether these discrepancies are significant enough to make the CO₂/crude oil estimation extremely inaccurate will be discussed in the following section.

6.2 Comparison of Literature MMP Values with Graphical Correlation

In order to test the proposed correlation, 157 MMP value from 20 investigators were compared with values predicted by the graphical correlations. Data pertaining to reservoir temperature, CO₂ impurities, live oil gases and references are found in Table 14. In some references light and intermediate oil gases as well as lean and enriching CO₂ impurities were lumped together. These lumped fractions were usually equally divided into separate fractions for individual components, with the exception of N₂ in oil, which was always kept below 2%.
TABLE 13

Binary Interaction Parameters Used in Generating the Graphical Correlation

<table>
<thead>
<tr>
<th></th>
<th>CO₂</th>
<th>CH₄</th>
<th>C₂</th>
<th>C₃</th>
<th>C₄</th>
<th>N₂</th>
<th>H₂S</th>
<th>SO₂</th>
<th>C₁₁-C₁₈</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>0</td>
<td>.092</td>
<td>.132</td>
<td>.124</td>
<td>.133</td>
<td>-.017</td>
<td>.097</td>
<td>.12</td>
<td>Fig. 21</td>
</tr>
<tr>
<td>CH₄</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>.046-.074</td>
</tr>
<tr>
<td>C₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>.023-.036</td>
</tr>
<tr>
<td>C₃</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>.011-.017</td>
</tr>
<tr>
<td>C₄</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>.0</td>
</tr>
<tr>
<td>N₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>.112*</td>
</tr>
<tr>
<td>H₂S</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>.03*</td>
</tr>
<tr>
<td>SO₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>.14*</td>
</tr>
<tr>
<td>C₁₁-C₁₈</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0</td>
</tr>
</tbody>
</table>

*Estimate.
TABLE 14
Predicted and Actual MMP Values for 157 Systems

<table>
<thead>
<tr>
<th>#</th>
<th>Ref.</th>
<th>T oC</th>
<th>CO₂ Impurities</th>
<th>MW C₅⁺</th>
<th>Live Oil Gases</th>
<th>Predicted w/ T.C.*</th>
<th>MMP w/o T.C.**</th>
<th>Actual MMP</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15</td>
<td>54.4</td>
<td>---</td>
<td>185.8</td>
<td>.054 C₁, N₂, .384 C₂-C₄, CO₂, H₂S</td>
<td>11.9</td>
<td>11.8</td>
<td>9.48</td>
</tr>
<tr>
<td>2</td>
<td>15</td>
<td>61.1</td>
<td></td>
<td>185.8</td>
<td>.054 C₁, N₂, .384 C₂-C₄, CO₂, H₂S</td>
<td>13.0</td>
<td>12.9</td>
<td>10.34</td>
</tr>
<tr>
<td>3</td>
<td>15</td>
<td>54.4</td>
<td></td>
<td>185.8</td>
<td>.05 C₁, N₂, .075 C₂-C₄, CO₂, H₂S</td>
<td>12.4</td>
<td>12.3</td>
<td>10.34</td>
</tr>
<tr>
<td>4</td>
<td>15</td>
<td>54.4</td>
<td></td>
<td>185.8</td>
<td>.229 C₁, N₂, .384 C₂-C₄, CO₂, H₂S</td>
<td>12.5</td>
<td>12.4</td>
<td>10.34</td>
</tr>
<tr>
<td>5</td>
<td>15</td>
<td>54.4</td>
<td>.075 C₁</td>
<td>185.8</td>
<td>.054 C₁, N₂, .384 C₂-C₄, CO₂, H₂S</td>
<td>14.23</td>
<td>14.</td>
<td>10.34</td>
</tr>
<tr>
<td>6</td>
<td>15</td>
<td>57.8</td>
<td></td>
<td>202.61</td>
<td>.005 C₁, N₂, .012 C₂-C₄, CO₂, H₂S</td>
<td>14.9</td>
<td>14.9</td>
<td>11.72</td>
</tr>
<tr>
<td>7</td>
<td>15</td>
<td>54.4</td>
<td></td>
<td>235.56</td>
<td>.054 C₁, N₂, .355 C₂-C₄, CO₂, H₂S</td>
<td>15.96</td>
<td>15.6</td>
<td>12.76</td>
</tr>
<tr>
<td>8</td>
<td>15</td>
<td>54.4</td>
<td>.10 C₁</td>
<td>185.83</td>
<td>.293 C₁, N₂, .403 C₂-C₄, CO₂, H₂S</td>
<td>16.1</td>
<td>15.7</td>
<td>13.10</td>
</tr>
<tr>
<td>9</td>
<td>15</td>
<td>37.8</td>
<td></td>
<td>235.56</td>
<td>.049 C₁, N₂, .019 C₂-C₄, CO₂, H₂S</td>
<td>11.20</td>
<td>11.1</td>
<td>10.54</td>
</tr>
<tr>
<td>10</td>
<td>15</td>
<td>67.8</td>
<td></td>
<td>203.81</td>
<td>.310 C₁, N₂, .229 C₂-C₄, CO₂, H₂S</td>
<td>17.8</td>
<td>17.8</td>
<td>16.89</td>
</tr>
<tr>
<td>11</td>
<td>34</td>
<td>76.1</td>
<td>.063 N₂, .062 C₄</td>
<td>227.0</td>
<td>.007N₂, .479C₁, .032C₂, .018C₃, .012C₄</td>
<td>18.1</td>
<td>20.</td>
<td>23.17</td>
</tr>
<tr>
<td>12</td>
<td>34</td>
<td>76.1</td>
<td>.088 N₂, .12 C₄</td>
<td>227.0</td>
<td>.007N₂, .479C₁, .032C₂, .018C₃, .012C₄</td>
<td>23.31</td>
<td>24.4</td>
<td>23.17</td>
</tr>
<tr>
<td>13</td>
<td>34</td>
<td>73.3</td>
<td>.107 C₁, .029 C₄</td>
<td>227.0</td>
<td>.007N₂, .479C₁, .032C₂, .018C₃, .012C₄</td>
<td>22.2</td>
<td>22.5</td>
<td>23.10</td>
</tr>
<tr>
<td>14</td>
<td>15</td>
<td>112.2</td>
<td></td>
<td>213.5</td>
<td>.327 C₁, N₂, .281 C₂-C₄, CO₂, H₂S</td>
<td>23.4</td>
<td>23.8</td>
<td>24.15</td>
</tr>
<tr>
<td>15</td>
<td>15</td>
<td>112.2</td>
<td>.0775 C₄</td>
<td>213.5</td>
<td>.327 C₁, N₂, .281 C₂-C₄, CO₂, H₂S</td>
<td>18.7</td>
<td>20.2</td>
<td>19.68</td>
</tr>
<tr>
<td>16</td>
<td>31</td>
<td>71.1</td>
<td>.049 C₁, .001 N₂</td>
<td>207.9</td>
<td>.044 C₁, N₂, .139 C₂-C₄, CO₂, H₂S</td>
<td>19.3</td>
<td>19.4</td>
<td>16.82</td>
</tr>
<tr>
<td>17</td>
<td>31</td>
<td>71.1</td>
<td></td>
<td>207.9</td>
<td>.044 C₁, N₂, .139 C₂-C₄, CO₂, H₂S</td>
<td>18.0</td>
<td>18.1</td>
<td>15.51</td>
</tr>
<tr>
<td>18</td>
<td>53</td>
<td>54.4</td>
<td></td>
<td>171.2</td>
<td>.295 C₁, N₂, .318 C₂-C₄, CO₂, H₂S</td>
<td>12.6</td>
<td>12.45</td>
<td>10.99</td>
</tr>
</tbody>
</table>

*With temperature correction for CO₂ impurities and live oil gases.

**Without temperature correction for CO₂ impurities and live oil gases.
<p>| | | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>19</td>
<td>53</td>
<td>54.4</td>
<td>.10 C₃</td>
<td>171.2</td>
<td>.295 C₁₄N₂ .318 C₂-C₄, CO₂, H₂S</td>
<td>15.7</td>
</tr>
<tr>
<td>20</td>
<td>54</td>
<td>42.8</td>
<td>196.1</td>
<td>.193 C₁₂N₂ .236 C₂-C₄, CO₂, H₂S</td>
<td>11.5</td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>55</td>
<td>117.2</td>
<td>169.2</td>
<td>.364 C₁₄N₂ .307 C₂-C₄, CO₂, H₂S</td>
<td>21.5</td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>56</td>
<td>54.4</td>
<td>.048 C₁ .002 N₂</td>
<td>302.5</td>
<td>.255 C₁₄N₂ .077 C₂-C₄, CO₂, H₂S</td>
<td>31.2</td>
</tr>
<tr>
<td>23</td>
<td>32</td>
<td>32.2</td>
<td>187.8</td>
<td>.006 N₂ .099C₁ .027C₂ .05C₃ .06C₄</td>
<td>7.72</td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>32</td>
<td>40.6</td>
<td>187.8</td>
<td>.006N₂ .099C₁ .027C₂ .05C₃ .06C₄</td>
<td>9.70</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>32</td>
<td>40.6</td>
<td>.25 H₂S</td>
<td>187.8</td>
<td>.006N₂ .099C₁ .027C₂ .05C₃ .06C₄</td>
<td>7.73</td>
</tr>
<tr>
<td>26</td>
<td>32</td>
<td>40.6</td>
<td>.50 H₂S</td>
<td>187.8</td>
<td>.006N₂ .099C₁ .027C₂ .05C₃ .06C₄</td>
<td>6.47</td>
</tr>
<tr>
<td>27</td>
<td>32</td>
<td>40.6</td>
<td>.10 C₁</td>
<td>187.8</td>
<td>.006N₂ .099C₁ .027C₂ .05C₃ .06C₄</td>
<td>12.6</td>
</tr>
<tr>
<td>28</td>
<td>32</td>
<td>40.6</td>
<td>.10 C₁ .225 H₂S</td>
<td>187.8</td>
<td>.006N₂ .099C₁ .027C₂ .05C₃ .06C₄</td>
<td>10.8</td>
</tr>
<tr>
<td>29</td>
<td>32</td>
<td>40.6</td>
<td>.10 C₁ .45 H₂S</td>
<td>187.8</td>
<td>.006N₂ .099C₁ .027C₂ .05C₃ .06C₄</td>
<td>9.56</td>
</tr>
<tr>
<td>30</td>
<td>32</td>
<td>40.6</td>
<td>.20 C₁</td>
<td>187.8</td>
<td>.006N₂ .099C₁ .027C₂ .05C₃ .06C₄</td>
<td>15.83</td>
</tr>
<tr>
<td>31</td>
<td>32</td>
<td>40.6</td>
<td>.20 C₁ .20 H₂S</td>
<td>187.8</td>
<td>.006N₂ .099C₁ .027C₂ .05C₃ .06C₄</td>
<td>14.20</td>
</tr>
<tr>
<td>32</td>
<td>32</td>
<td>40.6</td>
<td>.20 C₁ .40 H₂S</td>
<td>187.8</td>
<td>.006N₂ .099C₁ .027C₂ .05C₃ .06C₄</td>
<td>12.87</td>
</tr>
<tr>
<td>33</td>
<td>32</td>
<td>57.2</td>
<td>187.8</td>
<td>.006N₂ .099C₁ .027C₂ .05C₃ .06C₄</td>
<td>13.02</td>
<td></td>
</tr>
<tr>
<td>34</td>
<td>32</td>
<td>57.2</td>
<td>.25 H₂S</td>
<td>187.8</td>
<td>.006N₂ .099C₁ .027C₂ .05C₃ .06C₄</td>
<td>10.52</td>
</tr>
<tr>
<td>35</td>
<td>32</td>
<td>57.2</td>
<td>.50 H₂S</td>
<td>187.8</td>
<td>.006N₂ .099C₁ .027C₂ .05C₃ .06C₄</td>
<td>8.94</td>
</tr>
<tr>
<td>36</td>
<td>32</td>
<td>57.2</td>
<td>.10 C₁</td>
<td>187.8</td>
<td>.006N₂ .099C₁ .027C₂ .05C₃ .06C₄</td>
<td>15.73</td>
</tr>
<tr>
<td>37</td>
<td>32</td>
<td>57.2</td>
<td>.10C₁ .225 H₂S</td>
<td>187.8</td>
<td>.006N₂ .099C₁ .027C₂ .05C₃ .06C₄</td>
<td>13.41</td>
</tr>
<tr>
<td>38</td>
<td>32</td>
<td>57.2</td>
<td>.10C₁ .45 H₂S</td>
<td>187.8</td>
<td>.006N₂ .099C₁ .027C₂ .05C₃ .06C₄</td>
<td>11.83</td>
</tr>
<tr>
<td>39</td>
<td>32</td>
<td>57.2</td>
<td>.20 C₁</td>
<td>187.8</td>
<td>.006N₂ .099C₁ .027C₂ .05C₃ .06C₄</td>
<td>18.64</td>
</tr>
<tr>
<td>40</td>
<td>32</td>
<td>57.2</td>
<td>.20C₁ .20 H₂S</td>
<td>187.8</td>
<td>.006N₂ .099C₁ .027C₂ .05C₃ .06C₄</td>
<td>16.60</td>
</tr>
<tr>
<td>41</td>
<td>32</td>
<td>57.2</td>
<td>.20C₁ .40 H₂S</td>
<td>187.8</td>
<td>.006N₂ .099C₁ .027C₂ .05C₃ .06C₄</td>
<td>14.92</td>
</tr>
<tr>
<td>42</td>
<td>32</td>
<td>48.9</td>
<td>187.3</td>
<td>.009N₂ .335C₁ .088C₂ .077C₃ .054C₄</td>
<td>12.40</td>
<td></td>
</tr>
<tr>
<td>43</td>
<td>32</td>
<td>48.9</td>
<td>.10 C₂</td>
<td>187.3</td>
<td>.009N₂ .335C₁ .088C₂ .077C₃ .054C₄</td>
<td>11.98</td>
</tr>
<tr>
<td>44</td>
<td>32</td>
<td>48.9</td>
<td>.10 C₃</td>
<td>187.3</td>
<td>.009N₂ .335C₁ .088C₂ .077C₃ .054C₄</td>
<td>10.71</td>
</tr>
<tr>
<td>45</td>
<td>32</td>
<td>48.9</td>
<td>.10 C₄</td>
<td>187.3</td>
<td>.009N₂ .335C₁ .088C₂ .077C₃ .054C₄</td>
<td>10.13</td>
</tr>
<tr>
<td>46</td>
<td>32</td>
<td>48.9</td>
<td>.20 C₂</td>
<td>187.3</td>
<td>.009N₂ .335C₁ .088C₂ .077C₃ .054C₄</td>
<td>11.56</td>
</tr>
<tr>
<td>47</td>
<td>32</td>
<td>48.9</td>
<td>.20 C₃</td>
<td>187.3</td>
<td>.009N₂ .335C₁ .088C₂ .077C₃ .054C₄</td>
<td>9.45</td>
</tr>
<tr>
<td>48</td>
<td>32</td>
<td>65.6</td>
<td>187.3</td>
<td>.009N₂ .335C₁ .088C₂ .077C₃ .054C₄</td>
<td>15.1</td>
<td>15.1</td>
</tr>
<tr>
<td>-----</td>
<td>-----</td>
<td>------</td>
<td>-------</td>
<td>----------------------------------</td>
<td>------</td>
<td>------</td>
</tr>
<tr>
<td>49</td>
<td>32</td>
<td>65.6</td>
<td>187.3</td>
<td>.009N₂ .335C₁ .088C₂ .077C₃ .054C₄</td>
<td>14.6</td>
<td>14.6</td>
</tr>
<tr>
<td>50</td>
<td>32</td>
<td>65.6</td>
<td>.10C₂</td>
<td>187.3</td>
<td>.009N₂ .335C₁ .088C₂ .077C₃ .054C₄</td>
<td>13.1</td>
</tr>
<tr>
<td>51</td>
<td>32</td>
<td>65.6</td>
<td>.10C₃</td>
<td>187.3</td>
<td>.009N₂ .335C₁ .088C₂ .077C₃ .054C₄</td>
<td>12.4</td>
</tr>
<tr>
<td>52</td>
<td>32</td>
<td>65.6</td>
<td>.20C₂</td>
<td>187.3</td>
<td>.009N₂ .335C₁ .088C₂ .077C₃ .054C₄</td>
<td>14.1</td>
</tr>
<tr>
<td>53</td>
<td>32</td>
<td>65.6</td>
<td>.20C₃</td>
<td>187.3</td>
<td>.009N₂ .335C₁ .088C₂ .077C₃ .054C₄</td>
<td>11.6</td>
</tr>
<tr>
<td>54</td>
<td>32</td>
<td>98.9</td>
<td>190.7</td>
<td>.401C₁N₂ .030C₂-C₄, CO₂, H₂S</td>
<td>21.08</td>
<td>21.4</td>
</tr>
<tr>
<td>55</td>
<td>15</td>
<td>110.0</td>
<td>180.6</td>
<td>.325C₁N₂ .356C₂-C₄, CO₂, H₂S</td>
<td>20.49</td>
<td>21.</td>
</tr>
<tr>
<td>56</td>
<td>11</td>
<td>57.2</td>
<td>187</td>
<td>.3188C₁N₂ .0348C₂-C₄, CO₂, H₂S</td>
<td>13.71</td>
<td>13.65</td>
</tr>
<tr>
<td>57</td>
<td>11</td>
<td>57.2</td>
<td>183</td>
<td>.0C₁N₂ .0511C₂-C₄, CO₂, H₂S</td>
<td>12.32</td>
<td>12.3</td>
</tr>
<tr>
<td>58</td>
<td>11</td>
<td>87.8</td>
<td>187</td>
<td>.0C₁N₂ .0511C₂-C₄, CO₂, H₂S</td>
<td>17.14</td>
<td>17.2</td>
</tr>
<tr>
<td>59</td>
<td>11</td>
<td>57.2</td>
<td>183</td>
<td>.0C₁N₂ .0511C₂-C₄, CO₂, H₂S</td>
<td>15.23</td>
<td>15.1</td>
</tr>
<tr>
<td>60</td>
<td>11</td>
<td>54.4</td>
<td>171</td>
<td>.0C₁N₂ .0157C₂-C₄, CO₂, H₂S</td>
<td>11.51</td>
<td>11.5</td>
</tr>
<tr>
<td>61</td>
<td>57</td>
<td>42.7</td>
<td>204.1</td>
<td>.171C₁N₂ .2095C₂-C₄, CO₂, H₂S</td>
<td>11.96</td>
<td>11.65</td>
</tr>
<tr>
<td>62</td>
<td>57</td>
<td>39.4</td>
<td>199.7</td>
<td>.278C₁N₂ .2181C₂-C₄, CO₂, H₂S</td>
<td>10.99</td>
<td>10.6</td>
</tr>
<tr>
<td>63</td>
<td>57</td>
<td>85.6</td>
<td>247.8</td>
<td>.445C₁N₂ .1834C₂-C₄, CO₂, H₂S</td>
<td>25.12</td>
<td>25.6</td>
</tr>
<tr>
<td>64</td>
<td>15</td>
<td>71.1</td>
<td>221</td>
<td>.412C₁N₂ .07C₂-C₄, CO₂, H₂S</td>
<td>21.23</td>
<td>21.3</td>
</tr>
<tr>
<td>65</td>
<td>15</td>
<td>71.1</td>
<td>.05C₄</td>
<td>221</td>
<td>.412C₁N₂ .07C₂-C₄, CO₂, H₂S</td>
<td>18.11</td>
</tr>
<tr>
<td>66</td>
<td>15</td>
<td>71.1</td>
<td>.095C₃</td>
<td>221</td>
<td>.412C₁N₂ .07C₂-C₄, CO₂, H₂S</td>
<td>17.07</td>
</tr>
<tr>
<td>67</td>
<td>15</td>
<td>102.2</td>
<td>205</td>
<td>.513C₁N₂ .0984C₂-C₄, CO₂, H₂S</td>
<td>23.25</td>
<td>23.7</td>
</tr>
<tr>
<td>68</td>
<td>15</td>
<td>80.0</td>
<td>240.7</td>
<td>.533C₁N₂ .0868C₂-C₄, CO₂, H₂S</td>
<td>25.11</td>
<td>25.35</td>
</tr>
<tr>
<td>69</td>
<td>12</td>
<td>35.0</td>
<td>198.9</td>
<td>.23C₁N₂ .20C₂-C₆ (55)</td>
<td>9.35</td>
<td>8.9</td>
</tr>
<tr>
<td>70</td>
<td>12</td>
<td>47.8</td>
<td>198.9</td>
<td>.23C₁N₂ .20C₂-C₆ (55)</td>
<td>12.97</td>
<td>12.7</td>
</tr>
<tr>
<td>71</td>
<td>12</td>
<td>65.6</td>
<td>198.9</td>
<td>.23C₁N₂ .20C₂-C₆ (55)</td>
<td>16.1</td>
<td>16.1</td>
</tr>
<tr>
<td>72</td>
<td>12</td>
<td>88.9</td>
<td>198.9</td>
<td>.23C₁N₂ .20C₂-C₆ (55)</td>
<td>19.52</td>
<td>19.8</td>
</tr>
<tr>
<td>73</td>
<td>12</td>
<td>35</td>
<td>198.9</td>
<td>.40C₂-C₆</td>
<td>7.90</td>
<td>7.4</td>
</tr>
<tr>
<td>74</td>
<td>12</td>
<td>47.8</td>
<td>198.9</td>
<td>.40C₂-C₆</td>
<td>11.50</td>
<td>11.2</td>
</tr>
<tr>
<td>75</td>
<td>12</td>
<td>65.6</td>
<td>198.9</td>
<td>.40C₂-C₆</td>
<td>14.6</td>
<td>14.6</td>
</tr>
<tr>
<td>76</td>
<td>12</td>
<td>88.9</td>
<td>198.9</td>
<td>.40C₂-C₆</td>
<td>18.02</td>
<td>18.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>----</td>
<td>---</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>77</td>
<td>12</td>
<td>33.0</td>
<td>198.9</td>
<td>9.0</td>
<td>9.0</td>
<td>7.68</td>
</tr>
<tr>
<td>78</td>
<td>12</td>
<td>47.8</td>
<td>198.9</td>
<td>12.8</td>
<td>12.8</td>
<td>10.10</td>
</tr>
<tr>
<td>79</td>
<td>12</td>
<td>65.6</td>
<td>198.9</td>
<td>16.2</td>
<td>16.2</td>
<td>13.72</td>
</tr>
<tr>
<td>80</td>
<td>12</td>
<td>35.0</td>
<td>198.9</td>
<td>9.22</td>
<td>8.7</td>
<td>8.03</td>
</tr>
<tr>
<td>81</td>
<td>12</td>
<td>47.8</td>
<td>198.9</td>
<td>12.81</td>
<td>12.5</td>
<td>9.07</td>
</tr>
<tr>
<td>82</td>
<td>12</td>
<td>65.6</td>
<td>198.9</td>
<td>15.9</td>
<td>15.9</td>
<td>11.82</td>
</tr>
<tr>
<td>83</td>
<td>27</td>
<td>41.2</td>
<td>.03 N₂</td>
<td>237.1</td>
<td>.0054N₂ .1594C₁ .0748C₂ .0578C₃ .032C₄</td>
<td>20.64</td>
</tr>
<tr>
<td>84</td>
<td>27</td>
<td>41.2</td>
<td>.10 C₁</td>
<td>237.1</td>
<td>.0054N₂ .1594C₁ .0748C₂ .0578C₃ .032C₄</td>
<td>13.75</td>
</tr>
<tr>
<td>85</td>
<td>27</td>
<td>41.2</td>
<td>.19 N₂</td>
<td>237.1</td>
<td>.0054N₂ .1594C₁ .0748C₂ .0578C₃ .032C₄</td>
<td>36.69</td>
</tr>
<tr>
<td>86</td>
<td>27</td>
<td>41.2</td>
<td>.19 C₁</td>
<td>237.1</td>
<td>.0054N₂ .1594C₁ .0748C₂ .0578C₃ .032C₄</td>
<td>15.33</td>
</tr>
<tr>
<td>87</td>
<td>27</td>
<td>41.2</td>
<td>.27 C₁ .27 C₃</td>
<td>237.1</td>
<td>.0054N₂ .1594C₁ .0748C₂ .0578C₃ .032C₄</td>
<td>9.48</td>
</tr>
<tr>
<td>88</td>
<td>27</td>
<td>41.2</td>
<td>.28 C₁</td>
<td>237.1</td>
<td>.0054N₂ .1594C₁ .0748C₂ .0578C₃ .032C₄</td>
<td>17.02</td>
</tr>
<tr>
<td>89</td>
<td>27</td>
<td>41.2</td>
<td>.19 C₁</td>
<td>237.1</td>
<td>.0054N₂ .1594C₁ .0748C₂ .0578C₃ .032C₄</td>
<td>15.33</td>
</tr>
<tr>
<td>90</td>
<td>27</td>
<td>41.2</td>
<td>.25 H₂S</td>
<td>237.1</td>
<td>.0054N₂ .1594C₁ .0748C₂ .0578C₃ .032C₄</td>
<td>4.73</td>
</tr>
<tr>
<td>91</td>
<td>58</td>
<td>88.</td>
<td>205</td>
<td>20.5</td>
<td>20.5</td>
<td>14.55</td>
</tr>
<tr>
<td>92</td>
<td>58</td>
<td>88.</td>
<td>205</td>
<td>20.3</td>
<td>20.3</td>
<td>14.55</td>
</tr>
<tr>
<td>93</td>
<td>58</td>
<td>27.</td>
<td>249</td>
<td>6.7</td>
<td>6.7</td>
<td>8.00</td>
</tr>
<tr>
<td>94</td>
<td>58</td>
<td>38.</td>
<td>249</td>
<td>12</td>
<td>12.0</td>
<td>10.43</td>
</tr>
<tr>
<td>95</td>
<td>58</td>
<td>49.</td>
<td>249</td>
<td>18.4</td>
<td>18.4</td>
<td>12.82</td>
</tr>
<tr>
<td>96</td>
<td>58</td>
<td>55.</td>
<td>249</td>
<td>20.7</td>
<td>20.7</td>
<td>15.93</td>
</tr>
<tr>
<td>97</td>
<td>58</td>
<td>66.</td>
<td>249</td>
<td>23.8</td>
<td>23.8</td>
<td>21.44</td>
</tr>
<tr>
<td>98</td>
<td>58</td>
<td>42.</td>
<td>223</td>
<td>12.6</td>
<td>12.6</td>
<td>12.20</td>
</tr>
<tr>
<td>99</td>
<td>58</td>
<td>62.</td>
<td>227</td>
<td>19.3</td>
<td>19.3</td>
<td>16.00</td>
</tr>
<tr>
<td>100</td>
<td>58</td>
<td>43.</td>
<td>227</td>
<td>13.4</td>
<td>13.4</td>
<td>12.34</td>
</tr>
<tr>
<td>101</td>
<td>58</td>
<td>53.</td>
<td>227</td>
<td>17.6</td>
<td>17.6</td>
<td>14.34</td>
</tr>
<tr>
<td>102</td>
<td>58</td>
<td>62.</td>
<td>227</td>
<td>19.8</td>
<td>19.8</td>
<td>15.65</td>
</tr>
<tr>
<td>103</td>
<td>58</td>
<td>71.</td>
<td>227</td>
<td>21.2</td>
<td>21.2</td>
<td>17.03</td>
</tr>
<tr>
<td>104</td>
<td>58</td>
<td>75.</td>
<td>227</td>
<td>21.9</td>
<td>21.9</td>
<td>18.00</td>
</tr>
<tr>
<td>105</td>
<td>58</td>
<td>110.</td>
<td>227</td>
<td>26.6</td>
<td>26.6</td>
<td>22.27</td>
</tr>
<tr>
<td>106</td>
<td>58</td>
<td>43</td>
<td>201</td>
<td>11.8</td>
<td>11.8</td>
<td>9.65</td>
</tr>
<tr>
<td>-----</td>
<td>----</td>
<td>----</td>
<td>-----</td>
<td>------</td>
<td>------</td>
<td>------</td>
</tr>
<tr>
<td>107</td>
<td>58</td>
<td>53</td>
<td>201</td>
<td>14.1</td>
<td>14.1</td>
<td>10.82</td>
</tr>
<tr>
<td>108</td>
<td>58</td>
<td>62</td>
<td>201</td>
<td>15.6</td>
<td>15.6</td>
<td>11.79</td>
</tr>
<tr>
<td>109</td>
<td>58</td>
<td>71</td>
<td>201</td>
<td>17.1</td>
<td>17.1</td>
<td>14.76</td>
</tr>
<tr>
<td>110</td>
<td>11</td>
<td>54</td>
<td>171</td>
<td>11.41</td>
<td>11.4</td>
<td>12.17</td>
</tr>
<tr>
<td>111</td>
<td>11</td>
<td>57</td>
<td>183</td>
<td>13.56</td>
<td>13.5</td>
<td>13.89</td>
</tr>
<tr>
<td>112</td>
<td>11</td>
<td>66</td>
<td>219</td>
<td>18.5</td>
<td>18.5</td>
<td>15.27</td>
</tr>
<tr>
<td>113</td>
<td>11</td>
<td>85</td>
<td>219</td>
<td>21.38</td>
<td>21.5</td>
<td>20.10</td>
</tr>
<tr>
<td>114</td>
<td>21</td>
<td>41</td>
<td>198</td>
<td>10.95</td>
<td>10.75</td>
<td>8.20</td>
</tr>
<tr>
<td>115</td>
<td>21</td>
<td>120</td>
<td>188</td>
<td>22.57</td>
<td>23.1</td>
<td>32.51</td>
</tr>
<tr>
<td>116</td>
<td>21</td>
<td>88</td>
<td>200</td>
<td>21.20</td>
<td>21.05</td>
<td>21.48</td>
</tr>
<tr>
<td>117</td>
<td>21</td>
<td>101</td>
<td>178</td>
<td>20.21</td>
<td>20.55</td>
<td>23.27</td>
</tr>
<tr>
<td>118</td>
<td>21</td>
<td>54</td>
<td>171</td>
<td>12.51</td>
<td>12.4</td>
<td>12.86</td>
</tr>
<tr>
<td>119</td>
<td>21</td>
<td>40</td>
<td>171</td>
<td>11.02</td>
<td>10.55</td>
<td>11.48</td>
</tr>
<tr>
<td>120</td>
<td>27</td>
<td>87</td>
<td>218</td>
<td>21.73</td>
<td>22.05</td>
<td>17.34</td>
</tr>
<tr>
<td>121</td>
<td>21</td>
<td>43</td>
<td>204</td>
<td>12.16</td>
<td>11.85</td>
<td>10.45</td>
</tr>
<tr>
<td>122</td>
<td>21</td>
<td>39</td>
<td>200</td>
<td>10.86</td>
<td>10.5</td>
<td>13.89</td>
</tr>
<tr>
<td>123</td>
<td>21</td>
<td>86</td>
<td>278</td>
<td>29.18</td>
<td>29.75</td>
<td>34.58</td>
</tr>
<tr>
<td>124</td>
<td>21</td>
<td>32</td>
<td>205</td>
<td>8.1</td>
<td>8.72</td>
<td></td>
</tr>
<tr>
<td>125</td>
<td>21</td>
<td>58</td>
<td>170</td>
<td>13.1</td>
<td>13.2</td>
<td>10.2</td>
</tr>
<tr>
<td>126</td>
<td>19</td>
<td>58</td>
<td>171</td>
<td>12.2</td>
<td>12.86</td>
<td></td>
</tr>
<tr>
<td>127</td>
<td>19</td>
<td>74</td>
<td>171</td>
<td>14.8</td>
<td>17.0</td>
<td></td>
</tr>
<tr>
<td>128</td>
<td>19</td>
<td>74</td>
<td>267</td>
<td>26.9</td>
<td>30.44</td>
<td></td>
</tr>
<tr>
<td>129</td>
<td>19</td>
<td>54</td>
<td>254</td>
<td>21.0</td>
<td>17.0</td>
<td></td>
</tr>
<tr>
<td>130</td>
<td>19</td>
<td>74</td>
<td>254</td>
<td>25.5</td>
<td>23.55</td>
<td></td>
</tr>
<tr>
<td>131</td>
<td>19</td>
<td>74</td>
<td>214</td>
<td>19.8</td>
<td>20.78</td>
<td></td>
</tr>
<tr>
<td>132</td>
<td>19</td>
<td>74</td>
<td>113</td>
<td>11.4</td>
<td>13.89</td>
<td></td>
</tr>
<tr>
<td>133</td>
<td>13</td>
<td>57</td>
<td>170</td>
<td>12.0</td>
<td>11.03</td>
<td></td>
</tr>
<tr>
<td>134</td>
<td>13</td>
<td>36</td>
<td>221</td>
<td>9.7</td>
<td>7.79</td>
<td></td>
</tr>
</tbody>
</table>

**TABLE 14**

(Continued)
TABLE 14
(Continued)

| 135 | 13 | 49  | 187 | 11.3 | 9.93 |
| 136 | 13 | 49  | 240 | 17.0 | 11.38 |
| 137 | 13 | 28  | 240 | 16.9 | 16.82 |
| 138 | 23 | 40  | 238 | 12.5 | 17.53 |
| 139 | 23 | 88  | 186 | 17.8 | 21.89 |
| 140 | 23 | 83  | 221 | 22.3 | 23.21 |
| 141 | 23 | 75  | 193 | 16.9 | 21.48 |
| 142 | 23 | 66  | 257 | 24.6 | 21.79 |
| 143 | 23 | 70  | 194 | 16.2 | 22.19 |
| 144 | 23 | 90  | 240 | 25.7 | 18.24 |
| 145 | 23 | 40  | 231 | 12.2 | 19.66 |
| 146 | 42 | 98  | 227 | 25.2 | 21.28 |
| 147 | 42 | 137 | 188 | 23.5 | 29.19 |
| 148 | 42 | 137 | 223 | 28.0 | 29.89 |
| 149 | 42 | 111 | 187 | 21.3 | 20.98 |
| 150 | 42 | 111 | 227 | 26.9 | 21.79 |
| 151 | 42 | 111 | 263 | 29.5 | 26.35 |
| 152 | 59 | 71.1| 142 0.25C_2C_6 | 13.69 | 13.7 | 13.10 |
| 153 | 59 | 71.1| 142 0.30C_2C_6 | 13.58 | 13.6 | 13.10 |
| 154 | 59 | 48.9| 142 0.21C_2C_6 | 10.24 | 10.2 | 11.72 |
| 155 | 60 | 65.6| 139 0.20C_2C_6 | 12.4 | 12.1 | 14.00 |
| 156 | 61 | 48.9| 227 0.31C_2C_6 | 16.06 | 16.0 | 10.58 |
| 157 | 61 | 40.0| 205 0.31C_2C_6 | 10.8 | 10.7 | 8.78 |
These 157 systems were divided into four groups: (1) pure CO₂/stock tank oil; (2) pure CO₂/live oil; (3) impure CO₂/stock tank oil; and (4) impure CO₂/live oil. The correlation was first tested without the temperature correction for CO₂ impurities and live oil gases. The mean of the predicted to actual MMP ratio and the standard deviation of these individual groups as well as the entire group of data are presented in the parity plot, Figure 34. The mean was above unity for each group, averaging 1.07 for the entire set. The standard deviations for each of the groups were quite similar, averaging .20 for the 157 systems. Figure 35 illustrates the results obtained utilizing the temperature correction, with a mean of 1.09 and a standard deviation of .19. These mean values are comparable with those published in previous studies, but the standard deviations are high, with most other correlations falling in the .10 to .15 range. Previous correlations, however, were tested against much smaller data bases, the largest of which contained 68 systems. Unlike the current work, these correlations were developed by minimizing the difference between their predicted values and a data base of experimental results. Considering that the correlation was independent of a CO₂/crude oil data base, these results are quite satisfactory.
FIGURE 34: Comparison of Predicted and Actual MMP Values
FIGURE 35: Comparison of Predicted and Actual MMP Values, with Temperature Correction for CO₂ Impurities and Live Oil Gases
7.0 CONCLUSIONS

7.1 General Conclusions

A minimum miscibility pressure correlation based upon the phase behavior of model binary systems has been developed. Corrections to this correlation, based on the thermodynamic effects of additional components, such as methane and nitrogen, in the CO₂ and/or oil, were also incorporated.

An equation of state has been used for describing these effects and P-V-T-x experimental data has been taken which verifies the efficacy of this equation in predicting the thermodynamic (phase) behavior of model systems such as CO₂-N₂-tridecane. Simultaneously, STD experiments on the same systems were conducted to obtain minimum miscibility pressures and the result indicate that such pressures are near to or equivalent to the cricondenbars obtained in the P-V-T-x studies, with some correctable limitations at low temperatures.

Based upon these model system studies, the hypotheses that cricondenbar's are good (and sometimes exact) estimates of the minimum miscibility pressure and that an equation of state, with some empirical modifications, can be used to predict these cricondenbars (and hence MMP's) has been demonstrated.

The equation of state was then used to predict cricondenbars for crude oil-CO₂-additive systems. These results were then graphically prepared for general use in predicting minimum miscibility pressures (MMP's). These pressures were in good agreement with the miscibility pressures reported from over 150 sets of slim tube displacement experiments.
7.2 Evaluation of the Proposed Correlation

The PR EOS MMP graphical correlation can best be evaluated by summarizing, in detail, its strengths and limitations. The strengths include:

1. The correlation is based on miscibility of fluids;
2. Thermodynamic criticality is a necessary and sufficient condition for FCM displacement of an alkane by CO₂ which represents a limiting case of CO₂ displacement of oil. The correlation is exact for these simple systems;
3. The correlation accounts for the MW C₅⁺ of the oil, temperature, CO₂ impurities and live oil gaseous components;
4. The correlation is independent of a CO₂/crude oil MMP data base;
5. The correlation may be generated with the Peng-Robinson equation of state. Other equations are probably equally effective;
6. The correlation can be expressed in graphical form;
7. When tested against 157 MMP values from literature sources, a mean value of the predicted to actual MMP value of 1.09 was obtained with a standard deviation of 0.19.

The limitations of this correlation include:

1. The molecular weight distribution is only accounted for by the average molecular weight;
2. The crude oil C₅⁺ fraction is modeled using a single alkane, thereby replacing the MCM displacement with a FCM mechanism;
3. The critical loci of the CO₂/C₁₄H₃₀ and C₁₅/H₃₂ systems are interpolated, the CO₂/nC₁₇H₃₆ and C₁₈H₃₈ critical loci are extrapolated;
4. Temperature dependent interaction parameters must be used to generate the CO₂/n-alkane critical loci. Furthermore, a certain degree of
uncertainty exists in many of the pertinent binary interaction parameters;

(5) The PR EOS underestimated the shift due to cricondenbar loci by up to 30%.

(6) The correction breaks down for low-temperature high molecular weight systems, necessitating an empirical correction based on experimental trends observed in previous studies.

In conclusion, although the correlation may not be as accurate as previous ones, it gives reasonable results and is based on thermodynamic principles which provide insight into why the many parameters involved affect the MMP.

7.3 Extensions to High Temperature Conditions

The most striking difference between the predicted results of this correlation and others, particularly the Holm and Josendal correlation\(^{19}\) any modifications thereof,\(^{26, 29}\) is evident when the results of both are extended to temperatures above the current range of reservoir application. The critical loci of each of the \(\text{CO}_2/n\)-alkane systems of interest proceed from the critical point of \(\text{CO}_2\) (or a relatively low temperature, low pressure minimum) through a maximum pressure value and then terminate at the critical point of the alkane. Therefore, above the temperature at which this maximum occurs, any increase in temperature would lead to a decrease in the MMP of the system. This decrease will occur even in multi-component crude oils, for if one considers the temperature range above the critical temperature of the crude, both the \(\text{CO}_2\) and the oil would be supercritical and the MMP would be 0; the fluids would be miscible at all pressures. The MMP must, therefore, pass through a maximum value at some temperature and decrease thereafter. This is in direct contrast with the correlation of MMP with...
FIGURE 36: Temperature Above which MMP Predicted to Decrease
CO₂ density. As temperature increases, the pressure required to maintain a certain CO₂ density will steadily rise, no decrease will occur. The density correlations must, therefore, be restricted to the temperature range over which they were developed, for they fail to adequately account for the increased miscibility of hydrocarbons at elevated temperatures.

The approximate temperature at which the critical locus reaches its maximum value, and the value itself are plotted on Figure 36 as a function of molecular weight. These curves were derived from critical loci data.(23,46,47) For mixtures of CO₂ with C₈H₁₈, C₉H₂₀, C₁₀H₂₂, C₁₁H₂₄, C₁₂H₂₆, C₁₃H₂₈, and C₁₆H₃₄. To illustrate the use of the graph, consider a crude oil with a MW C₅⁺ of 170. Its maximum MMP value of 22 MPa would occur at 167°C. Thereafter, the MMP would decrease with an increase in temperature. Such high temperatures could only be encountered in extremely deep reservoirs or in CO₂/steam injection processes.

7.4 Extensions to Other Miscible Displacement Processes

There are four general categories or miscible displacement processes, vaporizing drive, condensing drive, CO₂ miscible drive (an efficient vaporization/extraction process) and first contact miscible drive. Unlike most of the other correlations, the same principle used in the development of the CO₂ miscible drive MMP correlation may also be applied to the other three processes. The MMP for FCM floods are defined by the critical loci of the drive slug/displacing slug systems, which typically decrease with temperature over the range of application. Correlations for condensing and vaporizing drive processes may also possibly be correlated to the criticalenb of a displacing/displaced fluid
system. Once again, it is obvious that slug density could not adequately describe the MMP requirements for these processes, especially FCM drive. The miscibility of fluids is a more logical and consistent approach for addressing each of these processes.
8.0 RECOMMENDATION

Several significant contributions could be made toward a more comprehensive understanding of the MMP using the basic principles described in this study, including:

(1) a comparison of paraffinic, aromatic and naphthenic hydrocarbon miscibility with CO$_2$ over a wide range of temperatures. This would clarify the influence of molecular structure on the MMP;

(2) the experimental determination of the CO$_2$/C$_n$H$_{2n+2}$ critical loci, where $n = 14$, 15, 17, 18 and 19. This would provide a more complete base of CO$_2$/alkane data;

(3) a complete study of N$_2$/alkane PVT behavior and N$_2$/crude oil STD's. This would not only fill in a substantial gap in the N$_2$/hydrocarbon data base, but may also lead to a similar correlation for this vaporizing gas drive process.
BIBLIOGRAPHY


22. Personal communication with Charles Arnold, Exxon Inc., Houston, Texas.


42. Goricnik, B. and Sarapa, M., "Relations between Oil Composition and Carbon Dioxide Minimum Miscibility Pressure," Proc. SZKFI and IFT International CO₂ EOR Symposium, Budapest.

43. Silva, M., "Component Partitioning in CO₂/Hydrocarbon Systems: The Effects of Chemical Type," Master's Thesis submitted to Faculty of the Graduate School of the New Mexico Institute of Mining and Technology (May 1984).

44. Holm, L. and Josendal, V., "Study Shows Best Use of CO₂ as EOR Agent," Oil and Gas Journal, October 22, 1984, pp. 131-134.


