PVT Study of the Interaction of Nitrogen and Crude Oil, Stage II

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ABSTRACT

The objective of this investigation is to study the impact of the injection of nitrogen/oxygen mixtures on the physical properties of crude oil and to determine its effect on oil composition. The mid-continent grade crude oil used in this study was obtained from the Big Andy field in Central Kentucky. This field is currently realizing enhanced oil recovery using nitrogen/oxygen injection.

As reported in Stage 1, results from the PVT studies using 3 different injection mixtures was used to develop a phase behavior model. The mixtures used consisted of 100 % nitrogen, 97 % nitrogen - 3% oxygen, and 86 % nitrogen - 14% oxygen. Six cycles of injection followed by a "soaking phase" and then withdrawal were performed for each gas mixture.

The results of the laboratory study indicated that striping of the crude oil (methane through decane plus) was being realized. The first injection using 100 % nitrogen indicated that the lighter components of the crude oil (methane through butane) were stripped from the crude oil. The volume realized 5 % shrinkage after 6 cycles for the 100 % N_2 test matrix. The results obtained for the other injection mixtures (97-3 % N_2O_2 and 86-14 % N_2O_2) showed shrinkage of 4 % volumetrically. The results obtained also indicated an increase in viscosity and density for all three injection mixtures after 6 injection cycles.

The phase behavior package developed modeled the results obtained from the PVT laboratory experiments. The model has shown that for a given initial mass of crude oil, there was 3 % shrinkage for a total of 8 cycles when injecting 100 % N_2. When varying the composition, the shrinkage did not show any significant variation from those obtained initially.

From the results obtained through the PVT cell and the phase behavior model, efforts to extend the results of these tests to the Big Andy field were undertaken to develop and understanding of the mechanisms attendant to the huff-and-puff technique. Analysis of the reservoir has suggested that the primary mechanism controlling gas movement during injection is the presence of naturally fractures. During the soaking-phase of the project the gas tends to migrate through gravity differences to the top of the formation and into the matrix. Also the operator has opted to use Carbon-Dioxide to act as a near wellbore clean-up mechanism.

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EXECUTIVE SUMMARY

The objectives of Stage I and Stage II of this study are to investigate the effects of nitrogen cyclic injection on the composition of crude oil and the extent to which nitrogen is vaporizing the crude oil and to optimize the project. The mid-continent grade crude oil used in this study was obtained from the Big Andy field in Central Kentucky. This field is currently realizing enhanced oil recovery using nitrogen/oxygen injection.

As reported in Stage 1, results from the PVT studies using 3 different injection mixtures was used to develop a phase behavior model. The mixtures used consisted of 100 % nitrogen, 97 % nitrogen - 3% oxygen, and 86 % nitrogen - 14% oxygen. A total of six cycles of injection followed by a "soaking phase" and then withdrawal were performed for each gas mixture.

The results of the laboratory study indicated that striping of the crude oil (methane through decane plus) was being realized. The first injection using 100 % nitrogen indicated that the lighter components of the crude oil (methane through butane) were stripped from the crude oil. The volume realized 5 % shrinkage after 6 cycles for the 100 % N_2 test matrix. The results obtained for the other injection mixtures (97-3 % N_2O_2 and 86-14 % N_2O_2) showed shrinkage of 4 % volumetrically. The results obtained also indicated an increase in viscosity and density for all three injection mixtures after 6 injection cycles.

The phase behavior package developed modeled the results obtained from the PVT laboratory experiments. The model has shown that for a given initial mass of crude oil, there was 3 % shrinkage for a total of 8 cycles when injecting 100 % N_2. When varying the composition, the shrinkage did not show any significant variation from those obtained initially.

From the results obtained through the PVT cell and the phase behavior model, efforts to extend the results of these tests to the Big Andy field were undertaken to develop and understanding of the mechanisms attendant to the huff-and-puff technique. Analysis of the reservoir has suggested that the primary mechanism controlling gas movement during injection is the presence of naturally fractures. During the soaking-phase of the project the gas tends to migrate through gravity differences to the top of the formation and into the matrix. Also the operator has opted to use Carbon-Dioxide to act as a near wellbore clean-up mechanism.

In terms of optimizing the process, we were unable to accomplish this objective during the course of these projects. The operator of the field is sponsoring work with us that will undertake optimization studies of the process that employ artificial neural networks. In addition, a second study is underway that utilizes the concept of dynamic programming for optimization. It should be also pointed out that we have received numerous enquiries into expanding this work for other reservoir environments. These include the First and Second Venango sands in northwestern Pennsylvania.

INTRODUCTION

1.1 Introduction

Improved oil recovery techniques (IOR) have increased in application over the past few decades because of lower production volumes and rising oil prices. Generally, oil companies must take into account two major factors when considering IOR processes. First, the feasibility of the technique to the specific field must be evaluated. Second, and most importantly, the economic soundness of the project must justify the application of the technique itself. The latter is primarily dependent upon regional oil prices and the cost/benefit of the additional oil recovery.

Among the IOR techniques used today, the most widely practiced in the United States are waterflooding, steamflooding and CO_2 injection. All of these methods have early applications that date back to the 1930's through the1950's. This is especially true of CO_2 and steam injection. Throughout the last decade, the application of nitrogen cyclic injection for immiscible processes, primarily pressure depleted reservoirs, has increased. The recovery process is very similar to that of steam stimulation practiced in the early 1930's. Whereas steam is used for heavy crudes, nitrogen cyclic injection is being used for comparatively light oils under low pressure conditions.

Despite the increase in the use of nitrogen for improved oil recovery, there has been little research supporting the use of it in shallow low pressured reservoirs containing comparatively light crude oil. Although nitrogen injection has shown promise as a technique, methods for screening reservoirs for applicability are necessary prior to implementation of the cyclic process.

1.2 Objective of the Study

The objective of this study is to evaluate the nitrogen huff and puff (i.e. cyclic injection) process in a dual porosity reservoir that is pressure depleted. The field is located in Eastern Kentucky and is operated by an independent oil company, Bretagne. To accomplish this objective, a PVT cell was fabricated, a laboratory study was designed and a phase behavior computer model developed. The laboratory work focused on the effects of nitrogen gas cycling

on the composition of the crude oil. Specifically the extent to which the oil is being vaporized by the injected nitrogen was to be examined. The physical properties of the crude oil, such as the viscosity and density, were monitored for changes.

The phase behavior model was developed to model the results obtained from the PVT cell, and the parameters controlling its performance tuned from the laboratory data obtained. The results obtained from the model were then used to quantify the amount of oil being vaporized by the injected nitrogen as the number of injection-withdrawal cycles increases. The model could then be used for vapor-liquid flash calculations.

From the perspective of the field setting, the focus of the study is the determination of nitrogen required for injection, the extent to which the crude oil is being contacted by the injected gas and most importantly, the crude oil shrinkage factor being observed after repetitive cycles of nitrogen injection and crude oil production. The work plan called for the use of data obtained from a field area where nitrogen injection had been ongoing for 4 years.

Another objective of this investigation is to identify the mechanisms attendant to the nitrogen huff and puff process and to use them to develop a screening guide for operators considering application of the process. Ultimately, field work coupled with the laboratory study of the cyclic process, should facilitate the design of reservoir compositional models for the study of huff and puff processes in specific fields.

1.3 Field Background

The Big Sinking field in Eastern Kentucky lies on the Western flank of the Appalachian basin. The field has been producing since the early 1900's. The underlying reservoir is pressure depleted with a remaining pressure of about 50-psig. The net thickness of the reservoir is about 40-ft and the depth to the top of formation is approximately 1300-ft. The reservoir has a porosity of approximately 16-% and has a matrix permeability of approximately 19-md. The average water saturation of the reservoir is approximately 50%. The crude oil's gravity is 36° API.

The current area of interest is the Big Andy field, an extension of the Big Sinking Field located on its Southeastern margin. The reservoir characteristics are similar since there are no discontinuities in the formation; however, the Big Andy reservoir is naturally fractured. Most of

the wells had been drilled in the early 1980's with a total of some 400 active wells. In the mid 1980's a waterflood pilot test was initiated in the Big Andy with no success due to the reservoir's natural fracture. As such, by the late 1980's other alternatives were investigated. CO_2 huff and puff was used as an alternative to waterflooding. Following CO_2 injection, membrane generated nitrogen was introduced.

The nitrogen huff and puff was initiated in 1998. Using membrane technology, nitrogen is generated on site at an approximate cost of $ 1.00/MSCF. One advantage of using nitrogen is its immiscibility in water and oil. As a consequence, of its immiscibility, the injected nitrogen remains in the gas phase. Additionally, nitrogen is environmentally benign, non-corrosive and easily disposed of through venting to the atmosphere. The nitrogen huff and puff process is a new technique with no prior field application (US patent # 6,244,341).

As such, the design of a PVT experimental study, matched by production data from the Big Andy field will help in the development of screening criteria necessary for wider application of the technology within the United States. Once the experimental framework is developed, a phase behavior model can be used and the parameters of the EOS tuned to fit the laboratory results. Ultimately, as the process becomes better understood, independent producers will have the capability to consider its application to other reservoirs.

1.4 Project Description

A PVT cell system was fabricated for the purpose of conducting the cyclic injection-withdrawal experiment using nitrogen and oxygen. The cell is manufactured by Temco™ and has an internal volume of 500 cc. In addition, the cell uses a hydraulic piston to vary the volume of the cell. Along with the PVT cell, an air bath has been installed surrounding the PVT cell, in order to vary the temperature of the cell. The current achievable temperature range is 65ºF to 100ºF.

Before using the cell it was necessary to validate the accuracy of the apparatus. Several tests were conducted using single as well as two and three-component systems. The results obtained were then compared with the results available in literature. For instance, a plot of pressure versus specific volume was constructed and compared to available data for the case of pure propane.

Also mixtures of propane-ethane and propane-methane were used to generate similar pressure-volume plots.

Testing was done to analyze the effects of bubbling nitrogen at a constant flow rate through a crude oil sample. Samples of gas were collected and the composition determined using a Gas Chromatograph (GC) unit. The observed trend was a decrease in composition of the lighter components of the crude, with time. The next step was to collect the liquid samples from the PVT cell which had been subjected to the nitrogen treatment. These samples were then analyzed for composition and determination of physical properties.

In conjunction with the experimental laboratory work, well head gas samples were taken and analyzed from several wells in the Big Andy field. The purpose of this was to initiate a study at the field scale of the impact of the repeated injection/withdrawal cycles of nitrogen on in situ crude oil.

EXPERIMENTAL

2.1 Experimental Apparatus

A PVT window cell was fabricated using a Temco™ (Serial # 2503) piston cylinder. The stainless steel cylinder has an internal volume of 500 cubic centimeters (cc) when the piston is fully retracted (see Figure). The maximum allowable working pressure is 5,000 psig, with a test pressure of 7,500 psig. The maximum allowable temperature is 350 º F. The piston cylinder is mercury free. The cell is mounted on two legs which allow it to move to an upward and downward position (for rocking purposes). This permits mixing and ensures equilibrium (for flash calculations) between the gas and liquid phases once fluids are injected into the cell. The cell contains a window at the front end which allows the fluids to become visible, hence facilitating measurements of liquid and/or vapor volumetric fractions. Figure **2.2** shows a picture of the PVT cell connected with the necessary equipment for conducting the experimental work. These include:

1. A linear variable differential transformer (LVDT) designed by Macro Sensors (model PR 812 – 4000).
2. Two OMEGA™ pressure transducers (PX 203-1KG5V) attached to the PVT cell.
3. A manual hydraulic pump (Enerpac PH 39) connected to the cell for piston displacement (see Figure **2.3**)
4. Two mass flowmeters (Omega FMA 1706) permit independent measurements of the flows of nitrogen and oxygen independently from the gas cylinders to the PVT cell.
5. A computerized data acquisition instrument, LabView™ which enables monitoring of pressure, temperature, volume and flow rates of injected gas into the cell.
6. A thermocouple to monitor temperature variations within the cell.
7. A Gas Chromatograph for analysis of the collected vapor samples (see Figure **2.4**)
8. A Brookfield viscometer for fluid viscosity measurement (see Figure **2.5**)

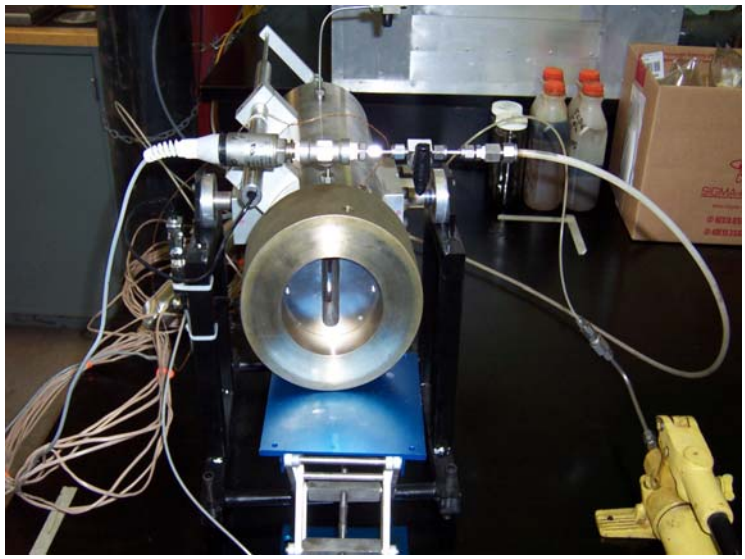


Figure **2.1**: Temco PVT Cell

Figure **2.2**: Complete Lab Set-up

Figure **2.3**: Enerpac Hydraulic Pump

Figure **2.4**: Shimadzu G.C. 17A

Figure **2.5**: Brookfield Viscometer

The gas chromatograph shown on Figure **2.4** is a Shimadzu brand, model G.C. 17A. The unit contains two detectors for analyzing different compounds. The first, an FID detector, is capable of detecting hydrocarbon compounds ranging from methane up to C_{20}. The second is a TCD column capable of detecting nitrogen, oxygen and carbon dioxide. Together, both detectors are used to determine the composition of the gas collected from the PVT cell.

In addition to the G.C. unit, a Brookfield viscometer is used to measure the viscosity of the crude oil sample before and after the injection process. The viscometer contains a circular plate where the liquid is placed, and a rotating shaft to measure the torque of the shaft against the fluid. The concept is to rotate the shaft at a certain known velocity which is translated into a

torque. The torque is a measure of the resistance of the fluid on the shaft. This torque measurement is then used to compute the viscosity.

2.2 Experimental Procedure

The objective of the experimental procedure was to inject nitrogen into the PVT cell containing crude oil, permit mixing of the N_2 with the oil sample, remove the vapor from the cell, and analyze it using a gas chromatograph (G.C.) instrument. Further, a period of 24-hours was used to permit the injected gas to reach equilibrium with the crude oil. It is worth noting that this time frame was chosen randomly and was not optimized during the experimental work. Following this 24-hour period, a sample of the vapor was withdrawn and analyzed to determine its composition. The following procedure was used to obtain the necessary data:

1. A sample of crude oil is selected from a well not previously treated with nitrogen. A volume of 400 cubic centimeters (cc) is chosen to facilitate the determination of vaporization. Mass and density are also measured for the sample to be analyzed. The oil sample is injected into the PVT cell at atmospheric conditions and the cell is sealed. Air is purged from the cell using nitrogen.
2. The piston is then pushed forward with the manual pump until the cell is completely filled with the oil (single phase) prior to injection.
3. A 500-cc cylinder is pressured up to 200-psig using nitrogen gas. The nitrogen gas is either 100 percent by molar composition or mixed with oxygen (up to 14 percent by volume) depending on the experiment. Table **2.1** contains the test matrix developed for varying the nitrogen-oxygen mixture injected into the PVT cell.
4. The nitrogen gas is then injected into the PVT cell until a pressure of 150-psig is reached. The 150-psig was selected to mimic field conditions. As mentioned previously, the cell is initially at atmospheric conditions.
5. The final step consists of allowing the fluids to reach thermodynamic equilibrium by permitting the crude oil and nitrogen to reside for 24 hours in the cell. Periodic rocking of the cell was used to promote mixing and the attainment of thermodynamic equilibrium.

6. A sample of vapor is then removed from the PVT cell and collected in a Teddlar bag designed for gas sample collection. The remaining vapor is vented from the cell, allowing only the liquid to remain in the cell. The PVT cell is then returned to its initial pre-injection conditions by moving the piston until only the remaining liquid can be seen through the window.
7. The Teddlar bag containing the vapor is then taken to the G.C. laboratory for analysis. Two samples of 300 micro liters (μL) are extracted using a 1 liter syringe. The first sample is injected into the FID column to analyze the composition of the hydrocarbons. The second sample is injected into the TCD column to determine the composition of nitrogen, oxygen and carbon dioxide.
8. The remaining vapor is vented from the cell, keeping only the liquid in the cell. The PVT cell is then returned to its initial pre-injection conditions by moving forward the piston until only the remaining liquid can be seen through the window.
9. Another cycle of gas is then prepared for injection and the process is repeated. Six cycles are performed using the PVT cell.
10. The crude oil's viscosity following the injection-withdrawal cycles was determined using the Brookfield viscometer

Table **2.1**: Nitrogen-Oxygen Test Matrix

Injection Gas / Oil Sample	N_2 (100) %	N_2-O_2 (97-3) %	N_2-O_2 (86-14) %
19P * (no prior N_2 injection)	6 Cycles	6 Cycles	6 Cycles
Pressure,Temp	150(psig), 70(ºF)	150(psig),70(°F)	150(psig), 70(ºF)

* Well 19P is located on the James Booth lease

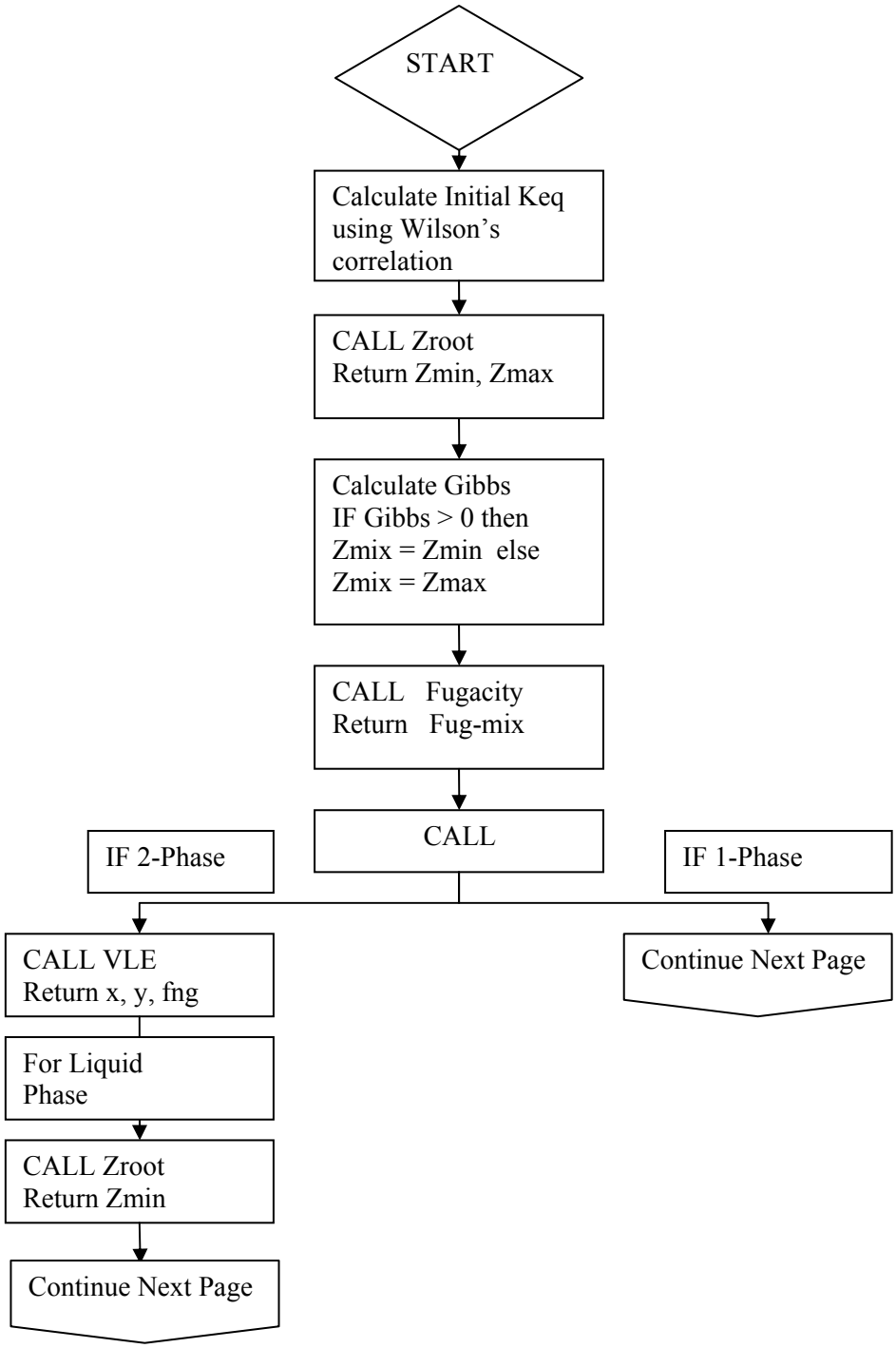
PHASE BEHAVIOR MODEL

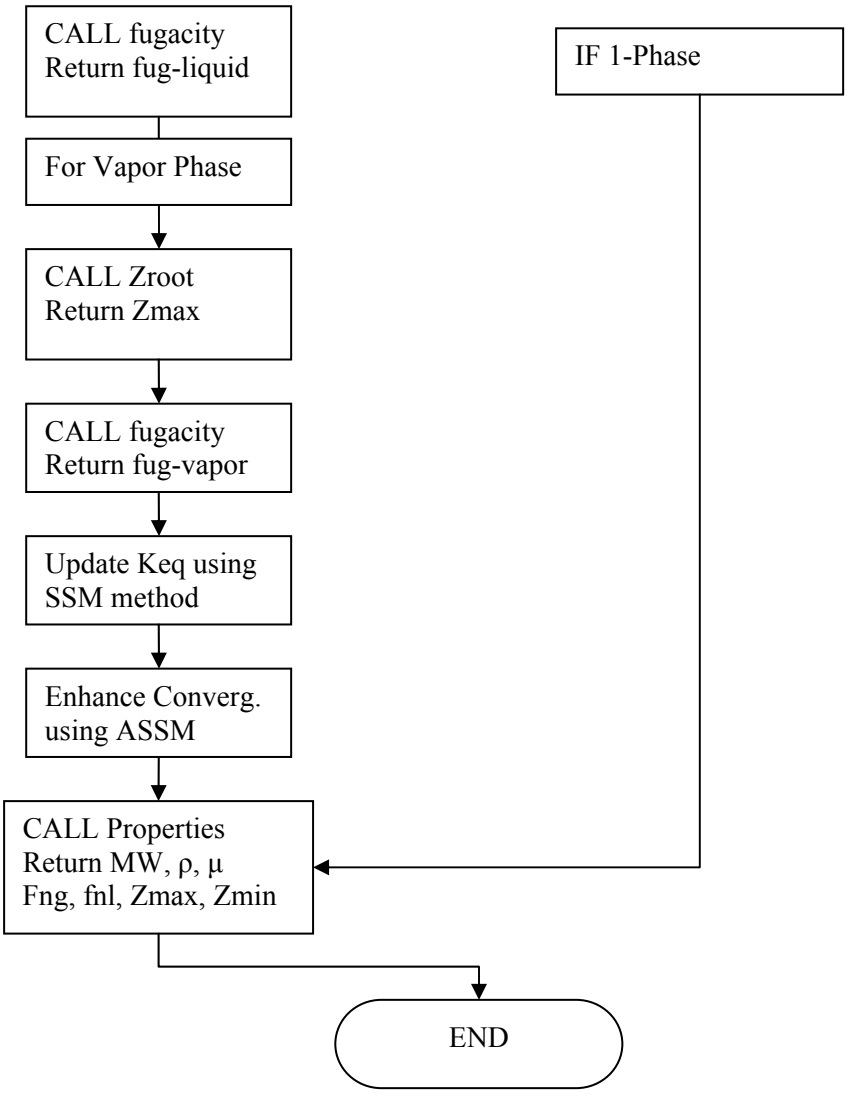
3.1 Objective and Problem Statement

Phase behavior prediction has always played an integral role in reservoir engineering. It is also important for production engineers concerned with the design of such things as pipelines and surface production facilities.

The purpose of this section is to familiarize the reader with the phase behavior model and the process by which it is used in conjunction with the experimental work. The phase behavior model discussed here is a set of algorithms written in FORTRAN® (formula translator) language in order to perform vapor liquid equilibrium (VLE) flash calculations - Figure **3.1** shows a flow chart of the overall algorithm. Realizing successful implementation, we can then determine whether a given composition will exist as a single phase or more, and the physical properties that characterize its behavior. The model will also permit a calculation of the change in composition as nitrogen is being cyclically injected, and equilibrium is realized during the "soaking" phase.

Figure **3.1**: Phase Behavior Model Flowchart




CALL fugacity
Return fug-liquid
IF 1-Phase
For Vapor Phase
CALL Zroot
Return Zmax
CALL fugacity
Return fug-vapor
Update Keq using
SSM method
Enhance Converg.
using ASSM
CALL Properties
Return MW, ρ, μ
Fng, fnl, Zmax, Zmin
END

3.2 Description of Modules

A comprehensive phase behavior model was developed to compute the properties of the gas and liquid phases. These properties include the densities, viscosities and molecular weights. The model was developed using several interdependent modules that are described in the following sections. The following sections discuss the procedures employed by each module.

- **Phase Stability Test**

In order to determine whether a hydrocarbon mixture will exist as a single-phase or as two phases, a "detection routine" was performed. This first module was formulated for the purpose of determining the mixture's phase.

In this module, the phase stability criterion proposed by Michelsen in 1982 was used [Michelsen, 1982]. The concept behind the stability test is the introduction of a "second-phase" inside the existing mixture. The stability test is then performed for two cases; a vapor-like "second-phase" and a liquid-like "second-phase". A requirement for successful testing is that the compressibility factor of the mixture must be chosen such that it minimizes the Gibbs free energy. When the test is performed, the outcome is either a single phase system or a two phase system. In the case where two phases are present, VLE calculations are initiated to determine the molar fractions of both the vapor and liquid.

- **Vapor Liquid Equilibrium Calculation (VLE)**

The VLE subroutine is used to determine whether the mixture will remain as a single phase or split into a two phase system. If two phases are present, the molar quantities of both vapor and liquid are determined. In order to do so, the Rachford-Rice Objective function (see Equation 1) was used to compute the equilibrium constant (K_i), which is the ratio of vapor molar fraction to that of liquid ($K_i = Y_i/X_i$) [Rachford and Rice, 1952].

In order to do so, Wilson's empirical correlation (Equation 2) is used to calculate a first estimate of the equilibrium constants. The equilibrium constants are later updated through the use of a more robust method, one which requires more rigorous thermodynamic principles.

$$g\left(f_{ng}\right)=\sum_{i=1}^{n_c}\frac{c_i\left(k_i-1\right)}{1+f_{ng}\left(k_i-1\right)} \qquad (1)$$

$$k_i = \frac{1}{P_{ri}} e^{\left[5.37\,(1+w_i)\left(1-\frac{1}{T_{ri}}\right)\right]} \qquad (2)$$

- **Compressibility Factor Prediction (Z-root)**

In order to predict the volumetric behavior of a hydrocarbon multi-component system, an equation of state (EOS) that describes the system is required. For this study, the Peng-Robinson Equation of State (PR-EOS) was chosen [Peng and Robinson, 1976]. The PR-EOS has the form:

$$P=\left(\frac{R\times T}{V_m-b_m}\right)-\left(\frac{\left(a\times\alpha\right)_m}{V_m^2+2b_mV_m-b_m}\right) \qquad (3)$$

In cubic form in term of the compressibility (Z):

$$Z^3 + a_1 Z^2 + b_1 Z + c_1 = 0 \qquad (4)$$

where:

$$a_1 = -\left(1-B)\right)$$
$$b_1 = A-3B^2-2B$$
$$c_1 = -\left(AB-B^2-B^3\right)$$

$$A = \frac{(a\alpha)_m P}{R^2 T^2} \qquad (5)$$

$$B = \frac{b_m P}{RT}$$

The task is to solve expression (4) for the compressibility factor of the hydrocarbon mixtures and then to move on to vapor liquid equilibrium calculation (VLE). The Peng and Robinson equation of state (EOS), Equation (3), was selected because it is widely used in the petroleum industry and most importantly, it is more reliable when applied to a wide range of hydrocarbon systems. In order to solve the cubic Equation (4), a numerical method is required. The Newton Rhapson technique is used for non-linear systems and can provide reliable results. It will be used to solve for the compressibility factor.

- **<u>IsoFugacity Criteria and SSM (successive acceleration method)</u>**

In the previous subroutine (VLE), an empirical method (Wilson's correlation) was used to calculate the equilibrium constant (K_i) of the composition. However, the values obtained were only estimates and did not represent an accurate thermodynamic evaluation. The fugacity will prove to be more accurate through the use of more rigorous thermodynamic equilibrium considerations. Thermodynamic equilibrium is achieved when all net transfer (heat, momentum, mass) is zero. Hence the potential must be the same under such conditions which in turn requires the fugacities (see Equation 6) of all components to be the same. Equation (6) is then related to the equilibrium constants through equation (7). When the fugacities of the components are obtained, they can then be updated using Wilson's initial prediction, through the SSM technique (8).

$$f_{li} = f_{gi} \text{ , for all i's} \qquad (6)$$

where:

f_{li} = fugacity of the i-th component in liquid phase

f_{gi} = fugacity of the i-th component in the vapor phase

$$K_i = \frac{\phi_{li}}{\phi_{gi}} = \frac{f_{li}/(x_i P)}{f_{gi}/(y_i P)} = \frac{y_i}{x_i}\left(\frac{f_{li}}{f_{gi}}\right) \tag{7}$$

and,

$$K_i^{n+1} = K_i^{n}\left\{\frac{f_{li}}{f_{gi}}\right\}^{n} \tag{8}$$

- **ASSM (Accelerated Successive Substitution Method)**

The SSM technique that was used previously to increase the convergence rate is more robust in predicting K-values than Wilson's method. However, it is slow to converge around critical points and another technique, which can be implemented at or near critical conditions, is required.

The SSM generates the first equilibrium-constant values, and a switching criterion is checked in order to implement the ASSM. If all the criteria are met, the SSM switches to the ASSM and updates the equilibrium values. The ASSM is then tested to determine if the solution is improving (fugacities are close to unity). If the ASSM does not generate improved solutions, its use is discontinued and the routine, switched back to the SSM without returning to it.

- **Property Prediction**

The final module computes the density, viscosity and molecular weights of the liquid and vapor compositions. These properties can be readily obtained since we have generated in the previous modules all the necessary tools. The molecular weights as shown in Equation (9) are generated using the molar fractions (liquid and vapor) that were calculated. From these, the densities are computed by implementing Equation (10).

$$MW_g = \sum_{i=1}^{n} y_i MW_i \quad (9)$$

$$MW_l = \sum_{i=1}^{n} x_i MW_i$$

$$\rho_a = \frac{P}{RT}\left(\frac{MW_a}{Z_a}\right) \quad (10)$$

The next step is to compute the viscosities of the phases. For determination of the gas viscosity, the Lee-Gonzalez-Eakin (1966) method was used. This predictive method is presented in Equation (11).

$$\mu_g = 1.10^{-4} k_v EXP\left(x_v\left(\frac{\rho_g}{62.4}\right)^{y_v}\right) \text{ (cp)} \quad (11)$$

where:

$$k_v = \frac{(9.4 + 0.02MW_g)T^{1.5}}{209 + 19MW_g + T}$$

$$y_v = 2.4 - 0.2x_v$$

$$x_v = 3.5 + \frac{986}{T} + 0.01MW_g$$

For determination of the liquid phase viscosity, Lohrenz, Bray and Clark correlation (1964) was used:

$$\mu_l = \mu^* + \xi_m^{-1}\left[\left(0.1023 + 0.023364\rho_r + 0.058533\rho_r^2 - 0.040758\rho_r^3 + 0.0093724\rho_r^4\right)^4 - 1.10^{-4}\right]$$

where:

$$\rho_r = \frac{\rho_l}{\rho_{pc}} = \left(\frac{\rho_l}{MW_l}\right)V_{pc}$$, reduced density of the liquid mixture

$\xi_m = \dfrac{5.4402 T_{pc}^{1/6}}{\sqrt{MW_l}\, P_{pc}^{2/3}}$ mixture viscosity parameter

u^* viscosity at atmospheric conditions, cp

T_{pc} pseudocritical temperature, °R

P_{pc} pseudocritical pressure, psia

RESULTS AND DISCUSSION

4.1 Field Work Analysis

The ongoing field operations of Bretagne GP in Eastern Kentucky provide the real– world basis for the experimental work that was performed at the Pennsylvania State University. As previously noted, nitrogen, is being injected into the Big Andy Field. Liquid production from the field has increased from 100 STBD to approximately 500 STBD using the nitrogen huff and puff technique. Based on these results and the analysis of gas collected from several wells in the field, it is recognized that there are at least two processes in play at the field level. The first is displacement where the nitrogen expands resulting in the flow of oil into the wellbore. The second process is the interphase mass transfer of the lighter components[1] from the liquid phase to the gas phase. Although the stripping process might not be desirable, a better understanding of its occurrence in the reservoir could help operators determine the ultimate recovery and number of cycles which can be performed on the field. While it is this second process which is being investigated in this work, it is worth noting that the field's production has increased as a result of the nitrogen huff and puff injection.

The process employed in the field amounts to the injection of approximately 1000 MSCF/Well of nitrogen-oxygen mixture. The well is then shut-in for approximately 30 days to permit soaking of the nitrogen with the oil and to permit percolation of this gas toward the top of the reservoir. For the field portion of this project, the James Booth lease was selected because the wells contained on this lease have little interference with wells located on adjoining leases. This minimizes the loss of injection gas to competing drainage patterns.

In this study the focus is the mass transfer realized between the injected nitrogen and the crude oil resident in the reservoir. To this end, gas samples were collected from the several wells

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[1] For the purpose of this study light components refer to methane through butane. Intermediate components refer to pentane through nonane, and heavy components, decane plus.

located on the Booth lease. These samples were collected and analyzed at the Pennsylvania State University using a gas chromatograph unit.

Figure **4.1** contain the results of the gas samples composition of the vapor phase taken from the wells after the soaking period and the production has been resumed. This plots show a significant amount of light hydrocarbons that have been transferred from the crude oil to the gas phase. It is this phenomenon that is the basis for the experimental work that was undertaken. Moreover, it is the impact of this vaporization on physical properties such as density and viscosity that was to be investigated.

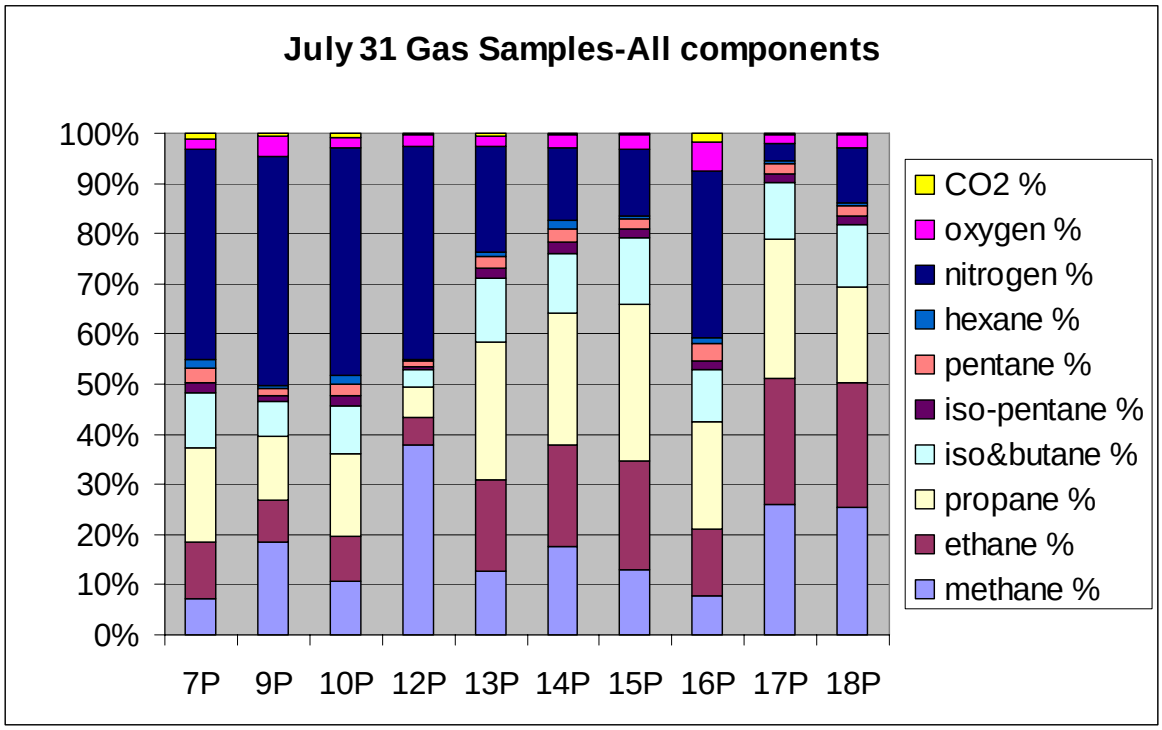

Figure **4.1**: G.C. Analysis J.B. Lease July 04

4.2 <u>Laboratory Data Analysis</u>

5 gallons of crude oil with no prior contact to nitrogen cyclic injection was obtained from well 19P in the James Booth lease (Figure **4.2**) located in the Big Andy field, Eastern Kentucky. The liquid sample was sent for analysis to Questar Applied Technology. The results obtained

(Table **4.1**) were then used as a starting reference for the experimental as well as modeling work to be performed later. The composition obtained shows that the crude oil is very light with an API gravity of 68.9. The specific gravity of the crude oil is 0.705 (density of water 1gm/ml) and the average molecular weight is 104.4 grams/mole.

A predetermined mixture of nitrogen-oxygen was injected into the crude oil. For the first test, pure nitrogen (100% molar fraction) was injected into the cell. The cell was brought to a pressure of 150 psig to be consistent with the average injection pressure realized during field operations. The temperature was also kept at 70°F. These parameters are maintained throughout the entire experimental study. The mixture of injected gas and crude oil was allowed to soak for 24 hours to ensure equilibrium before collecting a sample of vapor for analysis. The second series of tests were conducted using a 97-3 % N_2-O_2 mixture. The last series of tests were conducted using 86-14 % N_2-O_2 mixture. The soaking time was similar to that using 100 % N_2. Varying the composition of the injected gas would help identify any changes brought by the addition of oxygen to the injection process. While the vapor from the PVT cell was collected and analyzed with a gas chromatograph unit, the liquid was sent to Questar Applied Technology for analysis. The vapor from the PVT cell was collected in a 1 liter Teddlar bag. A volume of 300 micro liters (μL) was injected into the G.C. unit as required for detection of the desired hydrocarbons. The G.C. unit produces the appropriate peaks for each hydrocarbon component, which are then converted to a molar fraction. The remaining liquid in the PVT cell is kept in place and used for the subsequent injection cycle. The cell is also purged of any remaining vapor by moving the piston on the cell until the only phase that can be viewed by the operator through the window port is the liquid phase.

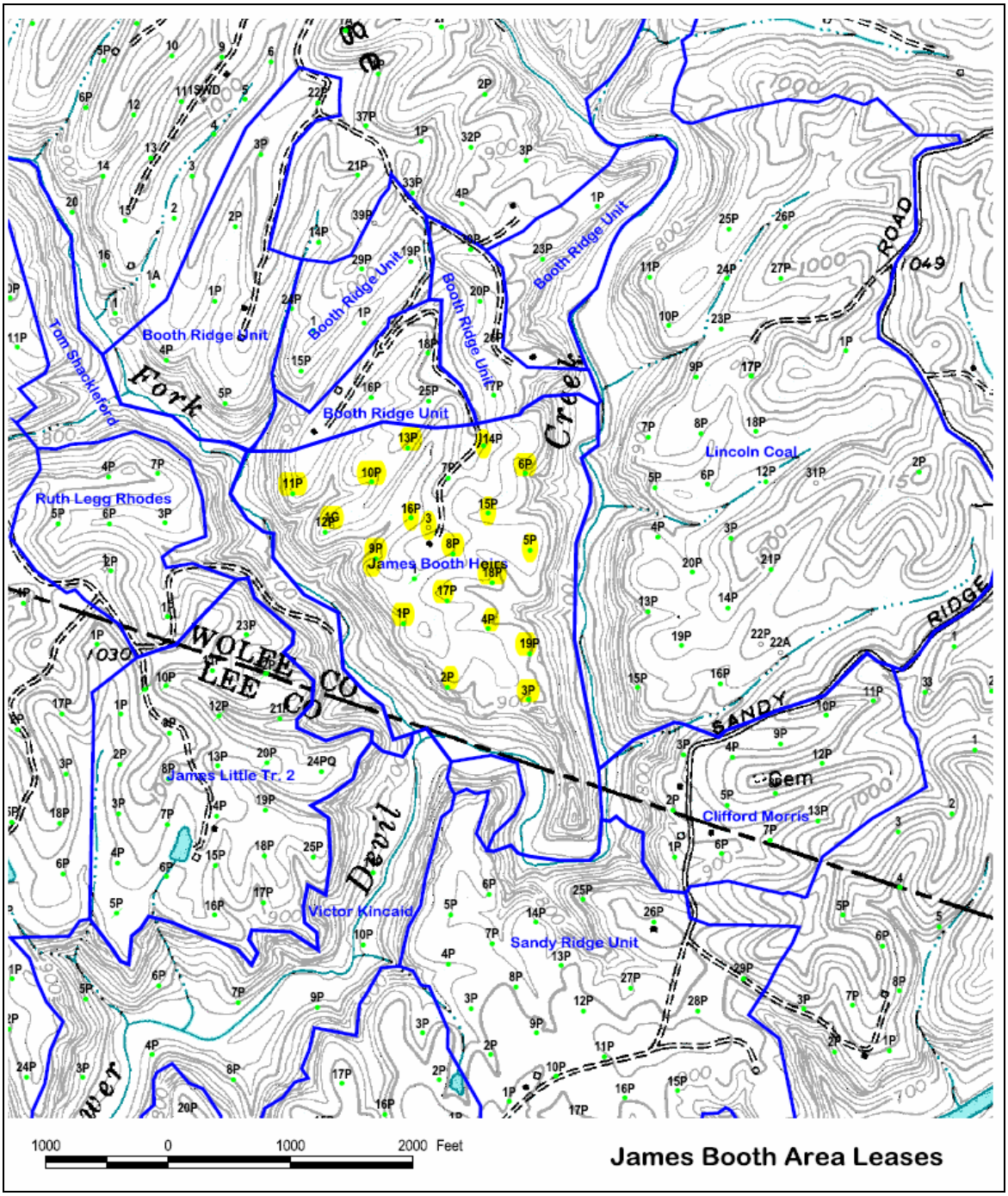

Figure **4.2**: Big Andy Field, Kentucky.

Table **4.1**: Sample 19P Composition Analysis (Pre-Injection)

Component	Mol%	Wt%	LV%
Methane	0.1725	0.0265	0.0624
Ethane	1.1076	0.3190	0.6335
Propane	5.4762	2.3127	3.2205
Isobutane	1.2196	0.6789	0.8515
n-Butane	7.5039	4.1772	5.0493
Neopentane	0.0107	0.0074	0.0087
Isopentane	3.6941	2.5525	2.8857
n-Pentane	6.8089	4.7047	5.2630
2,2-Dimethylbutane	0.0557	0.0460	0.0496
2,3-Dimethylbutane	0.8072	0.6662	0.7058
2-Methylpentane	2.7283	2.2517	2.4162
3-Methylpentane	1.6715	1.3795	1.4555
n-Hexane	5.8494	4.8275	5.1320
Heptanes	21.8014	20.1219	19.3788
Octanes	11.1952	11.9497	11.5999
Nonanes	8.8744	10.3474	9.6748
Decanes plus	20.9585	33.6139	31.5974
Nitrogen	0.0633	0.0170	0.0148
Carbon Dioxide	0.0000	0.0000	0.0000
Total	100.0000	100.0000	100.0000
Global Properties		**Units**	
Avg Molecular Weight	104.4210	gm/mole	
Pseudocritical Pressure	430.24	psia	
Pseudocritical Temperature	510.57	degF	
Specific Gravity	0.70598	gm/ml	Light Comp.
Liquid Density	5.8857	lb/gal	9.8172 %
Liquid Density	247.20	lb/bbl	
Specific Gravity	2.8158	air=1	Inter. Comp.
SCF/bbl	900.95	SCF/bbl	58.57 %
SCF/gal	21.4513	SCF/gal	
MCF/gal	0.0215	MCF/gal	Heavy Comp
gal/MCF	46.638	gal/MCF	31.597 %
Net Heating Value	4293.5	BTU/SCF at 60°F	
Net Heating Value	15511.8	BTU/lb at 60°F	
Gross Heating Value	4642.9	BTU/SCF at 60°F	
Gross Heating Value	16712.6	BTU/lb at 60°F	
Gross Heating Value	97784.3	BTU/gal at 60°F	
API Gravity	68.9		

The results using injection gas that is 100 % N_2 were obtained from the G.C. analysis of the produced vapor phase. The analysis on Figure **4.3** illustrates the components of the hydrocarbons being vaporized by the injected gas. Also, Figure **4.4** indicates that the after 6 injection cycles, the total produced vapor is composed of approximately 5 % hydrocarbons. These results also indicate that the lighter components of the hydrocarbons in the crude oil are being vaporized along with the intermediate components. The lighter components constitute approximately 60 % of the total hydrocarbons being stripped (3 % molar fraction). Mass transfer of these components occurs during the soaking period when equilibrium between the injected N_2 and the crude oil is achieved. The results also indicate that the quantity of the lighter component being stripped by the gas decreases gradually with every injection cycle as can be seen on Figure **4.4**. This means that there are less of the light ends in the crude oil after repetitive injection cycles. The trend also shows that the lighter components of the crude oil are more readily stripped than the heavier and intermediate ones. This is the result of the lighter component having higher vapor pressures than the heavier components and resulting in easier striping. The more volatile a gas is, the higher its vapor pressure. Hence the lighter, more volatile components will have less cohesive forces than the heavier components. This is also consistent with the observations made in the Big Andy Field.

Complementary to the results obtained from the G.C. unit, the liquid sample which was sent to Questar Applied Technology for analysis has also shown interesting trends. The results obtained (see Table **4.2**) have shown that after 6 cycles of 100 % nitrogen injection the molecular weight of the crude oil increases from 104.42 g/mole to114.07 g/mole. Also, the density increases from 5.88 lb/gal to 6.00 lb/gal and the API gravity decreased from 68.9 to 64.9 after 6 cycles. Most importantly, the crude oil's shrinkage was calculated given the data obtained and found to be around 6 % by volume for the case of 100 % N_2 injection (see Table **4.3**). When calculating the shrinkage for the injection cycles of 97-3 % N_2-O_2, and 86-14 % N_2-O_2 the numbers were slightly lower, and the shrinkage was found to be approximately 4 % by volume. The shrinkage by mass was also calculated for the three different injection cycles and found to be approximately 4 % for the case of 100 % N_2 injection and 2 % for the other two injections. The results obtained indicate that the 100 % N_2 injection has caused more shrinkage, both by mass

and by volume, than the 97-3 % N_2-O_2 and the 86-14 N_2-O_2. This could be caused by experimental error during analysis of the sample. Further work is needed to determine the role of oxygen in the stripping process.

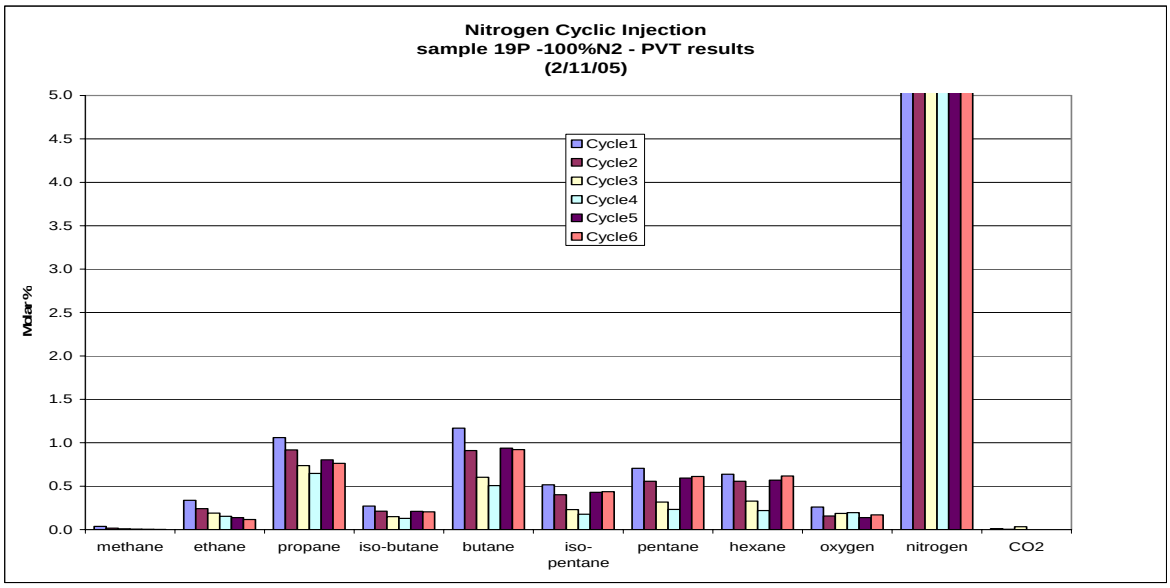

Figure **4.3**: G.C. Results Sample 19P-100%N_2

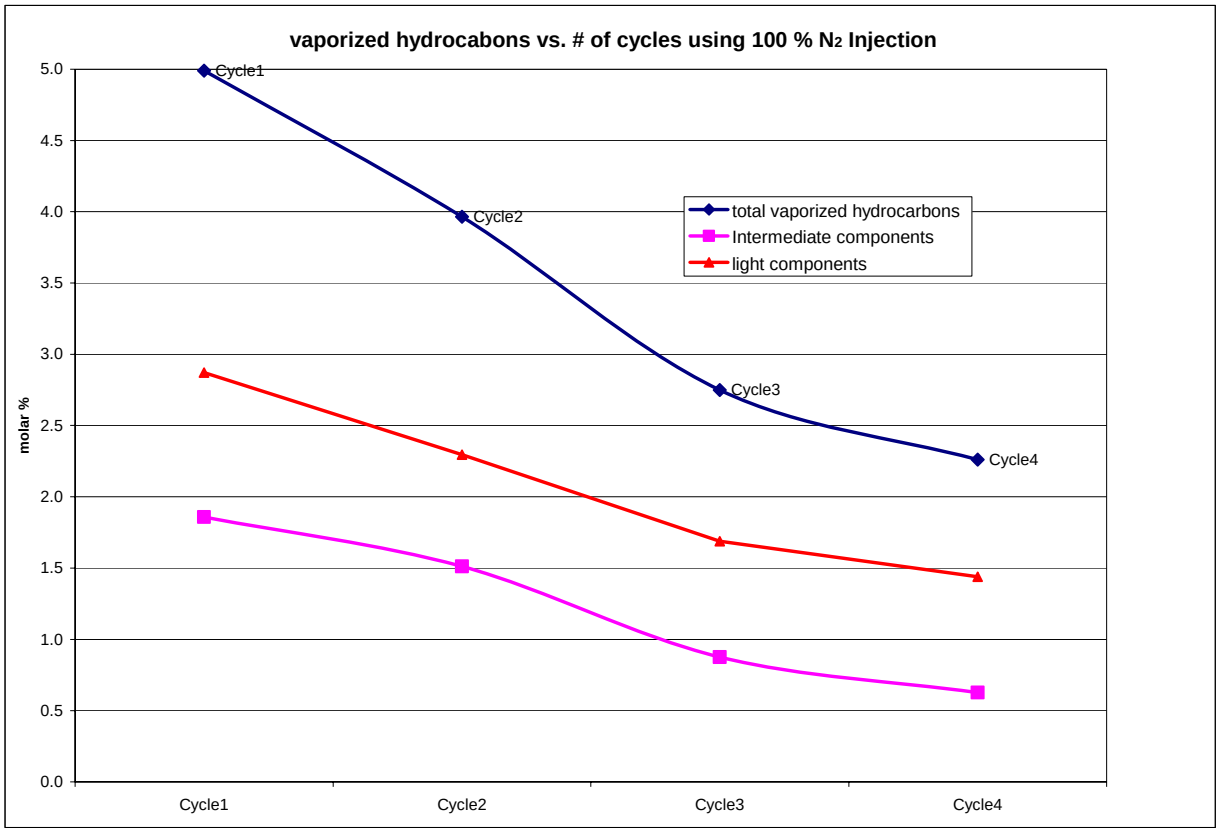

Figure **4.4**: Vaporized Hydrocarbons using 100 % N_2

Table **4.2**: Sample 19P – 100 % N_2 (Post Injection)

Component	Mol%	Wt%	LV%
Methane	0.0432	0.0061	0.0146
Ethane	0.0000	0.0000	0.0000
Propane	1.3981	0.5405	0.7682
Isobutane	0.6413	0.3267	0.4183
n-Butane	4.7840	2.4375	3.0076
Neopentane	0.0000	0.0000	0.0000
Isopentane	3.0418	1.9239	2.2202
n-Pentane	5.9442	3.7596	4.2930
2,2-Dimethylbutane	0.0540	0.0408	0.0450
2,3-Dimethylbutane	0.8838	0.6677	0.7221
2-Methylpentane	2.6412	1.9953	2.1854
3-Methylpentane	1.6988	1.2834	1.3821
n-Hexane	5.9487	4.4939	4.8766
Heptanes	23.6467	20.0148	19.6866
Octanes	12.2888	12.0432	11.9607
Nonanes	10.0812	10.8518	10.4372
Decanes plus	26.8184	39.5948	37.9635
Nitrogen	0.0852	0.0209	0.0186
Carbon Dioxide	0.0000	0.0000	0.0000
Total	100.0000	100.0000	100.0000
Global Properties		**Units**	
Avg Molecular Weight	114.0749	gm/mole	
Pseudocritical Pressure	403.12	psia	
Pseudocritical Temperature	551.64	degF	
Specific Gravity	0.72058	gm/ml	Light Comp.
Liquid Density	6.0074	lb/gal	4.2087 %
Liquid Density	252.31	lb/bbl	
Specific Gravity	2.9168	air=1	Inter. Comp.
SCF/bbl	842.07	SCF/bbl	57.808 %
SCF/gal	20.0492	SCF/gal	
MCF/gal	0.0200	MCF/gal	Heavy Comp
gal/MCF	49.907	gal/MCF	37.9635 %
Net Heating Value	4475.9	BTU/SCF at 60°F	
Net Heating Value	14805.0	BTU/lb at 60°F	
Gross Heating Value	4839.3	BTU/SCF at 60°F	
Gross Heating Value	15944.5	BTU/lb at 60°F	
Gross Heating Value	94856.5	BTU/gal at 60°F	
API Gravity	64.9		

Table **4.3**: Crude Oil Shrinkage

	100 % N_2	97-3 % N_2O_2	86-14 % N_2O_2
Mass shrinkage (%)	3.8	2.0	2.1
Volume shrinkage (%)	5.8	4.0	4.3

The results, using the second and last injection gases (97-3 % N_2-O_2 and 86-14 % N_2-O_2), were obtained from the G.C. analysis of the produced vapor phase. These were plotted on Figures **4.5** and **4.6**. The trend indicates that the composition of the vapor observed was not significantly different in comparison with the results obtained from the 100% N_2 injection. For instance the plots do not indicate any significant changes at the ethane and propane concentration (as well as other components) among the three injected gases. This would suggest that oxygen concentrations up to 14-% have little impact on the composition of the vapor after cyclic injection. The shrinkage difference could be the result of experimental error when collecting and analyzing the data.

The results obtained from the analysis of the liquid sample with the injection of 97-3 % N_2-O_2 and 86-14% N_2-O_2 are also presented in Tables **4.4** and **4.5** respectively. The results obtained were very similar to those with the 100 % N_2 injection. That is, there appears to be a similar trend with regards to the changes in physical properties before and after the injection process. For instance, the density increases from 5.88 lb/gal to 6.00 lb/gal with the injection of 97-3 % N_2-O_2 and 86-14 % N_2-O_2 respectively. The crude oil's average molecular weight increased from 104.42 gm/mol to 115.63 gm/mol.

The physical properties such as the viscosity and the density of crude oil samples from well19P were also measured in the laboratory before and after the injection process took place

(see Table **4.6**). The initial viscosity (prior to any injection cycles) was measured and found to be 7.2 centipoise (cp). At the end of 6 injection cycles, the viscosity was measured again. The results indicated an increase from 7.2 cp to 9.0 cp in the case when the 97-3 % N_2-O_2 gas was injected. The viscosity also increased with the injection of the gas mixtures. These results indicate a shifting of the physical properties to a more viscous and higher density crude oil. It has also been observed that the color of the crude oil after 6 injection cycles darkens and loses its initial brownish color. No major changes have been observed with the addition of oxygen in the injection gas.

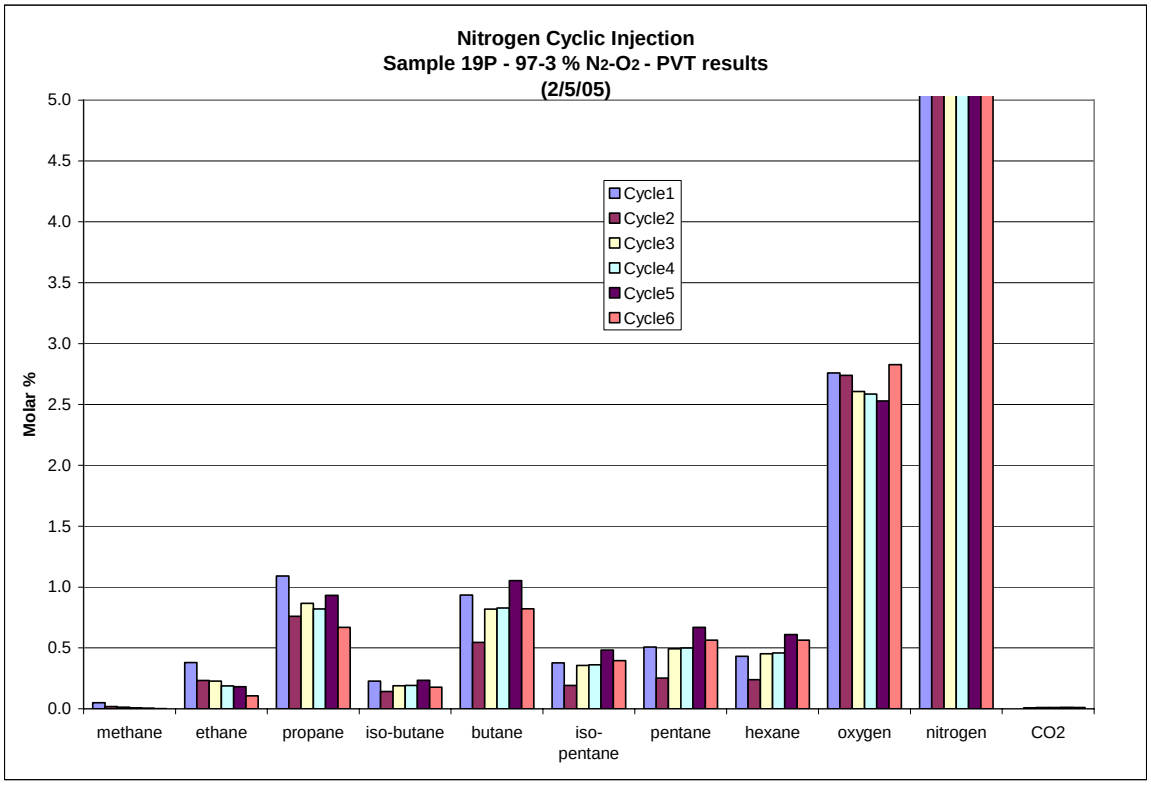

Figure **4.5**: G.C. Results Sample 19P – 97-3 % N_2O_2

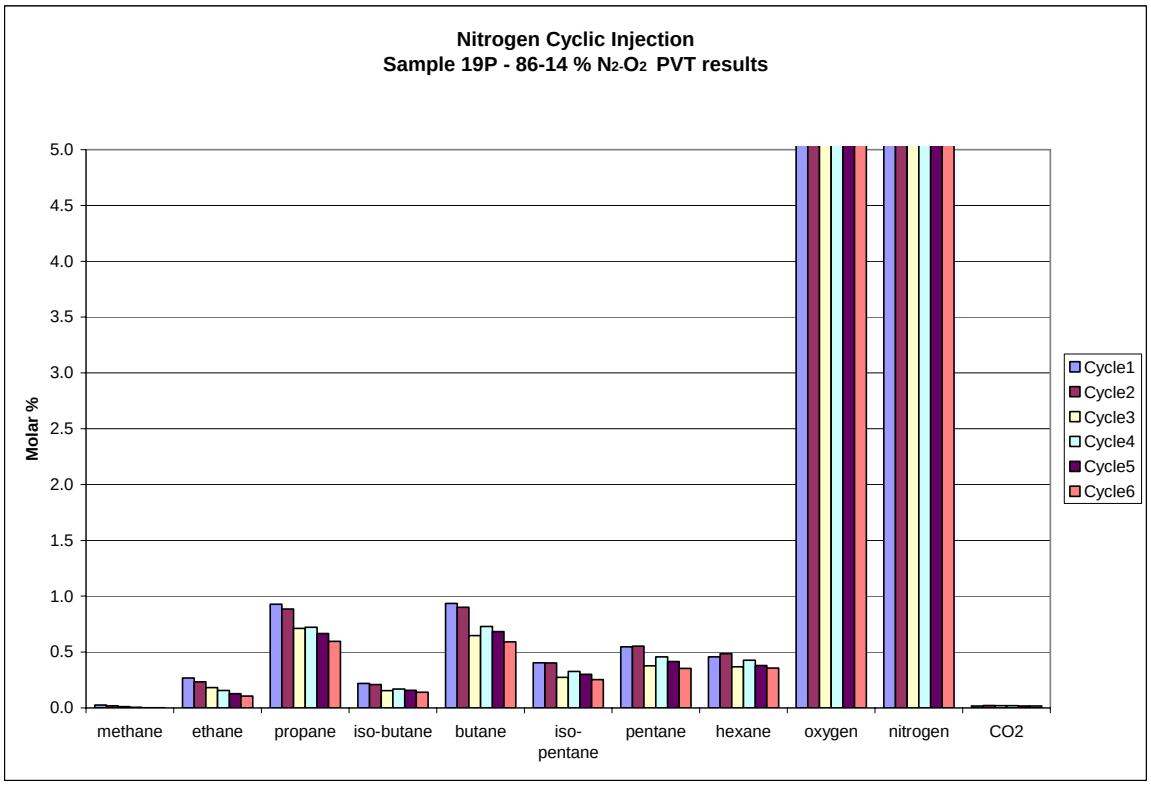

Figure **4.6**: G.C. results Sample 19P – 86-14 % N_2O_2

Table **4.4**: Sample 19P – 97-3 % N_2O_2 (post injection)

Component	Mol%	Wt%	LV%
Methane	0.0000	0.0000	0.0000
Ethane	0.0587	0.0154	0.0312
Propane	1.8697	0.7192	1.0223
Isobutane	0.6586	0.3339	0.4275
n-Butane	4.8849	2.4767	3.0560
Neopentane	0.0273	0.0172	0.0207
Isopentane	3.1034	1.9532	2.2540
n-Pentane	5.8983	3.7123	4.2390
2,2-Dimethylbutane	0.0500	0.0376	0.0414
2,3-Dimethylbutane	0.8388	0.6306	0.6820
2-Methylpentane	2.6150	1.9658	2.1532
3-Methylpentane	1.6975	1.2761	1.3743
n-Hexane	5.6683	4.2611	4.6239
Heptanes	22.6008	19.0347	18.7241
Octanes	11.6532	11.3596	11.2694
Nonanes	9.9459	10.6693	10.2760
Decanes plus	28.1286	41.4640	39.7389
Nitrogen	0.3013	0.0736	0.0655
Carbon Dioxide	0.0000	0.0000	0.0000
Total	100.0000	100.0000	100.0000
Global Properties		**Units**	
Avg Molecular Weight	114.6390	gm/mole	
Pseudocritical Pressure	401.71	psia	
Pseudocritical Temperature	550.84	degF	
Specific Gravity	0.72062	gm/ml	Light Comp
Liquid Density	6.0077	lb/gal	4.537 %
Liquid Density	252.33	lb/bbl	
Specific Gravity	2.8815	air=1	Inter. Comp.
SCF/bbl	837.91	SCF/bbl	55.65 %
SCF/gal	19.9503	SCF/gal	
MCF/gal	0.0200	MCF/gal	Heavy Comp
gal/MCF	50.157	gal/MCF	39.738 %
Net Heating Value	4402.5	BTU/SCF at 60°F	
Net Heating Value	14499.8	BTU/lb at 60°F	
Gross Heating Value	4764.4	BTU/SCF at 60°F	
Gross Heating Value	15616.8	BTU/lb at 60°F	
Gross Heating Value	92793.3	BTU/gal at 60°F	
API Gravity	64.9		

Table **4.5**: Sample 19P – 86-14 % N_2O_2 (post injection)

Component	Mol%	Wt%	LV%
Methane	0.0000	0.0000	0.0000
Ethane	0.0000	0.0000	0.0000
Propane	1.4614	0.5573	0.7939
Isobutane	0.5962	0.2997	0.3845
n-Butane	4.4831	2.2534	2.7865
Neopentane	0.0000	0.0000	0.0000
Isopentane	2.9454	1.8378	2.1255
n-Pentane	5.6814	3.5448	4.0568
2,2-Dimethylbutane	0.0523	0.0390	0.0430
2,3-Dimethylbutane	0.8568	0.6385	0.6921
2-Methylpentane	2.5504	1.9006	2.0864
3-Methylpentane	1.6442	1.2253	1.3225
n-Hexane	5.7745	4.3034	4.6802
Heptanes	23.1993	19.3753	19.1003
Octanes	12.0190	11.6116	11.5503
Nonanes	10.0413	10.6631	10.2797
Decanes plus	28.5371	41.7123	40.0654
Nitrogen	0.1579	0.0382	0.0341
Carbon Dioxide	0.0000	0.0000	0.0000
Total	100.0000	100.0000	100.0000
Global Properties		**Units**	
Avg Molecular Weight	115.6361	gm/mole	
Pseudocritical Pressure	399.36	psia	
Pseudocritical Temperature	556.36	degF	
Specific Gravity	0.72219	gm/ml	Light Comp
Liquid Density	6.0209	lb/gal	3.96 %
Liquid Density	252.88	lb/bbl	
Specific Gravity	2.9020	air=1	Inter. Comp.
SCF/bbl	832.49	SCF/bbl	55.936 %
SCF/gal	19.8212	SCF/gal	
MCF/gal	0.0198	MCF/gal	Heavy Comp
gal/MCF	50.480	gal/MCF	40.06 %
Net Heating Value	4407.7	BTU/SCF at 60°F	
Net Heating Value	14387.4	BTU/lb at 60°F	
Gross Heating Value	4768.3	BTU/SCF at 60°F	
Gross Heating Value	15494.1	BTU/lb at 60°F	
Gross Heating Value	92261.0	BTU/gal at 60°F	
API Gravity	64.4		

Table **4.6:** Physical properties after 6 injection cycles (PSU)

Sample 19P	100 % N2	97-3 N2-O2	86-14 N2-O2
initial viscosity	7.2 cp	7.2 cp	7.2 cp
final viscosity	7.8 cp	9.0 cp	8.3 cp
initial density	0.825 g/cc	0.825 g/cc	0.825 g/cc
final density	0.831 g/cc	0.834 g/cc	0.835 g/cc

4.3 Computer Model Data Analysis

The data obtained from the computer model were generated and compared with the data collected and analyzed from the PVT cell. Using the same initial composition shown in Table **4.2** and adding the required nitrogen-oxygen mixture, the new composition is then introduced to the computer model for phase splitting calculations. Once the pressure, temperature and overall composition are entered, the computer model generates new compositions of both the vapor and liquid phases along with their molar fractions and their physical properties. The result obtained from the liquid phase composition is then used to restart the splitting calculation for the next cycle with another batch of injection gas. The pressure and temperature used to simulate the laboratory data are kept constant at 150 psig and 70 °F. The amount of nitrogen injected is also kept constant. The initial results of the vapor composition were obtained using the initial interaction coefficients. These coefficients are then manipulated such that the results match as closely as possible those obtained from the laboratory model. The final coefficients are reported in Appendix A on Table A.4. A total of 8 cycles per injection mixture was used. This data can also be found in Appendix A and are contained in Tables A.1, A.2 and A.3

The results obtained from the model were then plotted. Figure **4.7** shows the composition of the vapor phase that result from the phase splitting calculations after injecting the crude oil with 100% N_2. Figure **4.8** shows the composition of the liquid phase after injection. For the 97-3%

N_2-O_2, Figures **4.9** and **4.10** were generated. Finally for the 86-14% N_2-O_2, Figures **4.11** and **4.12** were generated. In addition to these plots, shrinkage of mass as a function of the number of injection cycles were plotted for the 3 different injection mixtures. Figures **4.13, 4.14** and **4.15** contain these plots.

The most important observation was that the results obtained from the computer model have similar trends as those obtained from the laboratory analysis. These trends indicate a vaporization process which leaves the crude oil with less of its initial light components as the number of injection cycle increases. The number of cycles (8 for each gas mixture) did provide a good image of the change in composition as more nitrogen/oxygen is injected. The results obtained from Figures **4.7** to **4.12** also show that after 8 cycles a gradual decrease in vaporization is taking place. Hence the stripping effect seems to be diminishing. No significant changes have been observed when varying the composition of the injected nitrogen/oxygen mixture. This is also consistent with the data obtained from the PVT cell. It has also been found that the mass of the crude oil has decreased as a result of injection cycles. After 8 cycles, and for a given initial mass of oil, approximately 8.5% shrinkage on a mass basis was determined. This result is similar for all 3 injection mixtures with an insignificant difference among them. This shrinkage is important because it is consistent with observations obtained from the field and indicates that nitrogen injection causes vaporization and as a consequence shrinkage of reservoir fluid at the given conditions. It is also important because it allows further studies to focus on shrinkage in the crude oil caused by the nitrogen injection and to what extent the oxygen plays a role.

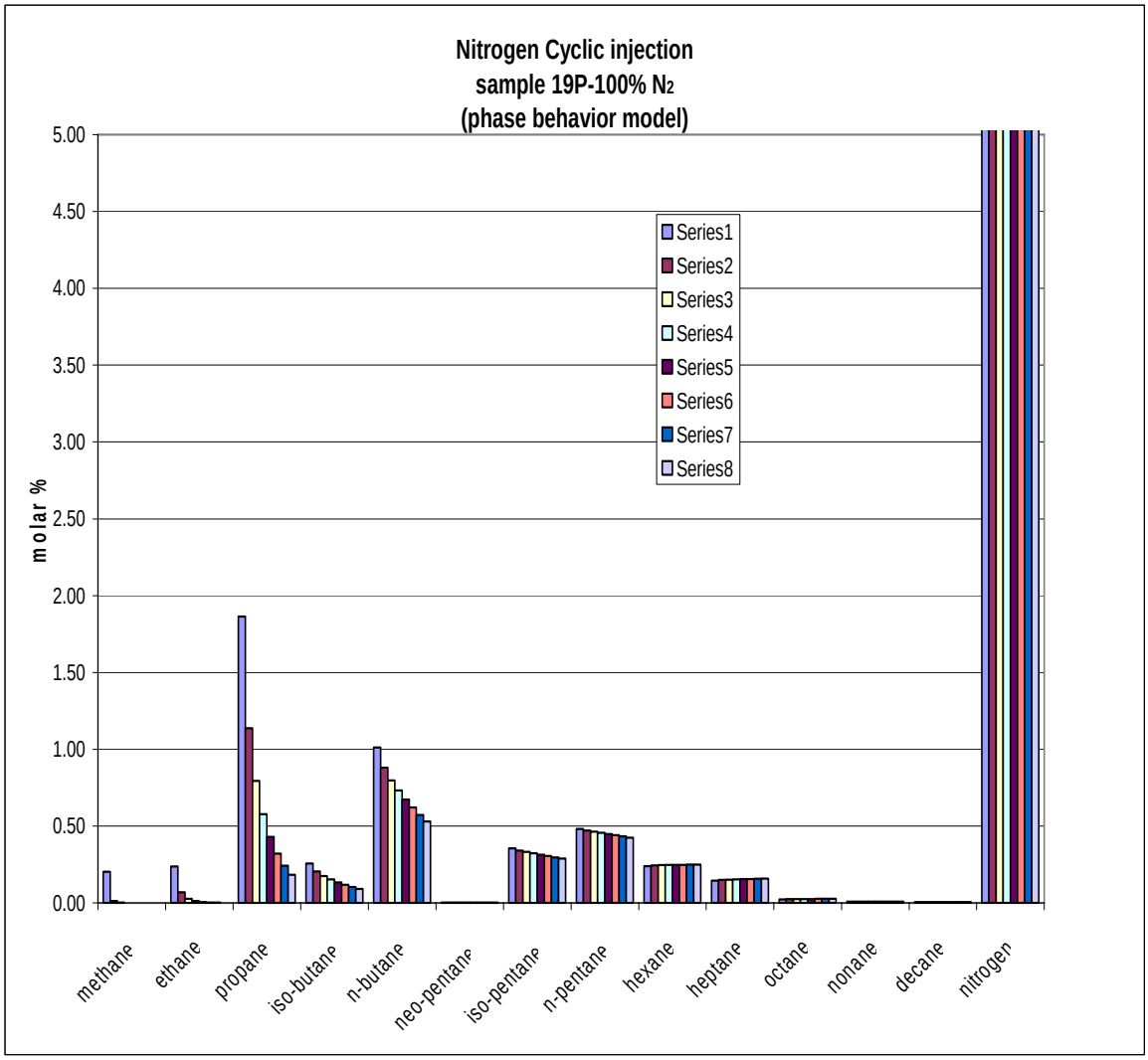

Figure **4.7**: Vapor Phase – Sample 19P – 100 % N_2

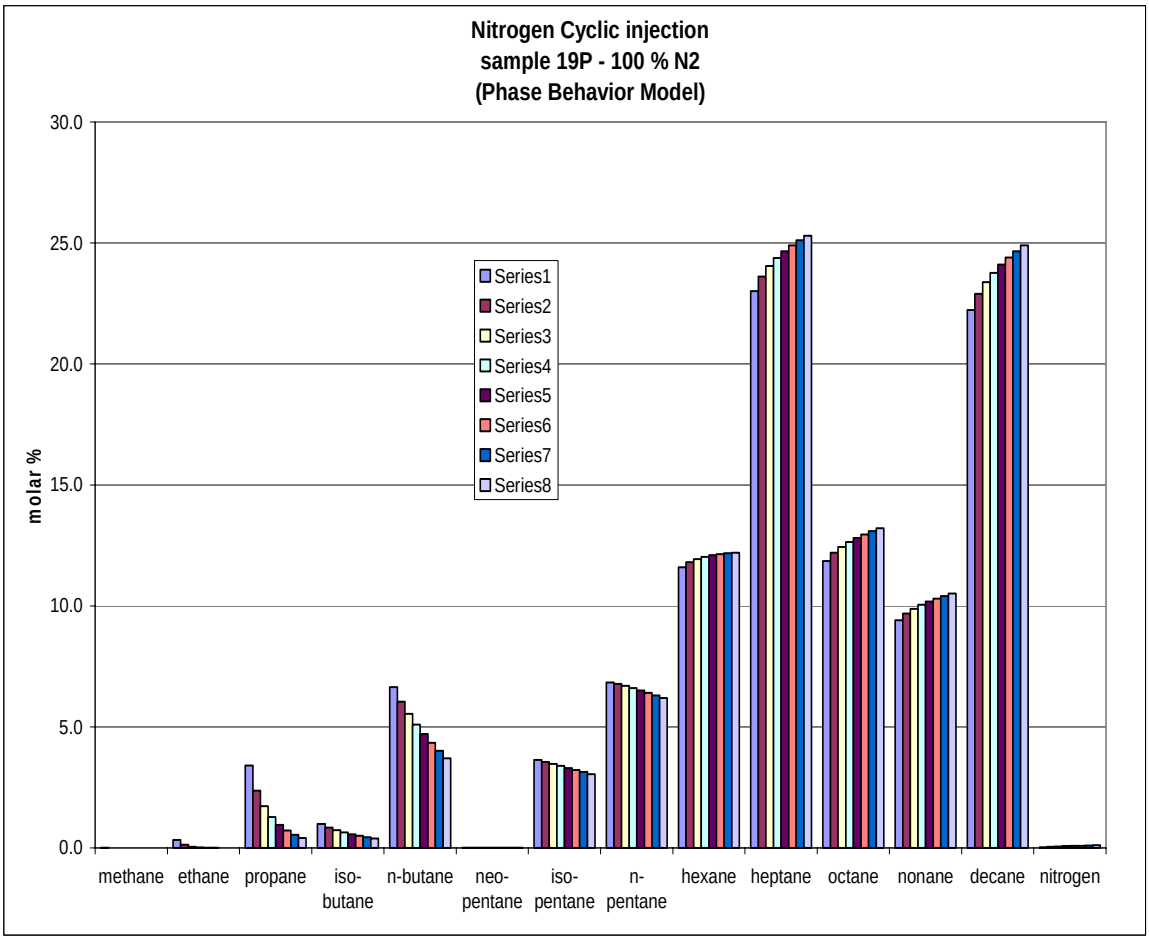

Figure **4.8**: Liquid Phase – Sample 19P – 100 % N_2

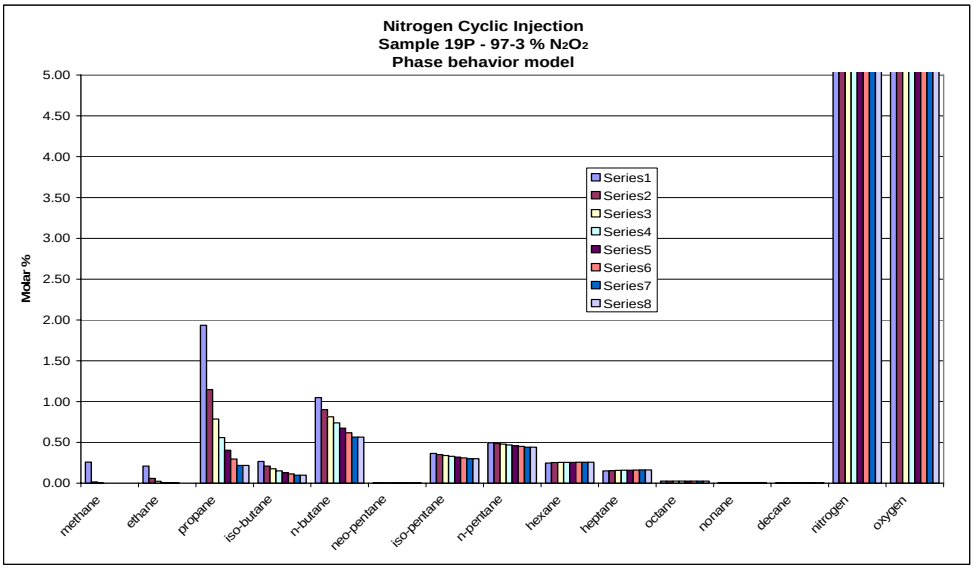

Figure **4.9** Vapor Phase – Sample 19P – 97-3% N_2O_2

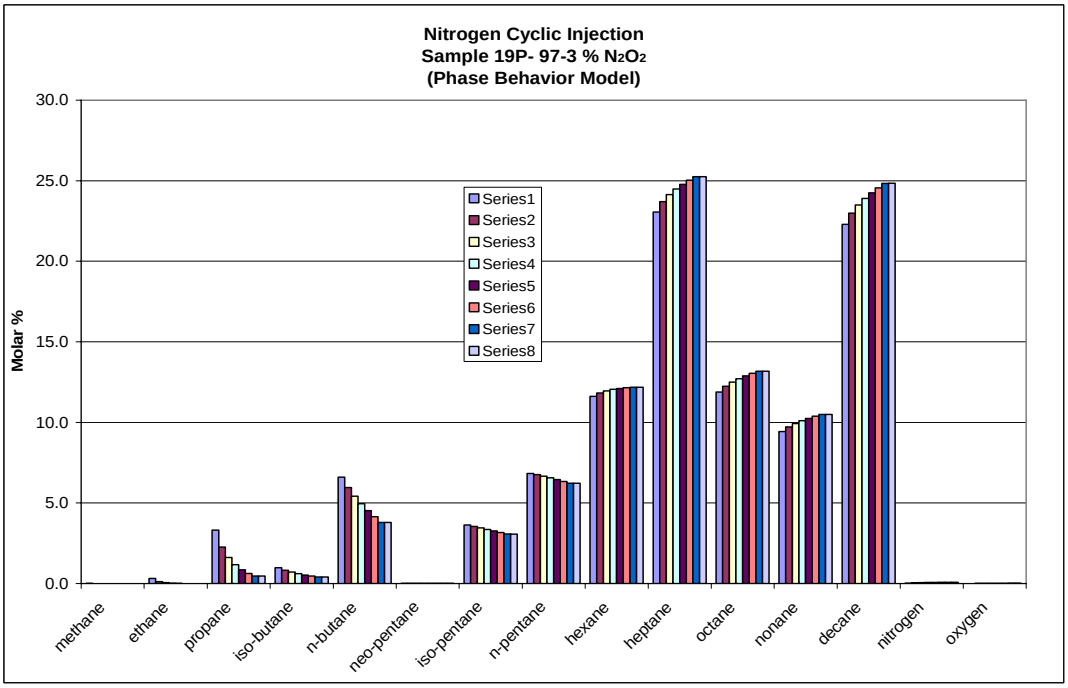

Figure **4.10**: Liquid Phase – Sample 19P- 97-3 % N_2O_2

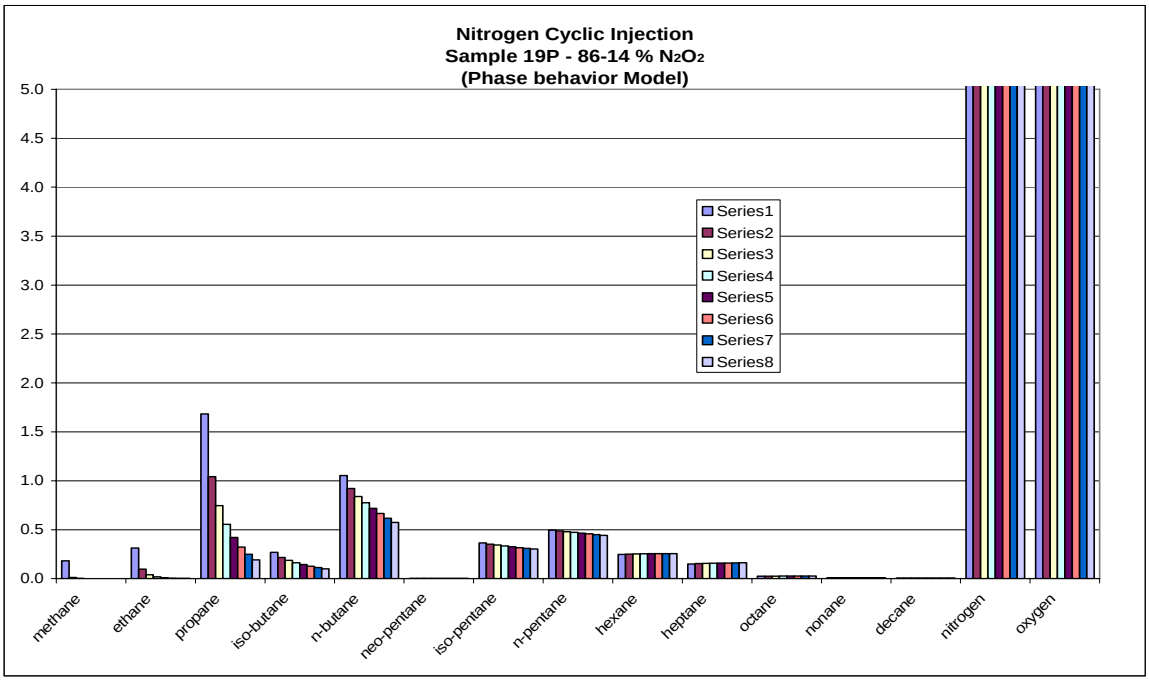

Figure **4.11**: Vapor Phase – Sample 19P – 86-14% N_2O_2

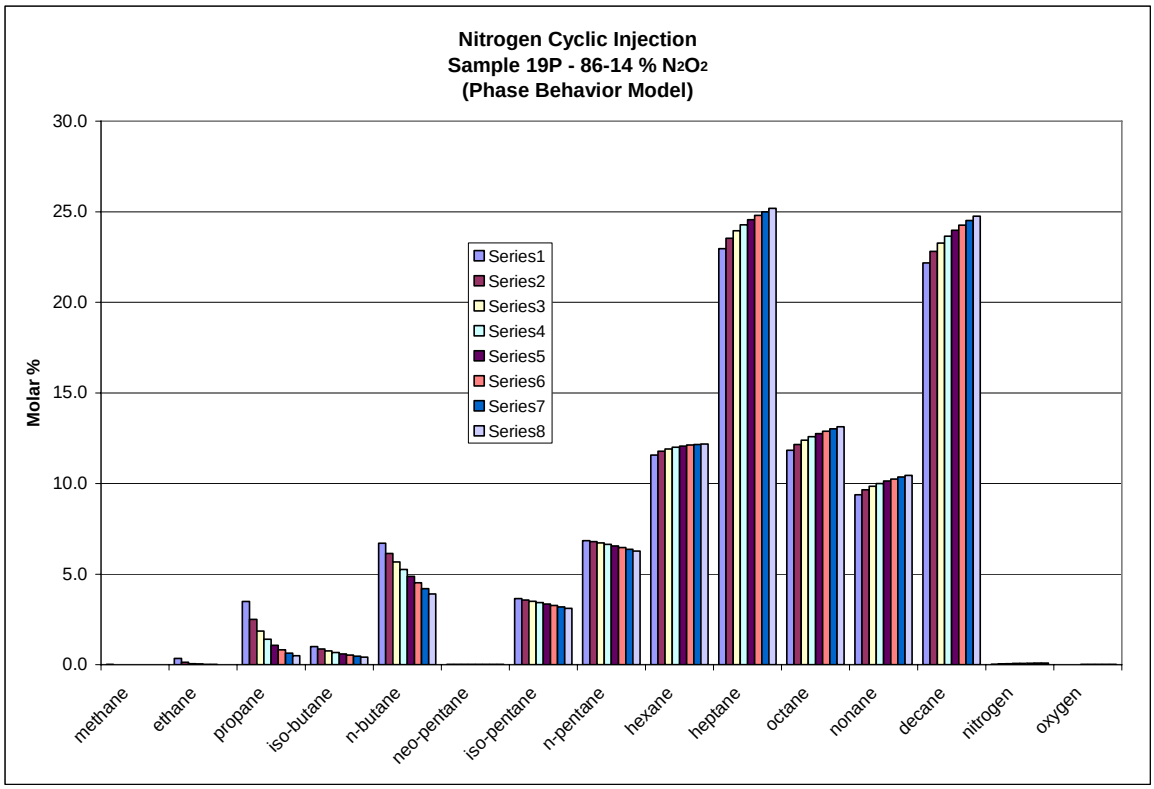

Figure **4.12**: Liquid Phase – Sample 19P – 86-14% N_2O_2

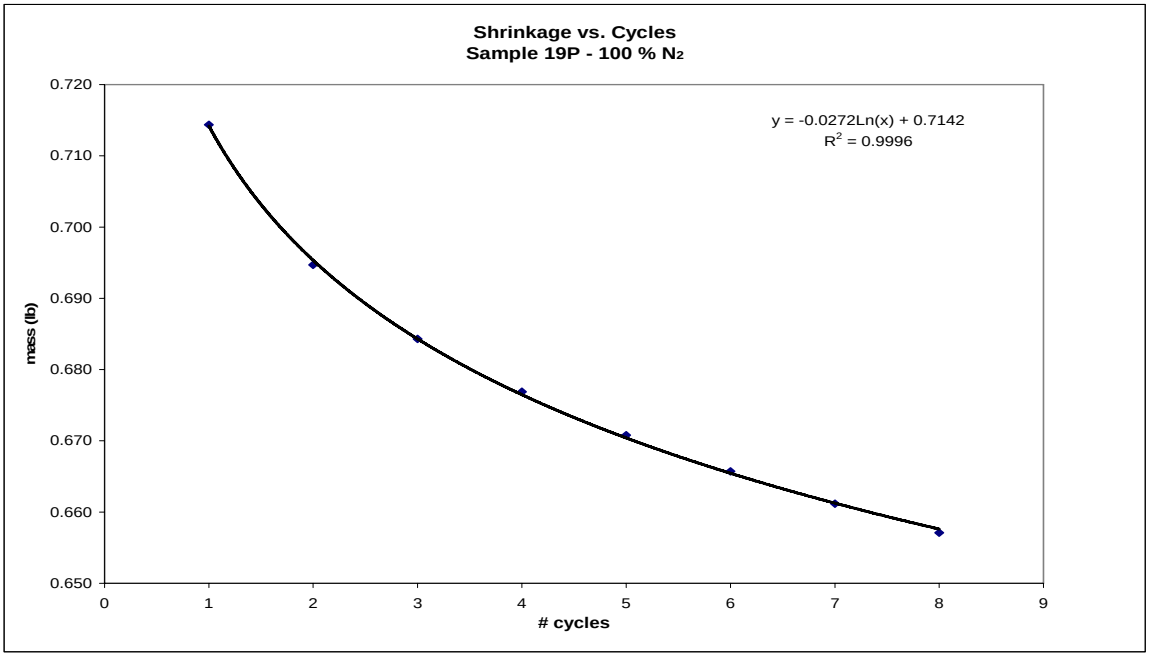

Figure **4.13**: Mass Shrinkage – Sample 19P – 100 % N_2

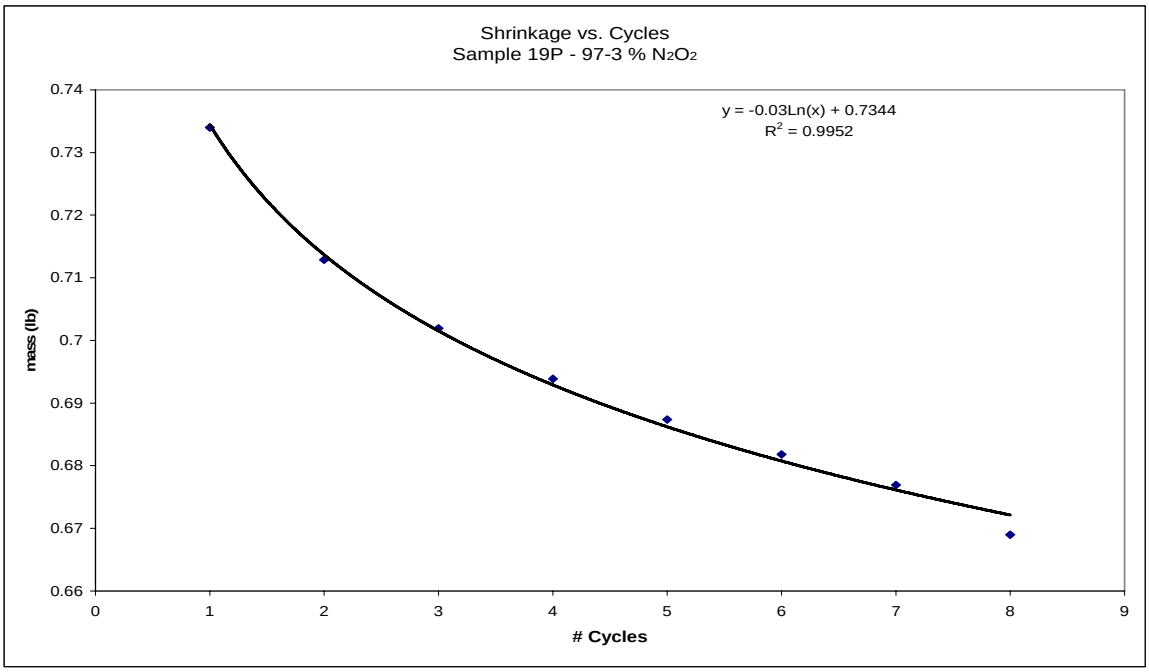

Figure **4.14**: Mass Shrinkage – Sample 19P – 97-3 % N_2O_2

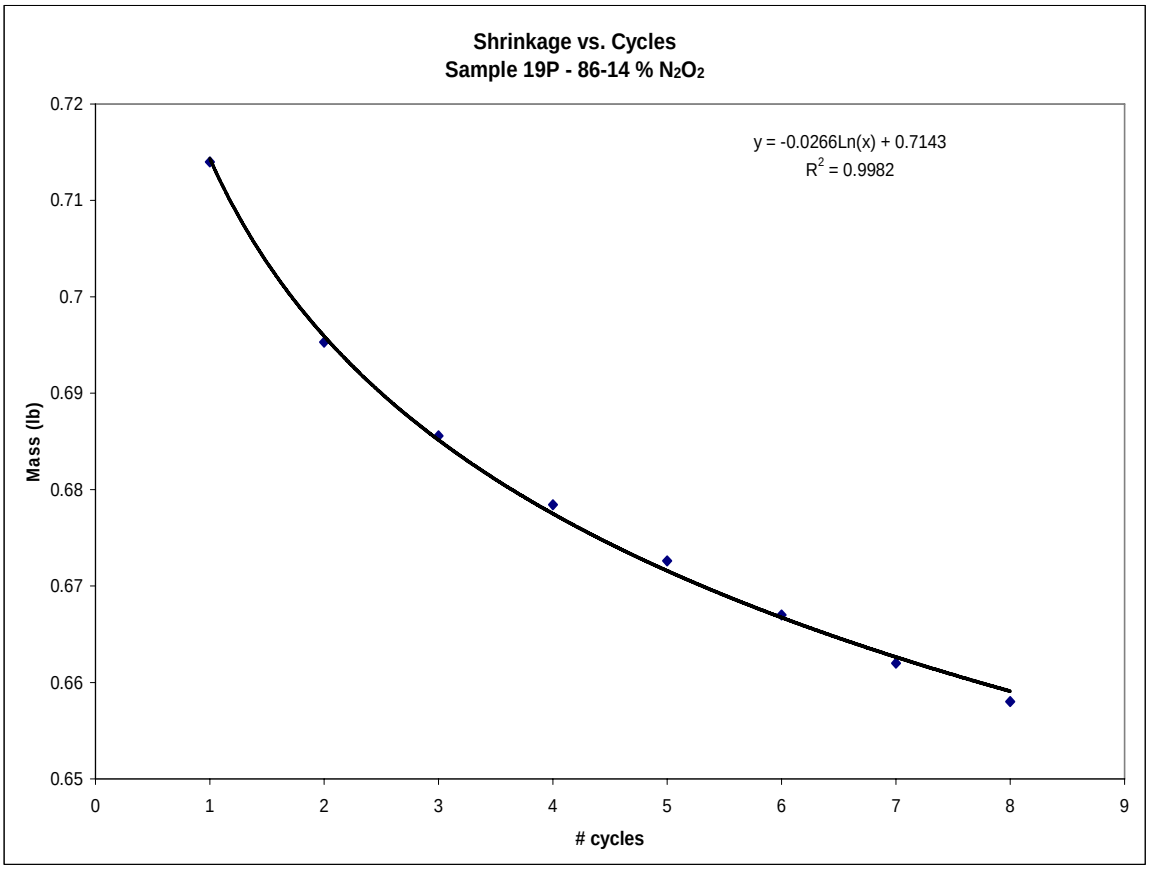

Figure **4.15**: Mass Shrinkage – Sample 19P – 86-14 % N_2O_2

CONCLUSION AND RECOMMENDATIONS

5.1 Summary and Conclusions

The objectives of Stage I and Stage II of this study are to investigate the effects of nitrogen cyclic injection on the composition of crude oil and the extent to which nitrogen is vaporizing the

crude oil and to optimize the project. In order to do so, a PVT cell was used to conduct laboratory experiments and a phase behavior package was developed to model the results obtained from the laboratory. Cyclic injection experiments were conducted using nitrogen-oxygen mixtures using mid continental crude oil. The mixture of injected gas and oil was permitted to reach equilibrium through the use of 24 hour soaking period before performing the next cycle. A total of 6 cycles were conducted for each experiment. The vapor phase withdrawn from the PVT cell was analyzed at the end of each cycle using a gas chromatograph (G.C.) unit. The liquid phase was sent out to Questar Applied Technology for analysis only at the beginning and end of the experimental runs. The same experiment was done numerically using a phase behavior model. The results obtained from the PVT experiment were then compared to the results obtained from the phase behavior computer model. The parameters of the computer model were manually tuned to match the laboratory data as closely as possible. A total of 8 cycles of gas injection were made using the computer model. Based on the results obtained from the experimental work and the phase behavior model, the following conclusions were made:

1. Analysis of gas samples collected from the PVT cell have shown that nitrogen huff and puff injection at low pressures and temperatures (150 psig, 70ºF) resulted in stripping of the lighter end hydrocarbons from the crude oil sample. The intermediate through heavy components by contrast remain in the liquid phase. These results are consistent with the fact that more volatile gases have higher vapor pressure, hence have less cohesive forces than heavier components.

2. After 6 injection cycles of nitrogen gas injection, the density and viscosity of the crude oil indicated an increasing trend. This trend also prevails when the crude oil is mixed with an injection of nitrogen/oxygen mixture. Hence, both nitrogen and nitrogen/oxygen injection have increased the viscosity and density of the crude oil.

3. Shrinkage of the crude oil was computed from the data obtained and was found to increase with additional cycles of gas injection. This shrinkage did not appear to be significantly different when oxygen was mixed with the injected nitrogen. Further

study will have to be conducted in order to better understand the effect of oxygen on the shrinkage of the crude oil.

4. Varying the composition of the injected gas (i.e. N_2-O_2 fraction) did not have a significant impact on the composition of the vapor resulting from the mass transfer of lighter hydrocarbons from the crude oil. This was evident from the data obtained both experimentally and from the computer model.

5. Results obtained with using a phase behavior model indicated the same trend in composition as seen using the PVT cell. After performing 8 injection cycles a gradual decrease in stripping effect was observed. In terms of vapor composition, results obtained from varying the composition of the injected gas were not different from those obtained with pure nitrogen injection.

6. Starting with a given mass of crude oil, and injecting a constant volume of nitrogen for each cycle, it was found using the model that after 8 injection cycles, the mass of crude oil shrank by approximately 8.5 % by mass. In this study, shrinkage was attributed to the vaporization of the lighter components of the crude oil.

In terms of optimizing the process, we were unable to accomplish this objective during the course of these projects. The operator of the field is sponsoring work with us that will undertake optimization studies of the process that employ artificial neural networks. In addition, a second study is underway that utilizes the concept of dynamic programming for optimization. It should be also pointed out that we have received numerous enquiries into expanding this work for other reservoir environments. These include the First and Second Venango sands in northwestern Pennsylvania.

5.2 Recommendations for Future Research

Based on the results that were obtained and the observations that were made during this investigation, the following recommendations for future research were made:

1. Testing the injection process at different pressures (particularly higher pressures) could further identify the role that increasing the pressure has on the miscibility and vaporization of the crude oil using nitrogen-oxygen mixtures.

2. Monitoring the soaking phase by varying the duration of the soaking time and analyzing its effect on the stripping process could help optimize the injection-soaking-production cycles. For the case of the field work, the current 30-day soaking phase has not been tested against different times. Also, the 24-hour soaking period for the experimental work was not optimized.

3. Expanding the test matrix to include more nitrogen/oxygen and even nitrogen/CO_2 mixtures could further improve our understanding of the role played by the oxygen coupled with nitrogen and/or CO_2 on vaporizing the lighter ends of the crude oil and impacting the density and viscosity of the remaining liquid.

4. Expanding the PVT runs to include more injection cycles could further determine the extent of the vaporization effect. It was found that 6 to 8 cycles would only give an indication of vaporization but not the full extent of vaporization.

5. Core flooding to test the mobility of the injected gas relative to the reservoir crude oil could improve our understanding of reservoir processes involved in displacement.

6. Finally, a compositional reservoir simulation incorporating the physical processes present would help in analyzing the reservoir and provide insight necessary for efficient operation and future design.

REFERENCES

There are no references for this report.

LIST OF ACRONYMS AND ABBREVIATIONS

A	Parameter of the Peng-Robinson equation of state
B	Parameter of the Peng-Robinson equation of state
$\mathbf{b_m}$	Parameter of the Peng-Robinson equation of state
$\mathbf{V_m}$	molar volume, ft^3/lbmol
P	Fluid pressure, psia
R	Gas constant**,** ft^3-psia/ lbmol -°R
T	Temperature, ºR
MW	Molecular Weight, lb/mol
$\mathbf{f_i}$	fugacity of component i
$\mathbf{X_i}$	liquid molar fraction
$\mathbf{Y_i}$	Vapor molar fraction
$\mathbf{K_v}$	Parameter for the Lee-Gonzalez-Eakin gas viscosity equation
$\mathbf{T_{pc}}$	Pseudo critical temperature, ºR
$\mathbf{P_{pc}}$	Pseudo critical pressure, psia
$\mathbf{K_i}$	Equilibrium constant
$\mathbf{K_{ij}}$	Interaction coefficient

Abbreviations

API	American Petroleum Institute
IOR	Improved Oil Recovery
FID	Flame Ionized Detector

TCD	Thermal Conductivity Detector
PVT	Pressure Volume Temperature
GC	Gas Chromatograph
MSCF	Thousand Standard Cubic Feet
MMSCF	Million Standard Cubic Feet
STB	Stock Tank Barrel
OOIP	Original Oil In Place
BOPD	Barrels of Oil Per Day
EOS	Equation of State
MIOR	Microbial Improved Oil Recovery
BBLS	Barrels
TIOR	Thermal Improved Oil Recovery

Greek

Σ	summation
μ	viscosity
ρ	density
ε	error
ω	Pitzer's acentric factor
ζ	Clark's correlation
Φ	fugacity
α	Molar fraction

Table **A.1**: Composition - Sample 19P – 100 % N_2

Sample 19P - 100 %N2 - Vapor Phase

	run1	run2	run3	run4	run5	run6	run7	run8
methane	0.20	0.01	0.00	0.00	0.00	0.00	0.00	0.00
ethane	0.24	0.07	0.03	0.01	0.01	0.00	0.00	0.00
propane	1.86	1.14	0.79	0.58	0.43	0.32	0.24	0.18
iso-butane	0.26	0.21	0.18	0.15	0.13	0.12	0.10	0.09
n-butane	1.01	0.88	0.80	0.73	0.67	0.62	0.57	0.53
neo-pentane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
iso-pentane	0.35	0.34	0.33	0.32	0.31	0.30	0.30	0.29
n-pentane	0.48	0.47	0.46	0.46	0.45	0.44	0.43	0.43
hexane	0.24	0.24	0.25	0.25	0.25	0.25	0.25	0.25
heptane	0.15	0.15	0.15	0.15	0.15	0.16	0.16	0.16
octane	0.02	0.02	0.03	0.03	0.03	0.03	0.03	0.03
nonane	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
decane	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.01
nitrogen	95.17	96.44	96.97	97.31	97.55	97.75	97.90	98.03

Sample 19P - 100 %N2 - Liquid Phase

	run1	run2	run3	run4	run5	run6	run7	run8
methane	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
ethane	0.33	0.13	0.05	0.02	0.01	0.01	0.00	0.00
propane	3.40	2.37	1.73	1.28	0.96	0.72	0.54	0.41
iso-butane	0.99	0.85	0.74	0.64	0.57	0.50	0.44	0.39
n-butane	6.65	6.04	5.54	5.10	4.71	4.34	4.01	3.71
neo-pentane	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
iso-pentane	3.64	3.56	3.48	3.39	3.31	3.22	3.14	3.06
n-pentane	6.84	6.77	6.70	6.61	6.51	6.41	6.30	6.19
hexane	11.59	11.81	11.94	12.03	12.10	12.14	12.18	12.20
heptane	23.01	23.62	24.04	24.38	24.66	24.90	25.11	25.30
octane	11.86	12.20	12.44	12.64	12.81	12.96	13.09	13.21
nonane	9.41	9.68	9.88	10.05	10.18	10.31	10.42	10.52
decane	22.23	22.90	23.38	23.77	24.10	24.40	24.66	24.90
nitrogen	0.03	0.05	0.06	0.08	0.09	0.09	0.10	0.11

Table **A.2**: Composition - Sample 19P – 97-3 % N_2O_2

Sample 19P - 97-3 %N2O2 - Vapor Phase								
Compositon	**run1**	**run2**	**run3**	**run4**	**run5**	**run6**	**run7**	**run8**
methane	0.26	0.02	0.00	0.00	0.00	0.00	0.00	0.00
ethane	0.21	0.06	0.02	0.01	0.00	0.00	0.00	0.00
propane	1.93	1.15	0.79	0.56	0.40	0.30	0.22	0.22
iso-butane	0.27	0.21	0.18	0.15	0.13	0.11	0.10	0.10
n-butane	1.05	0.90	0.81	0.74	0.67	0.62	0.57	0.57
neo-pentane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
iso-pentane	0.37	0.35	0.34	0.33	0.32	0.31	0.30	0.30
n-pentane	0.50	0.49	0.48	0.47	0.46	0.45	0.44	0.44
hexane	0.25	0.25	0.25	0.26	0.26	0.26	0.26	0.26
heptane	0.15	0.15	0.16	0.16	0.16	0.16	0.16	0.16
octane	0.02	0.03	0.03	0.03	0.03	0.03	0.03	0.03
nonane	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
decane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
nitrogen	72.32	72.77	73.11	73.33	73.49	73.60	73.69	73.70
oxygen	22.66	23.61	23.82	23.95	24.06	24.15	24.22	24.21

Sample 19P - 97-3 %N2O2 - Liquid Phase								
Compositon	**run1**	**run2**	**run3**	**run4**	**run5**	**run6**	**run7**	**run8**
methane	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
ethane	0.32	0.12	0.05	0.02	0.01	0.00	0.00	0.00
propane	3.32	2.27	1.61	1.17	0.85	0.63	0.46	0.46
iso-butane	0.98	0.83	0.71	0.61	0.53	0.46	0.40	0.40
n-butane	6.59	5.96	5.42	4.95	4.53	4.15	3.80	3.79
neo-pentane	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
iso-pentane	3.63	3.54	3.45	3.35	3.26	3.17	3.07	3.07
n-pentane	6.83	6.76	6.67	6.56	6.45	6.34	6.22	6.22
hexane	11.61	11.83	11.96	12.05	12.11	12.15	12.18	12.18
heptane	23.07	23.69	24.14	24.49	24.78	25.03	25.25	25.25
octane	11.89	12.24	12.50	12.71	12.89	13.04	13.18	13.18
nonane	9.43	9.72	9.93	10.10	10.25	10.38	10.49	10.49
decane	22.29	22.98	23.49	23.90	24.25	24.56	24.84	24.84
nitrogen	0.02	0.04	0.05	0.06	0.07	0.08	0.08	0.08
oxygen	0.00	0.01	0.01	0.01	0.01	0.02	0.02	0.02

Table **A.3**: Composition - Sample 19P – 86-14 % N_2O_2

Sample 19P - 86-14 %N2O2 - Vapor Phase

Comp	run1	run2	run3	run4	run5	run6	run7	run8
methane	0.18	0.01	0.00	0.00	0.00	0.00	0.00	0.00
ethane	0.31	0.10	0.04	0.02	0.01	0.00	0.00	0.00
propane	1.68	1.04	0.75	0.56	0.42	0.32	0.25	0.19
iso-butane	0.27	0.22	0.19	0.16	0.14	0.13	0.11	0.10
n-butane	1.05	0.92	0.84	0.78	0.72	0.67	0.62	0.58
neo-pentane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
iso-pentane	0.37	0.35	0.34	0.33	0.33	0.32	0.31	0.30
n-pentane	0.50	0.49	0.48	0.47	0.47	0.46	0.45	0.44
hexane	0.25	0.25	0.25	0.25	0.26	0.26	0.26	0.26
heptane	0.15	0.15	0.16	0.16	0.16	0.16	0.16	0.16
octane	0.02	0.03	0.03	0.03	0.03	0.03	0.03	0.03
nonane	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
decane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01
nitrogen	81.35	81.74	82.09	82.37	82.61	82.80	82.97	83.10
oxygen	13.85	14.69	14.82	14.85	14.86	14.84	14.83	14.82

Sample 19P - 86-14 %N2O2 - Liquid Phase

Comp	run1	run2	run3	run4	run5	run6	run7	run8
methane	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
ethane	0.34	0.14	0.06	0.03	0.01	0.01	0.00	0.00
propane	3.49	2.50	1.86	1.40	1.07	0.82	0.64	0.49
iso-butane	1.00	0.87	0.76	0.67	0.59	0.53	0.47	0.42
n-butane	6.70	6.14	5.67	5.25	4.87	4.52	4.20	3.90
neo-pentane	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
iso-pentane	3.64	3.57	3.50	3.42	3.34	3.27	3.19	3.11
n-pentane	6.84	6.79	6.72	6.64	6.55	6.46	6.37	6.27
hexane	11.58	11.78	11.91	12.00	12.07	12.12	12.16	12.18
heptane	22.96	23.54	23.95	24.28	24.55	24.79	25.00	25.18
octane	11.83	12.15	12.39	12.58	12.75	12.89	13.02	13.13
nonane	9.39	9.65	9.84	10.00	10.13	10.25	10.36	10.45
decane	22.18	22.81	23.27	23.64	23.97	24.25	24.51	24.74
nitrogen	0.02	0.04	0.05	0.06	0.07	0.08	0.08	0.09
oxygen	0.00	0.00	0.00	0.01	0.01	0.01	0.01	0.01

Table **A.4**: Tuned PR- Interaction Coefficients

	Methane	Ethane	Propane	Iso-butane	butane	neo-pent	iso-pent	pent	hexane	heptane	octane	nonane	decane	nitrogen
methane	0	0.005	0.01	0.015	0.015	0.018	0.018	0.018	0.019	0.02	0.025	0.03	0.035	70.018
ethane	0.005	0	0.002	0.003	0.003	0.005	0.005	0.005	0.007	0.01	0.015	0.017	0.021	40.039
propane	0.01	0.002	0	0.001	0.001	0.002	0.002	0.002	0.004	0.005	0.007	0.009	0.011	10.046
iso-butane	0.015	0.003	0.001	0	0.001	0.009	0.008	0.008	0.01	0.012	0.015	0.017	0.02	5.047
n-butane	0.015	0.003	0.001	0.001	0	0.001	0.001	0.001	0.003	0.005	0.007	0.009	0.011	5.047
neo-pentane	0.018	0.005	0.002	0.008	0.001	0	0.001	0.001	0.005	0.002	0.003	0.005	0.007	0.048
iso-pentane	0.018	0.005	0.002	0.008	0.001	0.001	0	0.001	0.003	0.005	0.007	0.009	0.011	0.048
n-pentane	0.018	0.005	0.002	0.008	0.001	0.001	0.001	0	0.002	0.003	0.005	0.007	0.009	0.048
hexane	0.019	0.007	0.004	0.009	0.003	0.005	0.003	0.002	0	0.003	0.005	0.005	0.008	0.05
heptane	0.02	0.01	0.005	0.01	0.005	0.002	0.005	0.003	0.003	0	0.005	0.006	0.007	0.055
octane	0.025	0.015	0.007	0.012	0.007	0.003	0.007	0.005	0.005	0.005	0	0.005	0.007	0.06
nonane	0.03	0.017	0.009	0.015	0.009	0.005	0.009	0.007	0.005	0.06	0.005	0	0.007	0.065
decane	0.035	0.021	0.011	0.017	0.011	0.007	0.011	0.009	0.008	0.07	0.007	0.007	0	0.07
nitrogen	70.018	40.039	10.046	5.047	5.047	0.048	0.048	0.048	0.05	0.055	0.06	0.065	0.07	0