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Quality controlled oil reservoirs PVT data

Master thesis by

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Abstract

This thesis focuses on the testing of the quality of the recovered oil samples and the PVT measurements performed in the lab. Firstly, a literature review of the sampling procedures is made, highlighting the problems, advantages, disadvantages and types of fluid that can be sampled each time. Then a quality testing for the samples is accomplished in order to judge the representativity of the oil sample by taking into account the reported sampling conditions and, if separator samples are used, the compatibility of the recombined gas and oil. The best samples undergo PVT tests in order to determine basic thermodynamic properties and composition. Confidence on the validity of the PVT report data is of upmost importance since it is applied to practically all reservoir or production engineering applications. So, a review of the quality check of the PVT experiments is accomplished by utilizing a mass balance method and other thermodynamic graphical techniques. Several tools are employed in Excel for testing the consistency of the reported phase behavior data of PVT study. Oil samples from Tunisia, Congo and unknown locations (fluid 9 and fluid X) are examined for their quality PVT report. It is concluded that the PVT properties of the given PVT analysis report are in most cases and tests well specified.

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List of symbols

<u>Symbol</u>	<u>Meaning</u>	<u>Units</u>
$A_1, A_o, a_o, a_1, a,$ $b, C_1, C_2, C_3, C_4,$ $C_5, M, P_f, M_o,$ A, B, C	Constants	
$^{\circ}API$	API gravity	$^{\circ}API$
B_g	Gas formation volume factor	ft^3/scf
B_o	Formation volume factor (FVF)	$bbbl/STB$
B_{ob}	FVF at bubble point	$bbbl/STB$
B_{od}	FVF from DLE	$bbbl/residual\ bbl$
B_{odb}	FVF from DLE at the bubble point pressure	$bbbl/residual\ bbl$
C_o	Isothermal oil compressibility	psi^{-1}
C_T	Isothermal compressibility	psi^{-1}
F	Moles of reservoir oil enter the flash separation	mole
F_g	Mole fraction of wellstream	
F_{gsp}	Mole fraction of wellstream that is gas in the primary separator	
F_i	Hoffman factor for the i component	
GOR	Gas to oil ratio	
K_i	Equilibrium ratios, K values	
K_w	Watson characterization factor	$^{\circ}R^{1/3}$
L	Moles of liquid phase from flash separation	mole
MMP	Minimum miscibility pressure	psia
$M_{C_{7+}}$	Molecular weight of the C_{7+}	$lbm/lbmol$
$M_{\bar{o}}$	Stock tank oil molecular weight	$lbm/lbmol$
M_{osp}	Separator oil molecular weight	$lbm/lbmol$
n	Mole	mole
P	Pressure	psia
P_b	Bubble point pressure	psia
P_{c_i}	Critical pressure for the i component	psia
P_{conv}	Convergence pressure	psia
P_i	Initial pressure	psia
P_r	Pseudoreduced pressure	
P_{sc}	Pressure at standard conditions	psia
P_{sp}	Separator pressure	psia
P_{wf}	Flowing bottom hole pressure	psia
R	Universal gas constant	$10.73 \frac{psia \cdot ft^3}{Rankine \cdot lbmol}$
R_s	Solution GOR	scf/STB
R_{sb}	Solution GOR from multistage separator	scf/STB

R_{sd}	Solution gas-oil ratio from DLE	scf/residual bbl
R_{sdb}	Solution gas-oil ratio from DLE at bubble point	scf/residual bbl
$R_{sp_{Lab}}$	Corrected separator gas oil ratio at laboratory condition	scf/STB
$R_{sp_{field}}$	Separator gas oil ratio based on rates calculated in the field	scf/STB
T	Temperature	°R
T_{bi}	Normal boiling temperature for the i component	°R
T_{ci}	Critical temperature for the i component	°R
T_r	Pseudoreduced temperature	
T_{sc}	Temperature at standard condition	°R
T_{sp}	Separator temperature	°R
V	Moles of vapor phase from flash separation	mole
V_b	Bubble-point volume	scf
V_{cell}	Original cell volume at saturation pressure in a PVT experiment	ft ³
V_o	Reservoir oil volume	scf
$V_{\bar{o}}$	Produced oil surface volume	STB
V_{ob}	Oil volume at bubble point	ft ³
$V_{\bar{o}r}$	Residual oil volume at reservoir temperature from DLE	residual bbl
$V_{o_{sc}}$	Volume of oil at saturation point measured at standard conditions	STB
V_p	Two phase volume at pressure P	scf
$V_{\bar{g}}$	Produced gas surface volume	scf
$V_{g_{sc}}$	Volume of gas at saturation point measured at standard conditions	scf
$w_{\bar{g}i}$	Weight fraction of surface sample of component i at gaseous phase	
$w_{\bar{o}i}$	Weight fraction of surface sample of component i at liquid phase	
x_i	Mole fraction of component i at liquid phase	
$x_{\bar{o}}$	Surface compositions of liquid phase at CVD	
Y	Y function	
$y_{\bar{g}}$	Surface composition of gas phase at CVD	
y_i	Mole fraction of component i at gaseous phase	
Z	Gas factor	
$Z_{g_{Lab}}$	Laboratory (true) separator gas Z-factor determined in the laboratory at conditions during gas metering	
$Z_{g_{field}}$	Separator gas Z-factor used in field calculation of gas rate	
z_i	Reservoir oil composition	

<u><i>Greek symbol</i></u>	<u><i>Meaning</i></u>	<u><i>Units</i></u>
γ	Specific gravity relative to water	
γ_g	Specific gravity of the gas	
$\gamma_{g_{Lab}}$	Separator gas gravity based on measured composition or direct measurement	
$\gamma_{g_{field}}$	Separator gas gravity used in field calculations of gas rate	
$\gamma_{\bar{o}}$	Specific gravity of the surface oil	
Δn_g	Moles of gas removed at CVD	mole
$\Delta \rho_{\rho}$	Compressibility correction	lbm/ft ³
$\Delta \rho_{\tau}$	Thermal expansion correction	lbm/ft ³
μ_{ob}	Viscosity at the bubble point	cp
μ_{od}	Dead oil viscosity	cp
μ_o	Undersaturated viscosity	cp
$\rho_{C_{7+}}$	Density of the C ₇₊	lbm/ft ³
$\rho_{\bar{g}}$	Surface gas density	lbm/ft ³
$\rho_{\bar{o}}$	Stock tank oil density	lbm/ft ³
ρ_{osp}	Separator oil density at separator conditions	lbm/ft ³
ρ_o	Crude oil density	lbm/ft ³

1. Introduction

Reservoir fluids are generally classified into five different fluid types: black oil, volatile oil, gas condensate, wet gas, and dry gas (American Petroleum Institute, 2003). Only the black and volatile oils are relevant to this thesis, so the analysis will be based on them.

Black oils are sometimes referred to as ordinary oils and are the most common type of oil reservoirs (Danesh, 1998). They are generally composed of more than 20% C_{7+} , indicating a large quantity of heavy hydrocarbon components. Therefore, their phase envelopes are the widest of all types of reservoir fluids, as can be confirmed by the following figure.

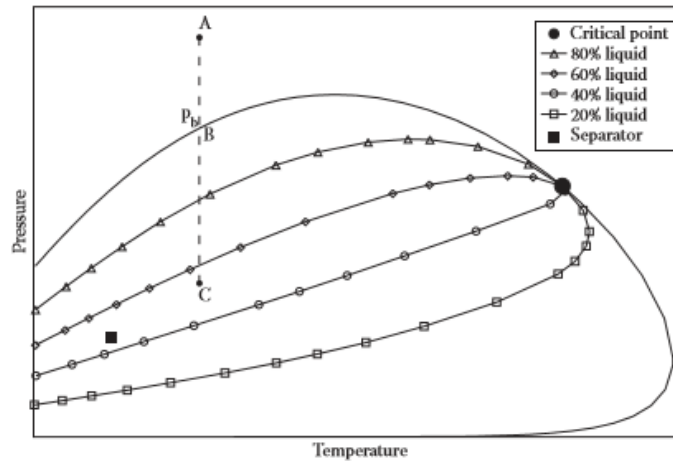


Figure 1.1: Phase envelope of a black oil.

The curves within the phase envelope are called quality lines and they merge at the critical point. They represent constant liquid volume, measured as percentage of total volume. The bubble-point curve and the dew-point curve can also be considered as 100% and 0% liquid volume. The vertical line ABC represents the pressure reduction in the reservoir at reservoir temperature. Reservoir pressures anywhere along line AB indicate that the oil is a single-phase liquid or is undersaturated, meaning that the oil is capable of dissolving more gas if present. As soon as the reservoir pressure reaches point B, the oil is at its bubble-point pressure and is said to be saturated. A continued reduction in the pressure anywhere along line BC results in the release of more gas to form a free gas phase in the reservoir. At each pressure below the bubble-point pressure, the volume of gas, on a percentage basis, equals 100% minus the percentage of liquid. *Figure 1.1* indicates that separator conditions are within the phase envelope in the two-phase region and a large amount of liquid arrives at the surface.

The phase envelope of a volatile oil is shown at *Figure 1.2*. The reservoir temperature is near the critical temperature, hence, volatile oils are referred to as near-critical oils. The iso-volume lines are tighter and closer near the bubble point curve, so, a small reduction of pressure below the bubble point vaporizes a significant fraction of the oil.

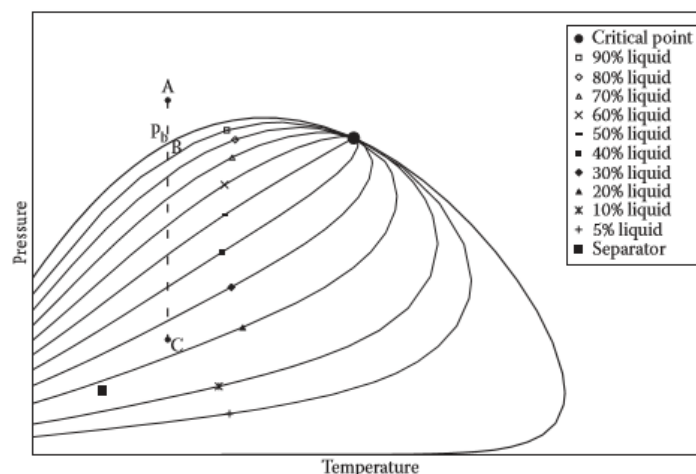


Figure 1.2: Phase envelope of a volatile oil.

Parameters for the classification of the reservoir fluids are presented at *Table 1.1* and *Figure 1.3*.

Table 1.1: Classification of petroleum reservoir fluids (Dandekar, 2013).

Reservoir fluid	Field data				Laboratory analysis		
	Initial producing GOR (scf/STB)	Initial API gravity of fluid	Color of stock tank liquid	Mol % of C ₇₊	Phase change in reservoir	Formation volume factor (res. bbl / STB)	Reservoir temperature
Black oil	250 – 1,750	<45.0	Dark	>20.0	Bubble point	< 2.0	< T _c
Volatile oil	1,750 – 3,200	>40.0	Colored	12.5 – 20.0	Bubble point	>2.0	< T _c
Gas condensate	>3,200	40.0-60.0	Lightly colored	<12.5	Dew point	-	> T _c
Wet gas	>50,000	Up to 70.0	Water white	trace amounts	No phase change	-	>Cricon dentherm
Dry gas	-	-	-		No phase change	-	>Cricon dentherm

Characteristic	Oils			Gases	
	Heavy Oils and Tars	Black Oils	Volatile Oils	Gas Condensates	Wet and Dry Gases
Initial fluid molecular weight	210+	70 to 210	40 to 70	23 to 40	<23
Stock-tank-oil color	black	brown to light green	greenish to orange	orange to clear	clear
Stock-tank oil-gravity, °API	5 to 15	15 to 45	42 to 55	45 to 60	45+
C ₇ -plus fraction, mol%	>50	35 to 50	10 to 30	1 to 6	0 to 1
Initial dissolved GOR, scf/STB	0 to 200	200 to 900	900 to 3,500	3,500 to 30,000	30,000+
Initial FVF, B_{oi} , RB/STB	1.0 to 1.1	1.1 to 1.5	1.5 to 3.0	3.0 to 20.0	20.0+
Typical reservoir temperature, °F	90 to 200	100 to 200	150 to 300	150 to 300	150 to 300
Typical saturation pressure, psia	0 to 500	300 to 5,000	3,000 to 7,500	1,500 to 9,000	—
Volatile-oil/gas ratio, STB/MMscf*	0	0 to 10	10 to 200	50 to 300	0 to 50
Maximum vol% liquid during CCE**	100	100	100	0 to 45	0
OOIP, STB/acre-ft (bulk)	1,130 to 1,240	850 to 1,130	400 to 850	60 to 400	0 to 60
OGIP, Mscf/acre-ft (bulk)	0 to 200	200 to 700	300 to 1,000	500 to 2,000	1,000 to 2,200

*At bubblepoint pressure. **Constant composition expansion of reservoir fluid.

Figure 1.3: Characterization of petroleum fluids (Petrowiki, 2015).

Reservoir fluids found in gas and oil fields around the world vary greatly in composition. In practice four types of fluid systems have been found in a given geological formation (Whitson, 1998):

- Undersaturated system with uniform composition
- Saturated system with uniform composition
- Undersaturated system with compositional gradient
- Saturated system with compositional gradient

Each fluid type has an impact at the decisions that concern field development plan and reservoir management. Some issues are the fluid sampling, design of surface facilities, prediction of hydrocarbon reserves and strategy for production.

This dissertation outlines the sampling procedure, the quality control of the samples, PVT analysis, as well as quality control of the PVT data report. In more details:

The *2nd chapter* reviews the sampling procedures. The sampling can be either surface or subsurface and the procedure of each one is explained. Also, the advantages and disadvantages are highlighted as well as the type of reservoir fluid that can be sampled each time. Whatever the case is, the main objective is to obtain a representative sample.

Chapter 3 summarizes the quality testing that the samples undergo in order to qualify their representativity to the reservoir fluid. The analysis of (bottom hole or separator) samples can be either at the wellsite or at the laboratory. At the end of the chapter the most widely utilized empirical correlations are presented.

In *chapter 4* the most significant PVT tests are described for their procedure and output parameters. The available techniques for compositional analysis are explained, as well as other less traditional tests. After the PVT analysis, the identification of fluid type can be confirmed, by studying the phase behavior of reservoir fluids (Dandekar, 2013).

The *5th chapter* proposes a quality testing procedure for the PVT report data in order to ensure validity. The process is based on mass balance, thermodynamic equilibrium and plots. Finally, an Equation of State PVT model can be built based on well established properties.

The application of the previously described quality control tests on reservoir oil PVT reports is described in *chapter 6*. Five oil samples are evaluated for their quality based on Excel environment.

The last chapter (*chapter 7*) presents the conclusions of this study and recommendations for future work.

2. Sampling procedures

The main objective of a successful sampling campaign is to obtain representative samples with adequate volume and determine PVT properties. Then, if it is required, it may be executed geochemical analysis for fluid source identification and reservoir continuity, as well as crude assay for refinery process (Speight, 2001; Speight, 2002; American Petroleum Institute, 2003).

Fluid samples provide useful information for the planning while special treatments may be required for the production (waxing tendency, asphaltene content, removal of hydrogen sulfide, etc) (Schlumberger, 2005):

- Sampling as an exploration tool: It reveals quantity of hydrocarbon that is present within the structure, reservoir compartmentalization, fluid contacts, hydrocarbon compositional gradient, fluid properties and composition. It forecasts recovery and predicts problems that may be encountered, downstream.
- Sampling during production: Optimize performance.

The rocks which contain reservoir fluids vary considerably in composition and in physical and flow properties (Speight, 2009). In certain cases, this can serve to complicate the sampling procedure. The most important considerations in designing a sampling procedure are (Lang and Donohue, 1985; American Petroleum Institute, 2003; American Petroleum Institute, 1966):

- Type of reservoir fluid (oil / gas, saturated / unsaturated, black oil / volatile oil / gas-condensate / wet-gas / dry-gas, single phase / multiphase)
- Well location: The composition and the physical properties of the reservoir fluid can vary significantly over the area of the reservoir
- Volume of sample required
- Design of well completion and surface (separation equipment)
- Cost
- Producing characteristics

The techniques used to collect reservoir fluids, depending on the location of sampling, are:

- **Subsurface Sampling** (*Chapter 2.1*)
 - ✓ Open hole (RFT / MDT)
 - ✓ Cased hole
- **Surface Sampling** (*Chapter 2.2*)
 - ✓ Separator samples
 - ✓ Isokinetic sampling
 - ✓ Thornton sampling
 - ✓ Wellhead sampling

It is strongly recommended that the following data are always reported in a general information sheet when sampling (Whitson and Brulé, 2000):

- Separator gas / oil ratio (GOR) in standard cubic feet / separator barrel
- Separator conditions at sampling
- Field shrinkage factor (B_{osp})

Also, it is advisable to report: the flowing bottom hole pressure (FBHP) during sampling, the static reservoir pressure, the minimum FBHP before and during sampling, the time and date of sampling, the production rates during sampling, the dimensions of sample container, the total number and types of samples.

The *Table 2.1* gives details for the type of sample and the quantity required.

Table 2.1: Guidelines for fluid sampling (Moffatt and Williams, 1998).

Type of sample	Comments	Quantity required
Surface separator	This method should be used routinely for all well tests where fluids are produced into a separator. It can be used as principal method or as a backup or cross check for other methods.	Minimum of 2 gas samples of 20 litre volume plus 2 liquid samples of 500cm ³ (more gas may be needed at pressures below 100 psia).
Bottom hole	This method is recommended for all reservoir oils, and may be successful with dense condensate fluids. Take back – up surface samples in case fluid is diphasic.	Minimum of 2 fluid samples of approximately 500cm ³ , or three is possible.
Wellhead	For dry gases or highly undersaturated fluids from high pressure high temperature wells. This method can avoid BHS costs. Take back-up surface samples in case fluid is diphasic at wellhead.	Minimum of 2 fluid samples of approximately 500cm ³ , for oils or high pressure gas fluids; standard 20 litre gas bottles can be used for low pressure dry gas wells.
Stock tank	Samples should be taken by flashing separator liquid, or from source of clean stock tank liquid.	Two cans of 1 litre volume, or more depending on tests required.
Water	Samples should be collected from water sight glass or clean sample tap on the water flowline.	Two glass or plastic bottles of 250 cm ³ volume, or more depending on tests required.

The choice of either the surface or downhole sampling method cannot be considered as simple or routine matter (American Petroleum Institute, 1966; American Petroleum Institute, 2003). *Table 2.2* shows the relative advantages of subsurface and surface sampling while the *Table 2.3* summarizes the applications of each method. For all the methods of sampling, flowing wells are the best candidates for fluid sampling (Anon, n.d.). In the next subchapters, each sampling procedure will be examined separately.

Table 2.2: Advantages and disadvantages of each method of sampling.

	Methods of sampling		Advantages	Disadvantages
Subsurface	Open hole	<i>RFT</i>	Fluids can be maintained at high pressure, time saving	Expensive, stuck tool, contamination, limited number of samples
		<i>MDT</i>	Environmental, economic, time-saving, data quality benefits	Stuck tool, expensive, contamination
	Cased hole	<i>Bottom hole sampling</i>	Avoids use of surface separators, no need of recombination of sample	Contamination with OBM, sand, small volume, mechanical obstructions, not applicable for highly viscous and foaming oils
Surface	<i>Standard</i>		Convenient, easy, cheap, large volumes	Need of recombination of samples
	<i>Isokinetic</i>		Tackles carry over	Need of homogeneous flow
	<i>Thornton</i>		Variety of conditions P, T	Sand erosion, hydrate problems, noticeable drop in production rate
	<i>Wellhead</i>		Cheap, easy, reliable results	Need of single phase flow

Table 2.3: Applicability of the sampling methods.

	Methods of sampling		Oils	Gases	Special cases
Subsurface	Open hole	<i>RFT</i>	Volatile Undersaturated oil		Consolidated and unconsolidated formations, compositional variation, for small diameter, abrupt change of angle
		<i>MDT</i>	Above bubble point	Above dew point	Consolidated and unconsolidated, containing asphaltene, compositional variation, deviated wells, deepwater
	Cased hole	<i>Bottom hole sampling</i>	Undersaturated oils		Viscous oils, high asphaltic content (SRS), trace analysis required (NRS)
Surface	<i>Standard</i>		Saturated oil, viscous and foamy oils	Gas condensate	Gas injection studies, asphaltene precipitation, emulsions, hydrates
	<i>Isokinetic</i>			Lean gas condensate	Fluid can have carry over
	<i>Thornton</i>			Gas condensate	Fluid can have carry over
	<i>Wellhead</i>		High pressure undersaturated oils, low GOR oil	Dry gas	Ideal for asphaltene studies, deep wells

2.1 Subsurface sampling

Subsurface sampling should always be the first choice when reservoir and well conditions permit (Schlumberger, 2005). Downhole sampling involves capturing reservoir fluid samples at reservoir conditions. The optimum situation, when the objective is to obtain a sample of the original reservoir fluid, is to collect samples before the bottom hole flowing pressure has dropped below the reservoir fluid saturation pressure (Whitson, 1998). When the pressure in the near-well region is reduced below the saturation pressure of the original reservoir fluid, the fluid separates into two phases (gas and liquid) having different compositions. This almost always gives rise to flow rates of gas and liquid that result in a fluid composition in the wellbore which differs from the original reservoir fluid. If the reservoir fluid is known to be undersaturated at the prevailing reservoir pressure (based on well test data and correlations for the saturation pressure estimation (Dake, 1978)), sampling may be delayed until other wells have been drilled. The permissible extent of this delay depends upon the degree of undersaturation and the rate of decline of reservoir pressure.

The bottom hole sampling must be chosen when (Thomas, n.d.):

- $P_{wf} > P_b$
- It is not required a big volume of sample
- Demand of asphaltene studies

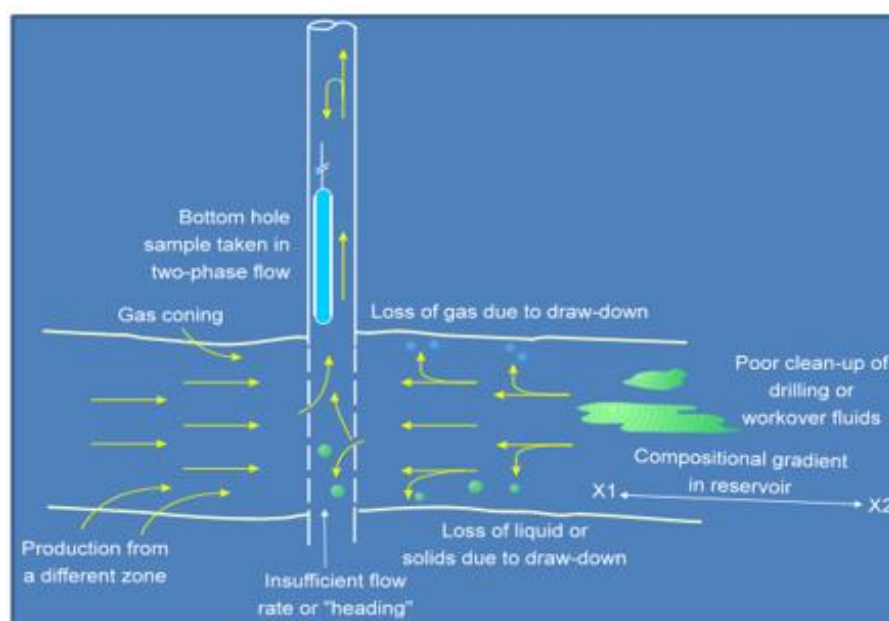


Figure 2.1: Problematic areas for subsurface samples (Moffatt, n.d.).

The issues that may complicate the subsurface sampling procedures are depicted at *Figure 2.1*. Namely (Ezekwe, 2011):

- Contamination from drilling fluids, mud filtrates and completion fluids: The use of oil based mud during drilling operations can lead to contamination of the near-wellbore region.
- Gas - oil or oil - water contacts: Generally, it is best not to sample from an oil well near a gas-oil contact in order not to take a sample containing volume of both contacts. In most instances, sampling for gas or oil should be done as far as feasible from a gas - oil, gas - water or oil - water transition zone.
- Mechanical obstructions (American Petroleum Institute, 2003): The tool may stuck (usually when it has been set at a given depth for a long time), the seal may failure (if the packer fails, the drilling mud will be sampled and the mud pressure will be recorded) and plugging may occur (sand grains from the formation may enter the tool and block the flow lines. This problem is reduced by the filter in the sampling probe, but fine grains may still get through).
- Variations in fluid composition: It is usual in very thick formations, large reservoirs or reservoirs subjected to recent tectonic disturbances (Speight, 2014; Levorsen, 1967).
- Two-phase flow in the wellbore
- Intermittent flow or heading
- Water production can be troublesome as far as it can cause alteration of the composition of the reservoir fluid through selective dissolution of constituents (CO₂, H₂S, aromatics).

Depending on whether the hole is open or cased, different tools and methods are applied. The open hole testers except from samplers, they (Varotsis, 1996):

- Measure pressure depth profile across the reservoir
- Allow definition of vertical and horizontal communication
- Provide an estimate of the formation permeability through the interpretation of pretest data recorded during drawdown and build up
- Monitor the fluid through resistivity and optical measurements
- Give early PVT data to engineers so that the characterization of the fluid, the different zones intervals and the composition grading are comprehensible
- Save time (real time well site decision)
- Reduce cost (no need of doing Drillstem tests) (Montel, 2008; Thomas, n.d.)

2.1.1 Open hole testers

The most important open hole samplers are presented in the following figure:

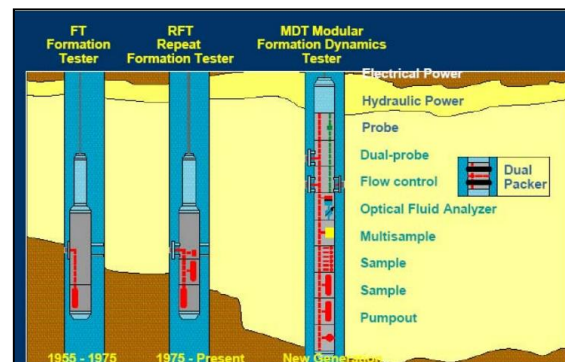


Figure 2.2: Open hole testers (Montel, 2008).

Nowadays the MDT tool is mostly used, as far as it is the improved version of the RFT. Firstly, an overview of the RFT will be given and then the MDT will be examined thoroughly.

2.1.1.1 Repeat formation tester (RFT) (Noah, 2014; Whitson, 1998; Glover, n.d.; Elshahawi, Fathy and Hiekal, 1999)

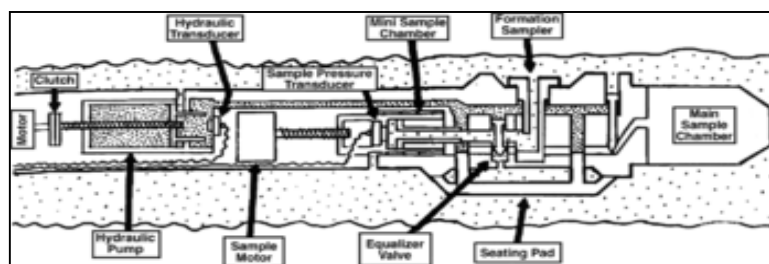


Figure 2.3: RFT tester.

The Repeat Formation Tester is an important tool for production and reservoir engineering and was designed to obtain fluid samples for further testing. Nevertheless its main use is focused on continuously recording the hydrostatic pressure of the fluids in the well, the pore pressure of the formation and the pressure transient induced by the withdrawal of samples. The tester can cope with consolidated and unconsolidated formations, and helps to establish a variation for reservoirs with (depth) compositional variation. Also it permits the logging engineer to test the formation for permeable formations before attempting to produce from them. It has the ability to re-set depth any number of times in order to accomplish a pretest, in which small samples of fluid are withdrawn from the formation and the fluid pressure in the formation is monitored. It should be noted that the RFT is expensive to be used if many fluid samples are required, as far as it is equipped with two sampling chambers. Each chamber can be used to sample the formation at two differing rates and stores it separately from the other. Since there are only two main sampling chambers in the tool, it may be required to empty the chambers in order to move on to another depth.

The tool is lowered by wireline means into the well to the depth required, which is recognized by comparing the gamma ray readings from a gamma ray sensor attached to the tool with previously taken logs. In this way an accurate depth may be fixed. The procedure and the pressure regime at RFT sampling is summarized in the *Figure 2.4*.

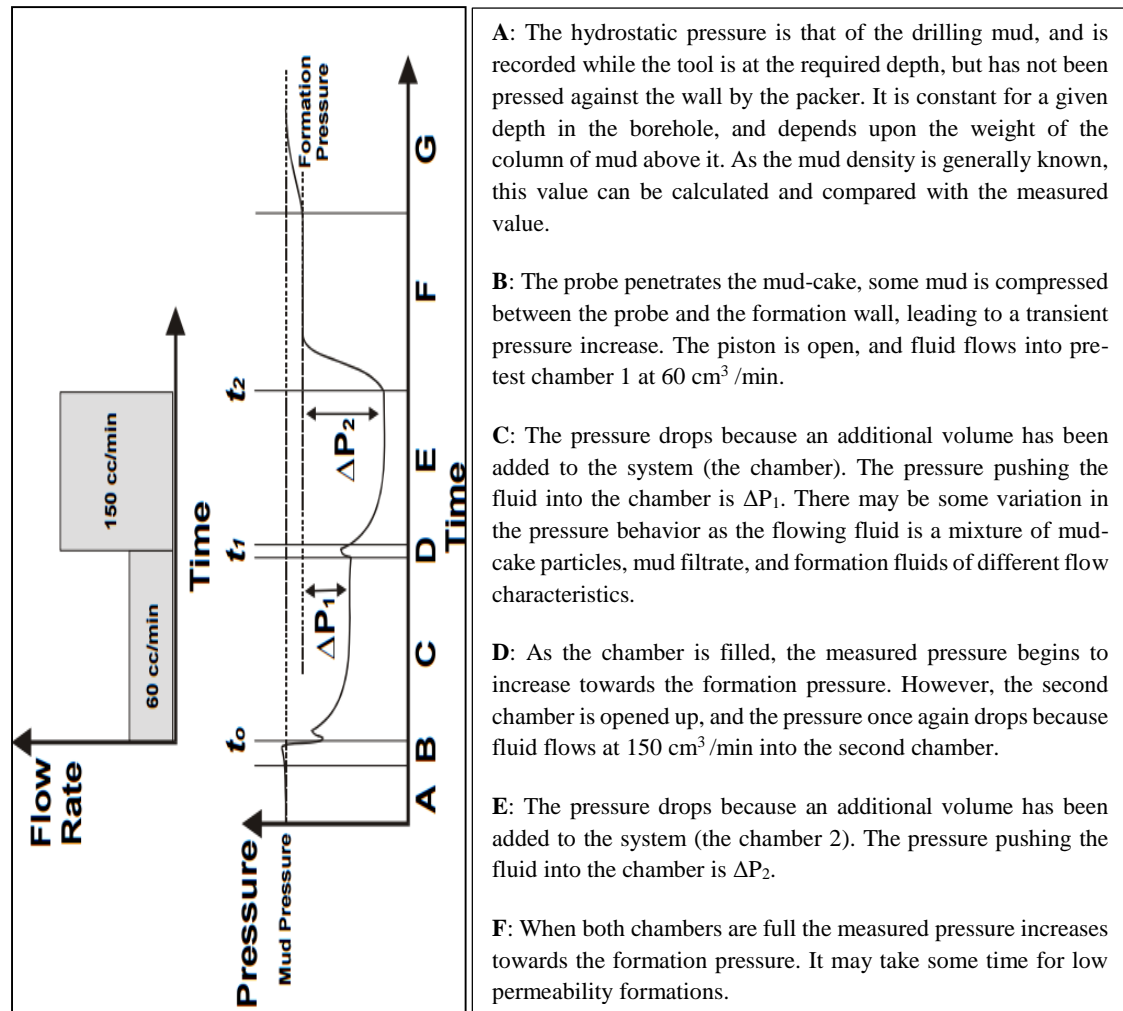


Figure 2.4: RFT pressure versus time (Glover, n.d.).

Evaluating the gradient of the formation pressure against depth provides information about the type of fluids, the fluid density and the contact between them (Serra, 1986). Also, it gives an indication of the productivity of fluids from the test depth.

The quality control of the RFT is described by Gunter and Moore (1987) and includes inspection of the tool, calibration, run quartz gauges and comparison of measured mud hydrostatic pressure against calculated mud hydrostatic pressure.

For small diameter boreholes and for wells with stability problems (hole restrictions, swelling formation, wells with abrupt change in angle), Schlumberger (n.d.2) has invented a Slimhole Repeat Formation Tester.

2.1.1.2 Modular formation Dynamics Tester (MDT) (Montel, 2008; Smits, et al., 1993; Schlumberger, 2005; Fujisawa and Yamate, 2013; Schlumberger, 2005; Schlumberger, 2008; Betancourt, et al., 2007; Anon., n.d.4; Crombie, et al., 1998; Khali et al., 2008; Zhaohui and Xiangdong, 2013; Kool, et al., 2001)

Real time, downhole analysis using MDT wireline tool is an extremely effective way to obtain accurate fluid data in a very short time frame. It is the evolution of the RFT and conducts three distinct services: real-time formation pressure tests, real-time in-situ measurements of fluid properties, and downhole capture - retrieval to the surface of fluid samples.

The basic MDT probe module is a retractable, hydraulically operated probe, embedded in a circular rubber packet that is forced through the mudcake to make a seal with the formation. The tool consists of individual modules that can be configured to meet almost any testing and sampling need, such as a variable rate and volume pretest chamber, flowline fluid resistivity measurement sensor, temperature sensor and pressure gauges (including a fast high precision Crystal Quartz Gauge that enables sensitive monitoring during the sampling process). The chamber of sampling is usually the Single Phase Multisample Chamber (SPMC) (*Figure 2.5*) which allows compensation for the temperature induced pressure drop. In that way SPMC ensures that the sample is above bubble point as it is returned to surface.

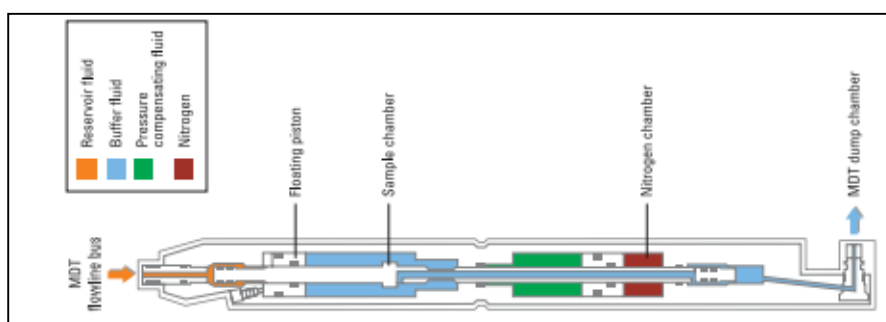


Figure 2.5: Single Phase Multisample chamber.

The MDT provides environmental, economic, time-saving and data quality benefits over traditional methods of reservoir characterization. Difficult cases such as highly deviated unstable formation in the Netherlands, near horizontal wellbores at an oil-bearing reservoir in Australia, deepwater at Gulf of Mexico and at Tahiti Field with asphaltene and sand presence, were sampled by the use of MDT tool.

The equipment that MDT can carry are examined on the following subchapters.

2.1.1.2.1 Low shock technique

The Low Shock Sampling technique is developed to limit pressure drawdown during fluid sampling and is frequently used in unconsolidated formations and for sampling above the bubble point. The shock is minimized by pumping formation fluids into the MDT tool against piston chambers held at borehole pressure, as opposed to drawing formation fluid into chambers at atmospheric pressure.

2.1.1.2.2 Fluid analysis

The downhole fluid analysis is a unique process that combines fluid identification and real time monitoring of a wide range of parameters (*Figure 2.6*). The most important analyzers are presented below.

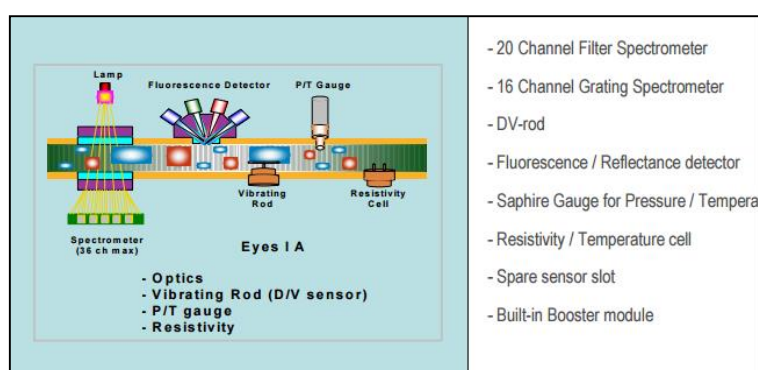


Figure 2.6: Downhole Fluid Analysis (Montel, 2008).

Composition fluid analyzer (CFA) contains a visible and near infrared absorption spectrometer for fluid discrimination. CFA measures the optical absorption as far as it is unique for C_1 , $C_2 - C_5$, C_6+ , CO_2 and H_2O (Mullins, et al., 2004). It can characterize complex mixtures, identify components (qualitative analysis) and determine the weight percent of each molecular group in a sample (quantitative analysis). The spectrometer is designed to withstand the temperatures and pressures prevailing in reservoirs, and the severe mechanical shocks and vibrations expected for oilfield uses. Light is transmitted through the fluid to an array of detectors turned to selected wavelength. The composition of the fluid is identified from the manner in which light attenuates during transmission through the fluid. The GOR can be derived through correlations based on measuring differences in color transmission in the lowest spectrometer channels, while the API gravity can be predicted by comparing the fluid absorption response in the visible wavelength channels with the response in the longer near IR wave length channels.

Live fluid analyzer (LFA) has a spectrometer which analyzes the components as the fluid flows through the MDT tool. The LFA analyzer detects and measures dissolved methane in live fluids and provides a predictable cleanup period for quality sample collection and reliable discrimination between water, oil and gas. Free gas is identified using two independent detectors.

Optical Fluid Analyzer (OFA): The OFA module (*Figure 2.7*) responds to two basic optical properties of the fluid in the flowline: (1) optical absorption in the visible and near-infrared region and (2) change in the index of refraction. The OFA is designed to measure accurately slight variations in coloration by using detection circuitry with a high signal to noise ratio. So, despite the fact that oil based muds and crude oil have the same components, their color distinct them (crude oil extends into near infrared beyond the visible range of the eye and provide a continuous measure of cleanup). Nevertheless, the analyzer does not provide enough information to differentiate scattering when phases emulsify.

- (1) The optical absorption is measured through a visible and near infrared absorption spectrometer and has the same operating principle as for the CFA. For the majority of the data points, the oil fraction detected by the OFA module is within 10% of the measured oil cut. The largest oil peak that can be seen using the OFA spectrometer is at 1,725nm (hydrogen – carbon bond).
- (2) A refractometer for free gas detection identifies the change in refractive index. A polarized infrared light shines at an angle on the interface between the sapphire window and the fluid flowline. The intensity of the reflected light measured at several angles indicates the presence or absence of gas in the flowline with a very rough estimate of its amount. Each gas has a different index of refraction (different critical angle) which varies with density and therefore with pressure and temperature. The gas detector responds only to free gas that is in contact with the surface of the window, which may not necessarily represent the volume fraction of gas present in the flow. For slug flow streams, the gas detector identifies 100% gas some of the time and 100% liquid the rest of the time. For bubble (and foam) flow streams, the gas detector sees the gas bubbles which flow near the surface of the gas detector window. Therefore, it is recorded less signal for a bubble flow.

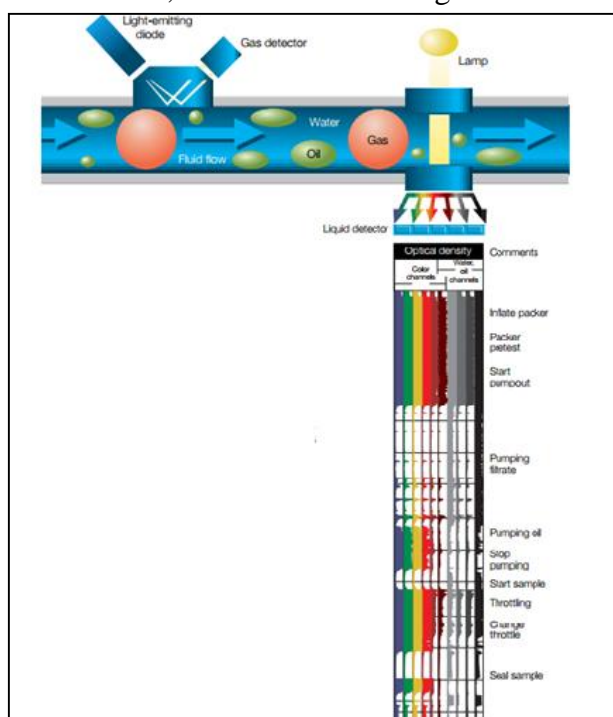


Figure 2.7: Optical Fluid Analyzer.

InSitu Fluid Analyzer (IFA): The InSitu Composition hydrocarbon fluid composition measurement introduces the first downhole deployment of a laboratory-grade grating (GR) spectrometer in addition to the conventional filter array (FA) spectrometer. The FA and GR spectrometers are optimized for the detection and analysis of hydrocarbons, color for relative asphaltene content, and CO₂ in crude oil and natural gas as well as determination of the water content and pH. Also, a reflection signal is measured. In *Figure 2.8*, a halogen tungsten light provides the light source for the spectrometer measurement. The transmitted light is collected by optical fiber bundles and guided into the filter array spectrometer and grating spectrometer. In addition to the spectrometer system, a ruggedized fluorescence detection unit is used for the optical emission from gas phase atoms that have been excited to higher energy levels by absorption of electromagnetic radiation. The gas phase emission can achieve great sensitivity since the fluorescence signal has a very low background. A blue light-emitting diode (LED) is the excitation light source and the fluorescence signals are detected at two different wavelengths. The fluorescence and reflection measurements are useful particularly when multiphase fluid is present in the flowline. Downhole normalization before each station consists of checking the source intensity and using that value to normalize the actual measured intensity. The compositional analysis is refined with an algorithm developed from Beer-Lambert's law, which establishes a linear relationship between the optical absorbance and the concentrations of species under investigation (Mullins, Schroer and Beck, 2000; Mullins, et al., 2000).

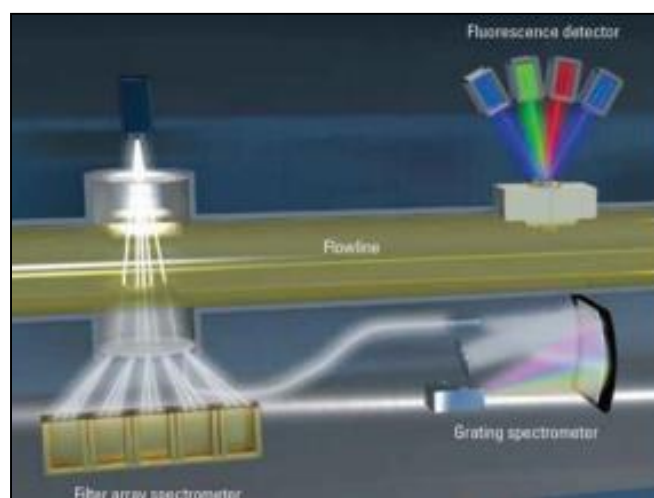


Figure 2.8: Developed system of a filter array spectrometer, a grating spectrometer and a fluorescence detector unit (Fujisawa and Yamate, 2013).

It is worth mentioning that MDT is weak on measuring the optical density of a fluid that does not transmit any light (dark oil, mud) and on instantaneous changes in the fluid (rapid movement of fluid).

InSitu Density: The density measurement is based on the resonance characteristics of a vibrating sensor that oscillates in two perpendicular modes within the fluid. Simple physical models describe the resonance frequency in relation to the fluid density. The resonance factor is related to the fluid density where added mass around the sensor decreases the resonance frequency; the heavier the fluid, the greater the release. Dual-mode oscillation is superior to other resonant techniques as far as the accuracy is concerned, because it minimizes the effects of pressure and temperature on the sensor through common mode rejection. The measurement is made under flowing conditions and the resonator is resistive to corrosive fluids.

InSitu Viscosity (Mishra, et al., 2014; LeCompte, Mishra and Barbosa, 2014): It measures viscosity across the range of light to heavy oil in downhole environment, from 0.2 to 300 cP at an accuracy of $\pm 10\%$. It relies on the principle that each medium has different vibration characteristics when it is at a vibrating wire. The more viscous the fluid, the more abruptly and rapidly the vibration of the sensing element lessens than compared with its behavior in a less-viscous fluid.

Vibrating Rod (Khali, et al., 2008): The Vibrating rod is a density / viscosity sensor. As with any vibrating object in a fluid media, the resonance frequency and quality factors are related to the fluid characteristics. The resonance factor is related to the fluid density as it is explained at the InSitu Density. The quality factor is mainly related to the fluid viscosity; the more viscous the fluid the more damping the sensing part will be subject to, and therefore, the lower the quality factor. The resonance factor and quality factor are measured from the ring down of the sensing element vibration. Density and viscosity are predicted through a complex physics modeling of the elastic properties of the sensing part and the Navier-Stokes equations describing fluid displacement around it.

2.1.1.2.3 Contamination level of reservoir fluid

The screening of contamination level of the reservoir fluid uses a pump-out modulus and a spectrometer. The objective of real time contamination monitoring is to continuously analyze the fluid pumped from the formation through the flowline using the spectrometer until an acceptable contamination level is measured. The faster pump-out results in less contamination of the sample and reduced rig time. Typical pump-out times vary from 20 minutes to 2 hours depending on the formation characteristic.

The contamination can either be miscible or immiscible with the hydrocarbon phase.

For immiscible contamination, the downhole optical spectrometer is capable of distinguishing water from oil by differences in optical absorption of light at visible and near infrared wavelengths (Smits, et al., 1995). Therefore for the case of water based mud the uniqueness and separation of absorption peaks permit differentiation of oil and water.

Contamination monitoring becomes much more critical when the fluids involved are miscible. This includes the formation crude oil invaded by oil based mud. Adding a dye to drilling mud can be used to quantitatively determine the contamination level. According to Schlumberger (2005), the contamination level due to oil based mud can fall to less than 1%, as far as the crude oil and the oil based mud filtrate have different color and gas content.

Hsu et al. (2008) detected oil based mud contamination by monitoring the optical density measurements at different wavelength channel (multichannel) by an optical spectrometer. Hsu's technique is better than OFA as far as it produces a single contamination estimate that is consistent with all the channel data. Akkurt et al. (2007) states that the Quicksilver Probe can be used for oil based muds at which contaminated fluid is pumped into one flowline, completely isolated from pure reservoir fluid and collected in a second sampling flowline.

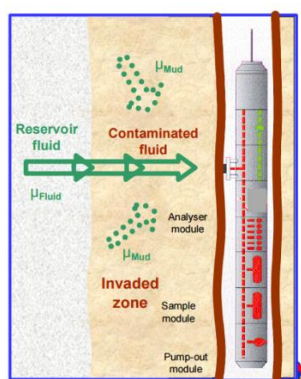


Figure 2.9: Contamination of reservoir fluid.

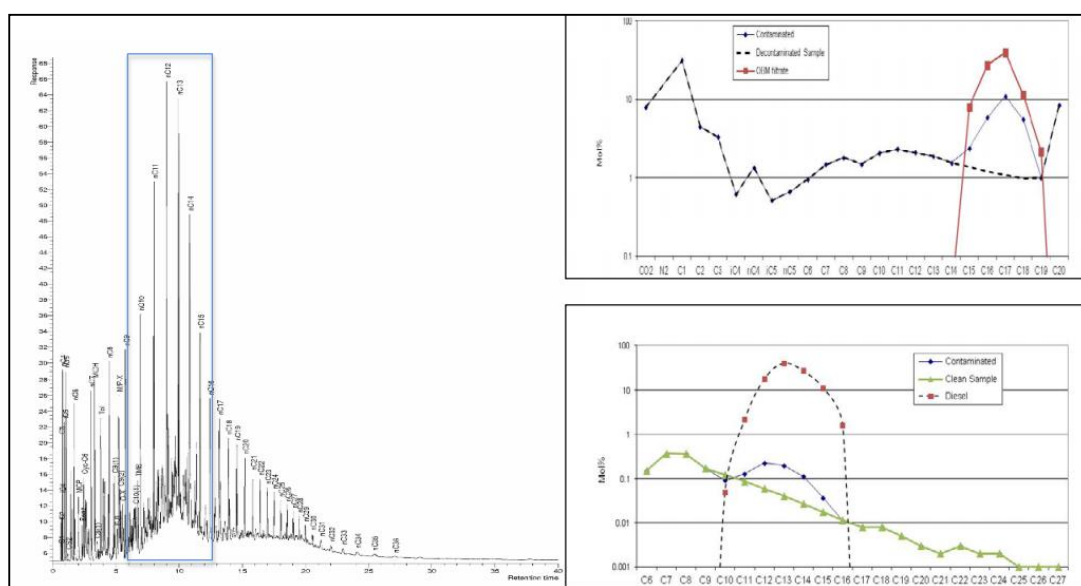


Figure 2.10: Contamination of reservoir fluid by oil based mud (Moffatt, n.d.).

The process of determining the composition of the reservoir oil is explained at the Chapter 4.1.6.

2.1.1.2.4 Special tests

If requested the MDT tool can be equipped with:

Downhole pH measurement: It is used in a production well to detect the pH, delineate the oil water contact, characterize the oil water transition zone and identify the sources of water in various layers (Raghouraman, et al., 2005b). The pH measurement is accomplished by injecting pH sensitive color dye into the formation (Baghuraman, et al., 2007; Raghuraman, et al., 2005a). The color of the reaction between the fluid and the dyes is detected through optical channels that operate at specific wavelengths and sensors.

Titration tests: Asphaltene stability in dead oils can be measured using titration tests, where an aliphatic solvent and a near infrared laser transmittance probe are used to detect the asphaltene flocculation (Guo, et al., 2005). As the titrant (typically heptane or pentane) concentration increases, the resulting mixture optical density decreases and the light transmittance through the fluid increases.

2.1.2 Cased hole

The cases of Cased hole Dynamic Tester and bottom hole sampling are presented below.

2.1.2.1 Cased hole Dynamic Tester (Burgess, et al., 2002; Andrews, et al., 2001)

As for the open hole environment, it has been invented a tester for the cased holes by Schlumberger and Gas Technology Institute. The Cased Hole Dynamics Tester (CHDT) tool was built in order to measure and collect samples from cased wells without compromising casing integrity. CHDT is the first tool to penetrate casing, cement and rock, acquire multiple formation pressures, retrieve high quality formation fluid samples and plug the test holes in a single trip. CHDT can be conveyed on wireline, on drillpipe or with tractor.

Firstly the tester is run to the target depth and then a hybrid bit starts to drill. The pressure surrounding the drill bit is monitored. As the drill advances through the casing into cement, small pressure variations result from the differences in volumetric changes and pore pressure of the cement. Cleaning cycles are used to enhance the drilling performance and remove debris. Once the bit encounters the formation, the measured pressure stabilizes at reservoir conditions and drilling can stop. The tool can drill up to 6in. CHDT samples are collected when suitable communication is established between the tool and the formation. The tool monitors resistivity for fluid typing and can be combined with the OFA, LFA and pump-out modulus for advanced fluid analysis.

2.1.2.2 Bottom hole sampling (BH)

Undersaturated oils are usually sampled by bottom hole sampling while the well is flowing at a relatively low rate. A pressure temperature survey is run to determine the location of the gas – oil and water – oil interfaces. These contacts can be determined by plotting the measured pressure versus depth and noting the points of slope change. The best place to sample is at the lowest point in the wellbore where the static pressure is above the estimated bubble point pressure (Lang and Donohue, 1985).

The samplers for BH sampling can be (Montel, 2008; American Petroleum Institute, 2003):

- Conventional bottom hole samplers: They incorporate the capability to open and/or close valves at specified times in order to capture a sample of the fluid existing at bottom hole conditions.
- Pistonned bottom hole samplers: A floating piston in the sample container separates the reservoir fluid sample from a hydraulic fluid on the back side of the piston. Due to the capability of controlling the rate of fluid sampling by applying back pressure, the possibility of single phase sampling is enhanced. Examples of pistonned bottom hole samplers are:
 - ✓ Single phase Reservoir Sampler (SRS): They are used when there is asphaltic content. SRS are pressure compensated by applying a back-pressure with nitrogen against a piston in the sample chamber. By maintaining the back pressure much higher than reservoir pressure, it is expected that monophasic conditions will be retained in the sample chamber. Asphaltenes may precipitate out of solution if the sampling conditions (temperature and pressure) are reduced.

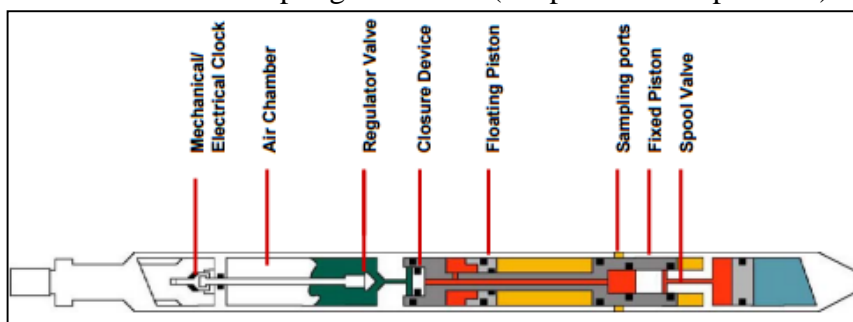


Figure 2.11: SRS Sampler.

- ✓ Nonreactive Reservoir Sampler (NRS) (Schlumberger, n.d.3): NRS is used for aggressive component studies. The chamber is coated in order to reduce the adsorption of the sample gases on the sample chamber.
- ✓ Exothermic samplers (Ezekwe, 2011): They are used mainly for samples that may contain asphaltenes. Exothermic samplers are similar to single phase samplers except that they are also designed to maintain the temperature of the sample with battery operated heating jackets.
- ✓ Slimline Single Phase Reservoir Sampler (SLS) (Schlumberger, n.d.2): SLS allows optimum sampling volume and can be used in a variety of sampler carrier designs.

As sample carrier in DST string is usually used the SCAR Inline Independent Reservoir Fluid Sampling (Schlumberger, 2013). It has five sample carrier choices to accommodate with different samplers and options to select from a broad range of size, pressure and temperature ratings. SCAR Inline Independent Reservoir Fluid Sampling delivers contaminant free reservoir fluid samples from deep within the reservoir. The activation of a sampler can be wireless or by pressure command (Schlumberger, 2013a).

Bottom hole samplers can be run conveyed by (McAleese, 2000):

- Slickline - Live digital slickline
- Electric line
- DST with surface control

Before sampling, a conditioning procedure is required.

2.1.2.2.1 Conditioning procedure for bottom hole sampling

Perhaps well conditioning is the most important, yet often misunderstood phase of the bottom hole sampling program and should be executed before sampling (Moffatt and Williams, 1998). The objective of well conditioning is to replace the non representative reservoir fluid located around the wellbore by displacing it into and up the wellbore with original reservoir fluid. A poorly conditioned well may still be producing drilling mud filtrate, work-over fluids, or reaction products. This thesis deals with oil reservoirs, so the procedure of conditioning an oil reservoir is examined as follows (Petrowiki, n.d.2; Moffatt and Williams, 1998):

Firstly, a **cleanup** of the well is executed. At the cleanup phase, the well produces long enough to the surface to remove any solids resulting from perforating activities, drilling mud or completion fluids in the well and mud filtrate or workover fluids that may remain in the formation near the wellbore. The production rate must provide a sufficient flow velocity in the production string to lift solids, hydrocarbon liquids and water to the surface. The cleanup period typically lasts from a few hours to 24 hours and progress is monitored by regular measurements of flowing wellhead pressure (P_{wf}) and basic sediment and water (BS&W). At the end of the cleanup phase, the monitored measurements must stabilize at small values. For the BS&W measurement a probe is equipped with an internal sensing device that measures the dielectric constant of the system. An adjusted value usually between 0.5 – 3% is set in order to monitor when this value is reached (Cameron, n.d.; Leffler, Pattarozzi and Sterling, 2003).

Then, shut in the well and build up to static pressure; produce at a low rate for long enough to remove all contaminants in the near-wellbore region, and begin sampling.

During well conditioning, the following field measurements are accomplished (American Petroleum Institute, 2003): wellhead pressure and temperature at tubing, gas rate, gas gravity, gas temperature, oil rate and water production rate.

2.1.2.2.2 Bottom hole sampling procedure

The typical procedure for bottom hole sampling is (Whitson, 1998):

- Conditioning the well
- Position sampler at the specified depth
- Produce the well at a low, stable rate
- Sample during the flow test (dynamic sample) or after shutting in the well (static sample)
- Bring the sampler to the surface
- Transfer the samples to suitable pressure vessel for transporting to the laboratory if requested. The procedure of the transfer includes (Whitson, 1998):
 - ✓ Measure the opening pressure of the BH sampler
 - ✓ Heat the BH sampler to about 80° C
 - ✓ Mix the sample by agitation / rotation
 - ✓ Transfer to sample container

A minimum of triplicate bottom hole samples should be collected in order to test their quality and have backup samples in case of leakage (Akpabio, et al., 2014).

The time that the bottom cased hole and surface sampling should be performed during the drill stem test (DST) is presented at the *Figure 2.12*:

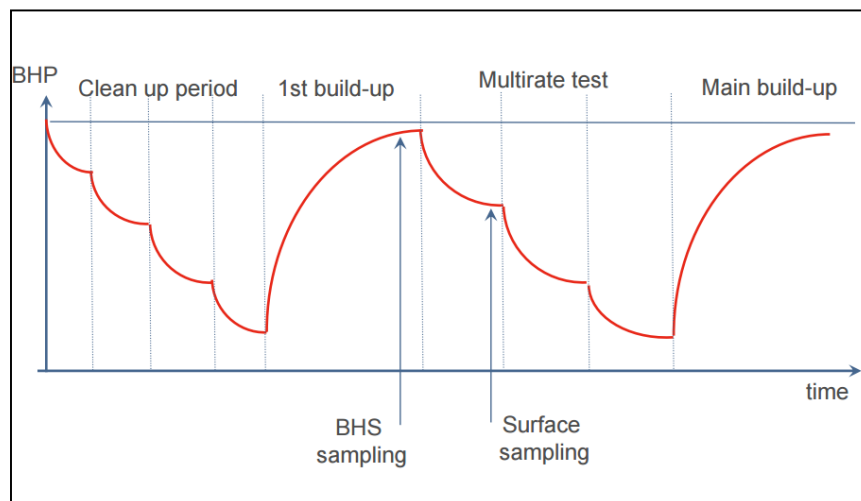


Figure 2.12: Bottom hole and surface sampling during Drill Stem Test (Montel, 2008).

2.2 Surface sampling

Surface sampling of reservoir fluids is by far the most common method of sampling pressurized hydrocarbon fluids as far as the surface sampling method is satisfactory for nearly all types of reservoir fluids (PetroWiki, n.d1.). Surface sampling from the wellhead, separator, and stock tank is performed routinely during most well tests and is occasionally required from production process lines (Schlumberger, n.d.). Cases have shown excellent agreement in measured fluid properties between recombined surface samples and subsurface samples (American Petroleum Institute, 2003).

According to Thomas (n.d.), the surface sampling must be chosen when:

- High water cut
- Large volume of samples are required
- $P_{wf} < P_b$

The accuracy of the separator flow rate measurements and stability of separation conditions are critical to the accurate determination of reservoir phase behavior from the recombined fluids (American Petroleum Institute, 2003). Therefore, the facilities for making these determinations must be in excellent condition.

Common errors encountered in surface sampling as can be seen in *Figure 2.13* are (Ezekwe, 2011):

- Fluid stream not equilibrated in the separator due to improper separator size, insufficient residence time, improper operation or poor mechanical condition
- Entrainment of liquid in the separator exit gas stream
- Gas carry-under in the separator exit liquid stream
- Emulsions in the separator exit liquid stream

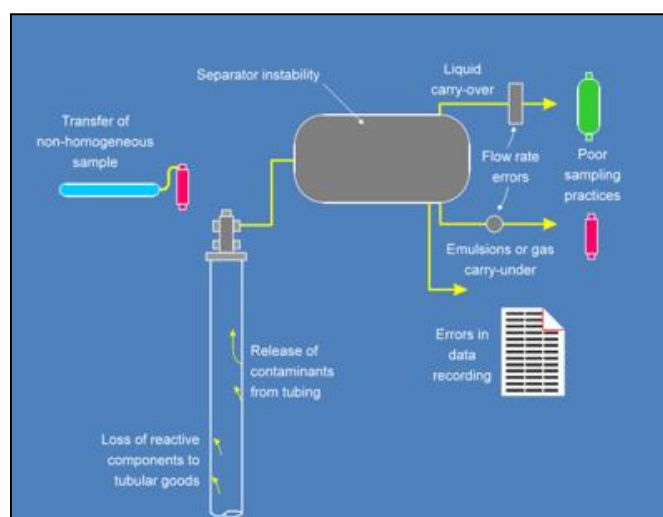


Figure 2.13: Errors for surface sampling (Moffatt, n.d.).

The surface sampling can be divided into subcategories (separator sampling, isokinetic sampling, Thornton sampling, wellhead sampling) but first conditioning of the well is required. All of the topics will be discussed at the following subchapters.

2.2.1 Conditioning

As for the subsurface sampling from cased holes, a conditioning procedure is required in order to take a representative surface sample. Firstly, a phase of cleanup is required as expressed in the chapter 2.1.2.2.1. Then, the flow rate is reduced in steps until the separator GOR does not change between choke sizes. The primary separator oil flow rate, the stock tank oil rate, and separator pressure and temperature are monitored. As long as the separator operating conditions of temperature and pressure are maintained stable and representative reservoir fluid arrives to the surface, the GOR should remain stable for different choke sizes. Another form of conditioning may be necessary if chemicals, such as antifoaming agents and demulsifiers, are used. If possible, any such injection should be stopped long enough before taking a sample (wait at least five times the residence time).

2.2.2 Separator sampling (Whitson, 1998; Montel, 2008; Thomas, n.d.; Petrowiki, n.d.1; American Petroleum Institute, 2003; Anon, n.d.)

Separator sampling is used for gas condensates and saturated oils. Separator samples are also taken for gas injection studies requiring large sample volumes and for special studies involving analysis of asphaltene precipitation, wax point, emulsions and hydrates. When multi-stage separation is used, the samples are taken from the first-stage (high pressure) separator. A good rule of thumb is that it takes about one-half hour to collect a set of separator samples.

The separator sampling method consists of taking simultaneous samples of separator oil and gas with concurrent and accurate measurements of the rates of separator oil and gas flow. According to Whitson (1998) separator pressure and temperature, liquid level and flow rates must be stable in order to take a valid separator sample. Good accuracy of flow rates often considered to be in the region of 5%, but if there is carry-over of liquid in the gas exit stream (or carry-under of gas in an oil with foaming tendencies) it becomes worse (Petrowiki, n.d.1). For that reason, it is proposed by American Petroleum Institute (2003) to use an isokinetic technique when carry over is taking place.

Figure 2.14 depicts the point from which each phase is being sampled.

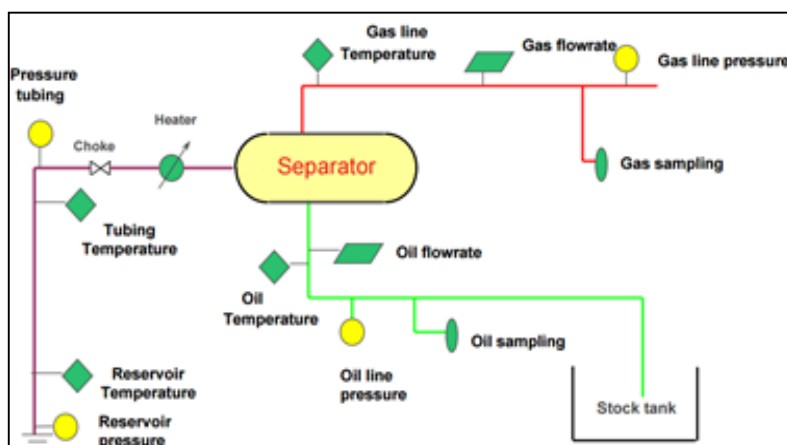


Figure 2.14: Separator sampling (Montel, 2008).

In line with current industry trends, recommendations are to use evacuated bottles for gases and piston bottles for liquids and avoid any use of mercury in sampling operations. At extremely low temperatures, piston bottles have been reported to leak past the piston seal, so sampling under such conditions should be avoided if possible. All the available methods of gas and liquid sampling are reviewed below.

Most separators will have at least one suitable valve tap for gas sampling. The preferred location is the top side of the gas outlet line. Special attention should be given when collecting gas samples from separators operating at low pressures because the lower density may result in the collection of insufficient weight of gas (Petrowiki, n.d.1). Other problems that may be encountered for gas sampling include entrained oil in the gas stream, reaction between corrosive gases (H_2S or CO_2) and steel container, and condensation of hydrocarbons within the container. The capacity of the containers is 20 liter and there are four basic methods for filling them:

Method 1 - Filling an evacuated container. It requires that the connecting line between the separator and sample container be purged with gas until the desired pressure is reached. Although this method requires that an evacuated container is available on location, it is the recommended method for gas sampling. Pressure on the container should be checked prior to sampling to ensure that vacuum exists.

Method 2 - Filling a Piston –type container. A hydraulic fluid must be pre-loaded behind the piston so that the piston position is fully toward the sampling end. They contain a floating piston that separates the sample side from the hydraulic-oil side of the container. The sample can be maintained at full separator pressure, but there is possibility of contamination if the seal of the piston leaks.

Method 3 - Filling an air-filled container after purging it with separator gas. It requires that the container is filled and emptied with separator gas several times in order to purge the container of air. The number of recommended successive purge cycles is inversely proportional to the separator's maximum gas pressure, as shown in *Table 2.4*.

Table 2.4: Recommended gas sample container purging cycles for surface separator sampling (American Petroleum Institute, 1966).

Maximum container pressure		Minimum purge cycles
psig	kPa	
10 – 14	70 – 100	16
15 – 19	100 – 150	13
20 – 29	150 – 200	10
30 – 59	200 – 400	8
60 – 84	400 – 600	5
85 – 149	600 – 1,000	4
150 – 450	1,000 – 3,100	3
> 450	> 3,100	2

Method 4 - Filling a liquid-filled container by displacement with separator gas. It requires that a two-valve sample container is filled with a liquid (salt water, glycol or water). The container is kept vertical while the upper valve is connected to the separator and the lower valve is opened to withdraw the liquid. When all the liquid is displaced, the valves are closed and the container is removed for shipment.

Liquid samples should be taken at full pressure from the oil line. Liquid sampling should be preceded by slowly draining about 100 cc of oil into a cup to clean the valve and to be sure that oil, not water, is being produced. The problems that can occur during oil sampling, include vaporization within the container (lower separator temperature than container's) and reaction between corrosive gases (H₂S or CO₂) and steel container. The basic methods for liquid sampling are:

Method 1 - Displacement of a liquid-filled sample container. This method consists of collecting a sample by displacing a liquid that is insoluble in the oil (typically water, glycol-water mixture, or brine) from a sample container initially pre-loaded with the liquid to be displaced. It is an easy and safe method to follow.

Method 2 - Filling an Evacuated Container. This method can yield excellent samples. It is based on either using an already evacuated container or a vacuum pump to evacuate the container on place. When the container is full, the valves are closed and the sampler is disconnected.

Method 3 - Filling a Piston – type Container. It has the advantages that the liquid sample can be kept at the saturation pressure throughout the collection process and it does not come into contact with any other fluids during sampling or transfer to the laboratory. The hydraulic fluid must be preloaded behind the piston so that the piston position is fully toward the sampling end. The appropriate valve is opened to allow oil to flow inside the container and displace the resident liquid. When the desired volume is collected, the valves are closed and the container is disconnected. There is possibility of contamination of the sample due to leakage of the seal.

Method 4 - Purging the container with separator oil. The separator oil flows from bottom to top through the sample container at a pressure equal to the separator pressure. After several container volumes have flowed through the container, the valves are closed. A portion (10 %) of the container volume is quickly released from the bottom valve with the container in a vertical position. This method requires considerable care to ensure that dissolved gas is not released into the container during flow.

Method 5 - Displacement of a gas-filled sample container (separator gas). It requires that the container is first filled with separator gas at separator pressure by using the method 3 for gas samples. With a pressure gauge installed on the top of the container, the bottom of the container is connected through a purged line to the separator. The sample is taken by opening the bottom valve and bleeding off the gas through the top valve, adjusting the rate so that no appreciable pressure drop occurs in the container. When oil flows from the top valve, both valves are closed and the container is disconnected.

2.2.3 Multi phase sampler (Afanasyev, et al., 2009; Dalen, 2012; Montel, 2008)

Multi Phase Sampler is designed for sampling from areas within the surface flow stream where one phase is dominant and the oil, gas and water are at equilibrium. The Multi Phase Sampling equipment enabled the collection of oil, gas, and water samples directly from the Multiphase flowmeter (MPMF) at line conditions during production testing. The multiphase flowmeter (MPMF) is based on differential pressure measurement in a venturi spool by adding a nuclear component to measure total mass flow rate and the holdups, or fractions, of gas, oil and water. Through a sampling trap, three probes are placed in the flowline's multiphase stream in a way that the venturi is in front of the probes. This positioning ensures that the sample is well mixed and not affected by fluid slugs or similar flow anomalies and is therefore representative of the flow being measured by the venturi. Two probes are placed at the top and at the bottom and face upstream to capture mostly liquids; a third probe is positioned in the middle of the flow path, facing downstream, to capture gas. The captured fluid enters a sample chamber where an optical phase detector distinguishes between oil, water and gas. The non target phases are displaced from the chamber back into the flowline by a hydraulically activated piston.

2.2.4 Isokinetic sampling (Whitson, 1998; Petrowiki, n.d.1; Danesh, 1998; Riley, et al., 1979; Williams, 1998; Fevang and Whitson, 1994; Boniface and Zakka, 2015)

Isokinetic sampling, also known as split-stream sampling, involves collecting samples from well production in two-phase flow. It is recommended for lean gas condensates with documented low separator efficiency, characterized by significant carry over of separator oil into the separator gas stream.

The isokinetic sampling system consists of four essential parts: three tube sampling probes, pressure sensors, flow calorimeter (used as a heat exchanger) and a purge system. The probe can either be at fixed or adjustable position and consists of a sampling tube for obtaining the fluid sample and two pressure sensing tubes to control hydrodynamic conditions at the entrance to the sampling tube. The sampling is achieved by requiring that the kinetic energy of the stream phase entering the sampling probe is identical to that in the free stream at the top of the probe. Schraub (1969) has shown that this is true when the static pressure of the free stream is identical to the static pressure within the entrance of the sampling tube. The isokinetic method samples gas twice:

- A sample of the oil-free gas is taken by sampling in the same direction as gas flows by using a sample probe facing downstream.
- A sample of the gas containing the entrained (carry over) oil is taken by sampling against the direction of gas flow at a properly controlled sampling rate (isokinetically).

Although isokinetic sampling has been in use for more than fifty years, there are challenges of ensuring that the small split stream flow is withdrawn at the same velocity as the main well production stream (*Figure 2.15*), and of achieving a homogeneous flow of the diphasic fluid upstream of the sampling probe. Nevertheless, by inserting a mixing section ahead of the sampling tube, the gas can be more homogeneously distributed in the tubing flow.

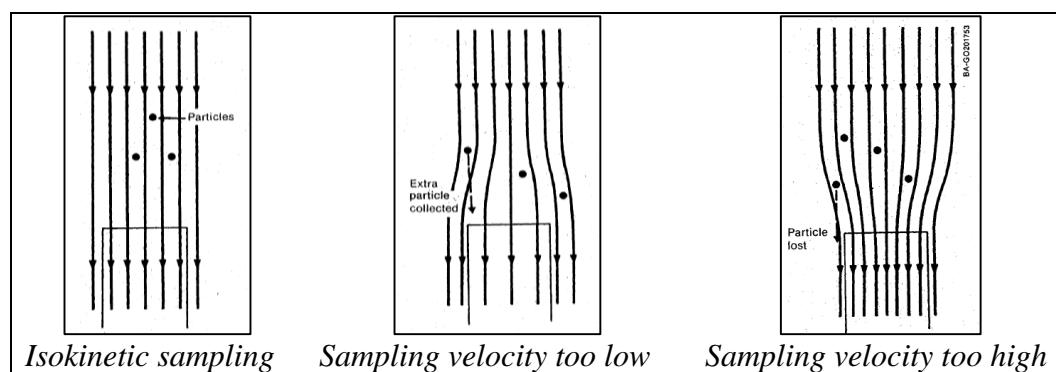


Figure 2.15: Isokinetic sampling.

2.2.5 Mini-Laboratory (Thornton) sampling (Whitson, 1998; Montel, 2008; Ebbrell, 1984; Scheele and de Jong, 1984; Anon, n.d.2; Anon, n.d.3)

The Thornton testing equipment is used for gas condensates and includes a sample manifold and a miniature laboratory containing the split phase sampling unit. The sampling manifold is positioned in the flow line between the well head and the choke manifold, and incorporates a mixing device in one leg. After passing through the phase mixing device, a homogeneous side stream is directed isokinetically, via a sample probe, to a miniature laboratory. At the miniature laboratory small scale liquid - gas separations are held, up to a maximum of three separation stages. The conditions of separation may be varied to suit any anticipated extremes of use (summer and winter conditions). Gas collected at high pressures in the first two separation stages are flashed to atmospheric pressure in order to determine the liquid / gas ratio for these separations and to provide samples. Sequential recombination of the analyzed phase compositions in the measured mole ratios appropriate to each separation will then yield a detailed composition of the original sample stream.

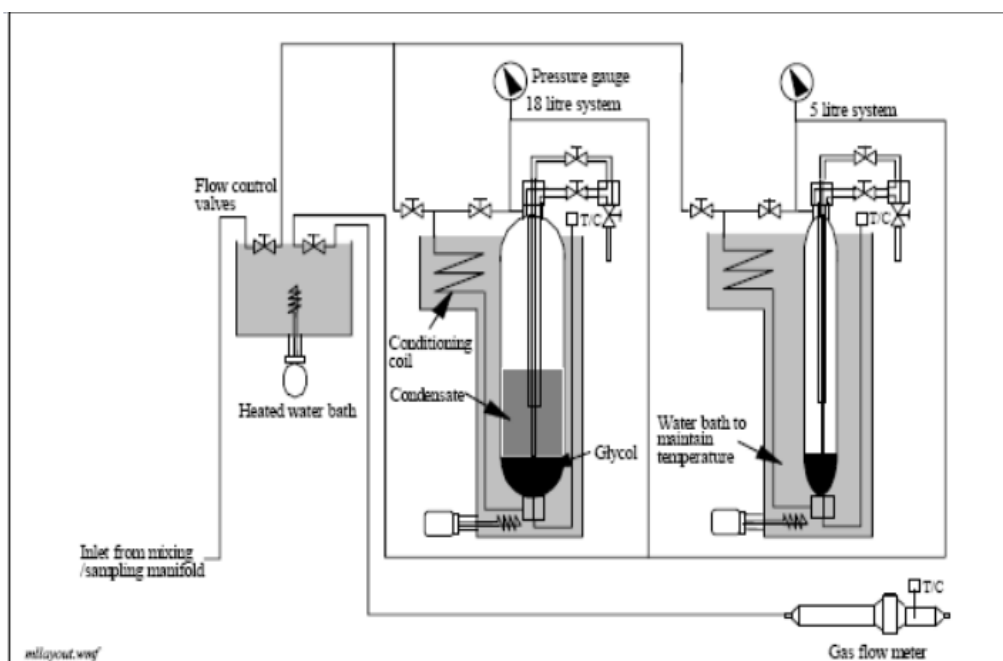


Figure 2.16: Mini laboratory.

The mini-laboratory sampling approach is expensive and therefore not usually recommended. It has been used for wells in Norway and observed in some cases sand erosion (sand trap bypassed during sampling), hydrate problems (emanate from the Thornton manifold itself) and noticeable drop in production rate when flow passed through Thornton manifold.

2.2.6 Wellhead sampling (Montel, 2008; Whitson, 1998; Petrowiki, n.d.1; Thomas, n.d.; American Petroleum Institute, 2003)

Wellhead sampling, more commonly known as flowline sampling is a less common alternative to the previously mentioned approaches despite the fact that it is a cheap and easy way to sample. Typically, wellhead samples can only be taken from high-pressure, deep wells that are highly undersaturated at wellhead conditions and for dry gases. Successful wellhead samples should be very accurate if the fluid is still in one phase condition at the wellhead conditions and temperature is above the wax appearance point (WAP). As far as the state of the fluid is not usually known with certainty, separator sampling also should be performed if possible, as a backup.

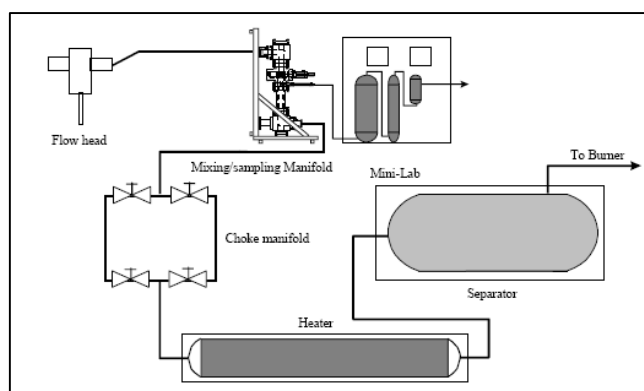


Figure 2.17: Wellhead sampling.

The procedure of wellhead sampling involves the collection of a fluid sample at the surface from the wellhead itself or from the flowline or upstream side of the choke manifold. The used wellhead sampling methods are filling a membrane sampler by displacing the backpressure fluid and filling a piston cylinder sampler.

An example of the cylinder sampler is the Wellhead Sampling Manifold of Schlumberger (2012) which is applicable for high pressure fluid samples at the wellhead during well testing operations. It is safe as far as the exposure time of personnel at high pressure wellhead and the risk of hydrocarbon release during sampling are reduced.

2.3 Conclusions

There are many methods of reservoir fluids sampling, each one having drawbacks and advantages. The choice of sampling method depends on many parameters, and firstly to the kind of the reservoir fluid. The engineers are presented with a series of technical challenges, such as, selection of the correct zone for sampling, contamination of reservoir fluid, maintenance of single phase for samples and transportation of unaltered samples to surface and laboratory facilities. In order to perform PVT studies on the recovered samples (chapter 4), firstly the quality of the samples must be evaluated (chapter 3).

2.4 Bibliography

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3. Quality control of the recorded samples

Quality control (QC) of collected samples and data must be performed before, during and after sampling (Osfouri, et al., 2014; Mawlod and David, 2015). Improper QC or any error in recorded data can be misleading in the next steps of fluid modeling, fluid properties measurement, and construction of thermodynamic model for representative reservoir fluid.

Williams (1994) listed the occurring errors in two major categories, error sources due to the nature of reservoir fluid and due to human operations (error during sampling or transfer, contaminated sample containers and leaks during shipment). The range of allowance for some parameters is presented in the Table below:

Table 3.1: Relative and absolute allowance for some parameters (Osfouri, et al., 2014).

Parameter	Relative allowable tolerance	Absolute allowable tolerance
Wellhead pressure	$\pm 1\%$	± 20 psia
Wellhead temperature	$\pm 3\%$	± 5 °F
Separator pressure	$\pm 3\%$	± 15 psia
Separator temperature	$\pm 5\%$	± 5 °F
Oil flow rate	$\pm 2.5\%$	± 10 bbl/day
Gas flow rate	$\pm 5\%$	± 1 MMscf/day
BS&W		$\pm 5\%$

The objective of reservoir fluid sampling is to collect a sample that is representative of the fluid present in the reservoir at the time of sampling. A non representative sample may not exhibit the same properties as the reservoir fluid, so quality checks are essential to evaluate the validity of the collected fluid. Besides visual inspection for possible leaks, damaged fittings, etc., specific tests are conducted to determine the sample representativity, such as contamination level, pressure and properties examination (Petrowiki, n.d.4; Ganzer, n.d.). Some of the samples will be removed because of invalidity, improper condition of sampling, insufficient laboratory data, inconsistency and incompatibility between samples (Behnaman, Maghsoudloojafari and Khalili, 2014). The available techniques to evaluate the quality of the samples depend on the type of sample (subsurface / surface). The methods can be also subdivided by whether they are accomplished at the wellsite or at the laboratory. Besides evaluating the representativity of the sample by an experiment, a correlation can provide an estimation of a property (*Chapter 3.3*).

3.1 Quality control of bottom samples

Bottom hole samples quality is tested through composition and pressure comparison at wellsite and at the laboratory (Akpabio, et al., 2015).

3.1.1 Wellsite quality control of bottom hole samples

Firstly, the *opening pressure* of the sampler is compared to the formation pressure at the time of sampling as far as it is an indication of whether any leak or loss occurred during the trip from the bottom of the well up to the surface (Varotsis, 2014). An error of $\pm 2\%$ is acceptable (Varotsis, 1966). Opening pressures depend on the tool design, fluid type, temperature and volume collected (American Petroleum Institute, 2003; American Petroleum Institute, 1966). In the case of SRS then due to pressure compensation, the opening pressure cannot be associated with the bottom hole pressure unless an electronic memory gauge is placed in the sampler to record pressure and temperature throughout the sampling operation.

Another validity check on bottom hole samples is the measurement of *bubble-point pressure* at reservoir or at ambient temperature (Dandekar, 2013). In reality the measurement at reservoir temperature is rarely done. The bubble point pressure at ambient temperature is performed on each sample, while the fluid sample is still in the sampler or after the sample has been transferred to a shipping container. Both methods require a modest equipment set-up including a calibrated hydraulic fluid injection pump and an accurately calibrated pressure measuring device. The saturation pressure comes from the intersection of lines at a plot of volume injected by the pump versus pressure. After considering the temperature effect, it is decided whether to send the sample at the laboratory or not.

3.1.2 Laboratory control of bottom hole samples

To ensure that representative bottom hole samples have been obtained at the laboratory, the bubble point pressure is re-examined while a flash test confirms the present phases (Guidry, 2013).

The *bubble point pressure* is measured by monitoring the compressibility of the oil both at monophasic and diphasic conditions and determining the pressure at which sharp change in the system's compressibility occurs (*Figure 3.1*). To ensure that representative samples have been obtained, at least two (and preferably three) BH samples should have the same bubble point pressure at ambient temperature, within 3 to 4% (Whitson, 1998) or within 2% (American Petroleum Institute, 2003). The calculated bubble point pressure should also be less than the flowing bottom hole pressure if the well has been conditioned properly (McAleese, 2000).

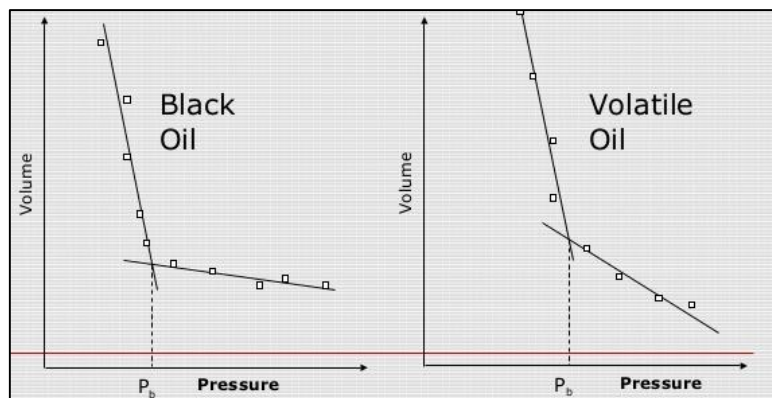


Figure 3.1: Quality check of sample (American Petroleum Institute, 2003).

For a black oil (low volatility), the discontinuity in volume at the bubble point is sharp and the bubble point pressure and volume are easily read from the intersection of the pressure-volume trends in the single-phase and the two-phase regions.

Volatile oils do not exhibit the same clear discontinuity because as the ratio of the gas dissolved in the oil increases and the reservoir temperature approaches the critical temperature of the fluid, the oil becomes more compressible. In that case, the p-V curve is practically continuous in the region of the bubble point. Bostrom, et al. (2005) introduced an ultrasonic method of cavitating fluids at or near their thermodynamic bubble point for bubble point determination. The apparatus includes transducers (to detect bubbles), fluid handling system, electronics and data system and the bubble point is determined by measuring acoustic power and depressurization rate. The cavitated bubbles produce fluctuations in the acoustic properties of the fluid that are detected by measuring the fluctuations of the transducer's electrical properties. The variance of electrical properties increases by orders of magnitude in the presence of bubbles.

A *flash test* is accomplished for the determination of the equilibrium phase compositions (Dandekar, 2013). A large volume of the live single-phase sample is flashed at standard temperature and pressure; the stabilized separated gas and oil phases are analyzed for their composition (chapter 4) and representativity of the original fluid (Pedersen and Christensen, 2007).

The following chart revises the procedure of quality control of bottom hole samples introduced by Pedersen and Christensen (2007):

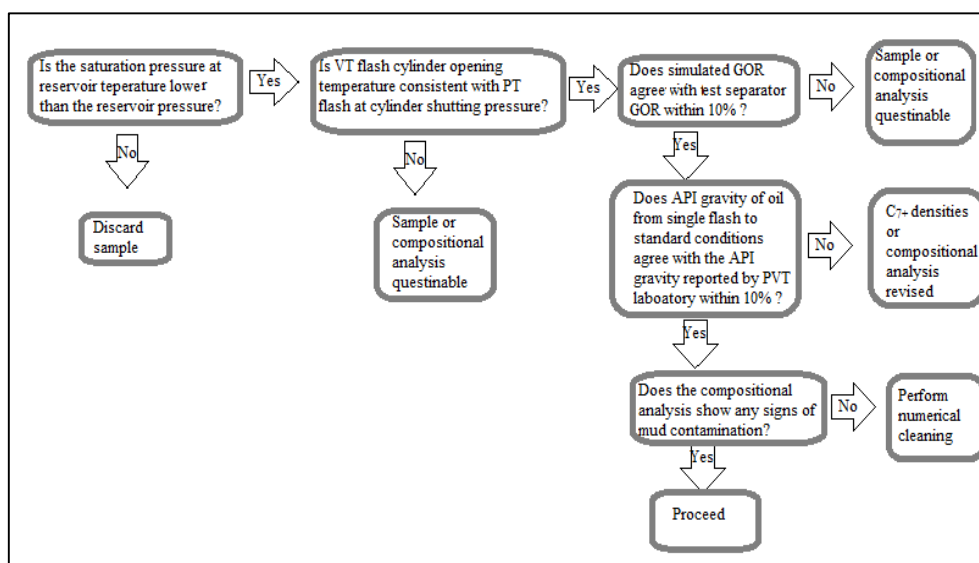


Figure 3.2: Quality control of bottom hole samples (Pedersen and Christensen, 2007).

3.1.3 Recommended transfer procedure of recovered bottom hole samples

The primary concern in transferring a bottom hole sample is to maintain the integrity of the sample during the transfer process (American Petroleum Institute, 1966). The container must be thoroughly cleaned before the transfer of the sample, in order to avoid contamination from trace amounts of heavy components derived from previous use. In addition, the sample composition must not be altered by leaks of hydraulic fluid coming from piston type samplers and by selective absorption of components from the sample into a transfer fluid when they are in direct contact (Pedersen and Cristensen, 2007). The transport of the sample must certify that the fluid in the sampler is maintained in a single-phase condition or, if the fluid is in a two-phase condition, that the entire content of the sampler is transferred. The single-phase state is the preferred situation and can be accomplished by pressurizing and agitating the sample. The vessel of transportation must be under closely controlled temperature and pressure conditions and certified that all applicable transportation safety regulations are satisfied. An irreversible change of fluid that may occur if the conditions aren't controlled is asphaltene precipitation, while reversible ones such as wax precipitation and gas evolution may also happen (Moffatt, n.d.).

3.2 Quality control of separator samples

The separator samples must be examined for the validity of each phase (gas / liquid) and the compatibility between them. The wellsite and laboratory quality control of the separator samples are overviewed.

3.2.1 Wellsite quality control of separator samples

The separator gas phase is subjected to specific gravity measurement through a gravitometer (Ranarex), content of H_2S by the reaction between the gas sample and the reagent contained at a tube, and CO_2 content which is measured by the same manner as for hydrogen sulfide (McAleese, 2000). Also the opening pressure of the gas container can be measured and compared to the separator pressure.

The density of the separator liquid is measured by weighing a precisely known volume of oil. The liquid phase is flashed to atmospheric conditions to collect tank gas and oil, measure GOR and to analyze the two phases by gas chromatography. Also, the opening pressure of the liquid sample can be measured and compared to separator pressure. Lastly, the bubble point pressure of the liquid phase can be determined at ambient temperature. On the rig site, the BS&W is measured by centrifuging the sample (McAleese, 2000). The centrifuge tubes are filled with solvent and sample in ratio 50:50. A demulsifier can also be added if emulsion content is suspected. After centrifuging the tubes the volume of water, sediment and emulsion are read.

3.2.2 Laboratory quality control of surface samples

If phase separation occurs at the sample, then a number of tests can be performed to reveal whether the sampled separator gas and separator oil are representative of the separator pressure and temperature. The sequence of laboratory analysis provided by Nnabuo et al (2014) is described in the following figure:

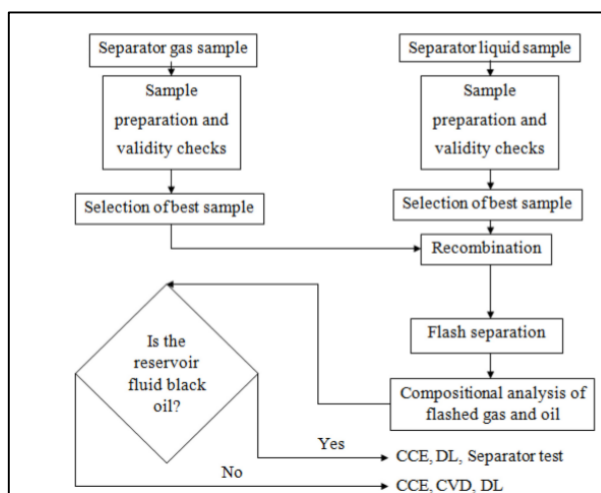


Figure 3.3: Flow diagram for laboratory analysis of separator samples (Nnabuo, et al., 2014).

Firstly each phase of the separator is studied separately.

For separator gas samples, the quality checks should be made when the sample bottles have been heated to, or slightly above, separator temperature (Williams, 1994):

- Determination of opening pressure and comparison to the separator pressure (Varotsis, 2014). The minimum difference value qualifies the best sample (Pedersen and Christensen, 2007).
- Compositional analysis, including air content (minimum air content is desired as far as the presence of air is indicative of poor sampling techniques (Ganzer, n.d.))
- Determination of residual liquids, possibly from carry over

Separator liquids transported with a gas cap must be homogenized by pressurization and agitated. The controls that should be performed are (Williams, 1994; Batzer, 2009):

- Determination of initial opening pressure
- Determination of bubble point pressure at ambient temperature and comparison with separator pressure. If the measured bubble point is within 1-2% of the separator pressure then the oil sample is considered valid (Whitson, 1998).
- Check for presence of sediments or an aqueous or mud phase (through centrifuge)
- Flash separation to give gas / oil ratio (GOR), shrinkage, gas gravity and composition

Afanasyev et al. (2008) state that for quality purposes, the acceptable deviation of measured bubble point from sampling is $\pm 5\%$ and for the dew point $\pm 20\%$. The separator oil and gas should be saturated at separator conditions. So, the bubble point pressure of the oil and the dew point pressure of the gas at separator temperature should be equal to the separator pressure. Expressed differently, the phase envelopes of the separator oil and separator gas should meet at the separator temperature and pressure (Pedersen and Christensen, 2007).

The sequence for validity checks provided by Pedersen and Christensen (2007) is expressed below:

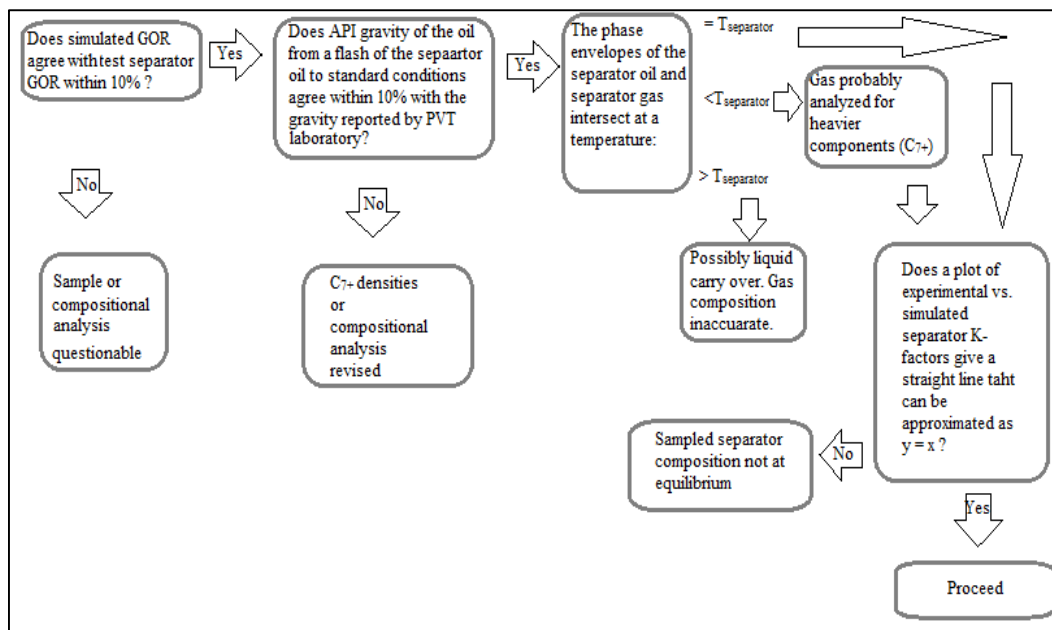


Figure 3.4: Quality control of surface samples (Pedersen and Christensen, 2007).

The separator oil and gas compositions should be checked for their thermodynamic consistency using one of the k value methods, described next.

3.2.2.1 Thermodynamic consistency of separator samples

Equilibrium ratios play a fundamental role in the understanding of phase behavior of hydrocarbon mixtures. They are important in predicting compositional changes under varying temperature and pressure in reservoirs, surface separations, production and transportation facilities. In particular, they are critical for reliable and successful compositional reservoir simulation. Equilibrium ratios, more commonly known as k values, relate the vapor mole fractions, y_i , to the liquid fraction, x_i , of a component i by the expression:

$$k_i = y_i / x_i$$

In a fluid mixture consisted of different chemical components at high pressure, k values are dependent on pressure, temperature and composition of the mixture, while for lower pressure k values are independent of composition (Whitson and Brulé, 2000). There are several methods for determining equilibrium ratio, most of which demand critical properties and acentric factor (PETE 310, n.d.). The most well known methods are (Younger, 2004):

- Plot of k value of different components versus Hoffman factor or second order of critical temperature (*Subchapter 3.2.2.1, 3.2.2.1.2*). Then compare the tendency of the line with the anticipated behavior. In *Figure 3.5* Moffatt (n.d.) visualizes some trends at a k plot.
- Correlations such as Standing (*Subchapter 3.2.2.1.3*) and Galimberti (*Subchapter 3.2.2.1.4*)
- Data Book along with the proper convergence pressure (*Subchapter 3.2.2.1.5*)
- An equation of state for both vapor and liquid phase (*Subchapter 3.2.2.1.6*)

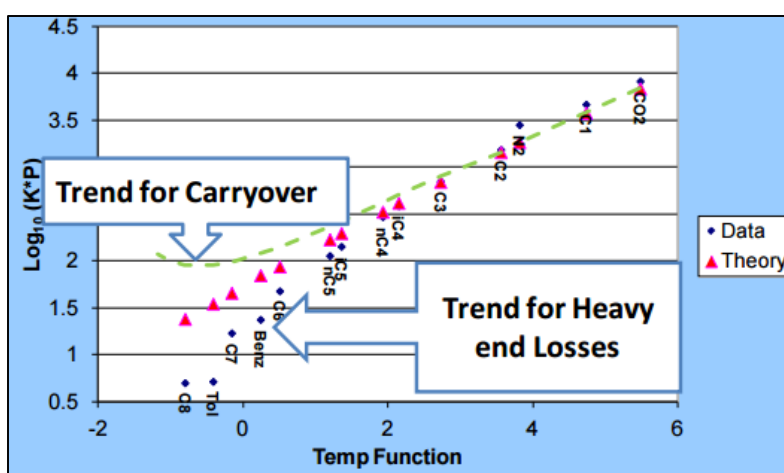


Figure 3.5: k plot (Moffatt, n.d.).

For black oils, simple k value correlations are accurate but volatile oils have more complex behavior as far as small changes in the pressure and temperature, lead to an incremental change of fluid composition (PETE 310, n.d.). For nonhydrocarbon components, Lohrenz et al. (1963) reported k values for H_2S , N_2 and CO_2 as a function of pressure, temperature and convergence pressure.

3.2.2.1.1 Hoffman et al. method (Hoffmann, Crump, and Hocott, 1953; Osfouri, et al., 2014; Nnabuo, et al., 2014; Varotsis, 2014; Whitson, 1998; Lawrence and Gupta, 2009; Crump and Hocott, 1953; Akpabio, Isehunwa and Akinsete, 2015; Ahmed, 2007)

Hoffman plot is referred to a qualitative test to evaluate consistency of separator samples through k values. According to Suwono et al. (2012) and Imo-Jack & Emelle (2013) it is a fast and reliable technique. Hoffman, Crump and Hocott published their method in 1953 which utilizes a log-linear plot of k value versus Hoffman factor, F by the expression:

$$\log(k_i \cdot P_{sp}) = A_1 \cdot F_i + A_o$$

Where:

k_i : k value for the i component

F_i : Hoffman factor for the i component given by the expression:

$$F_i = \frac{\log\left(\frac{P_{ci}}{P_{sc}}\right)}{\frac{1}{T_{bi}} - \frac{1}{T_{ci}}} \cdot \left(\frac{1}{T_{bi}} - \frac{1}{T_{sp}}\right)$$

A_1 : intercept at the plot

A_o : slope of the line at the plot

P_{sp} : separator pressure (psia)

P_{sc} : standard pressure (psia)

P_{ci} : critical pressure for the i component (psia)

T_{sp} : separator temperature (°R)

T_{bi} : normal boiling temperature for the i component (°R)

T_{ci} : critical temperature for the i component (°R)

The semi log plot of k_i versus Hoffman factor (F_i) leads to a linear trend for components C_2 until C_6 , as can be seen at *Figure 3.6*. Some curvature might occur for heavier hydrocarbons, but extreme curvature can be indicative of potential data issues, often losses of heavy components in the vapor phase. Light nonhydrocarbons should be close to the behavior of light hydrocarbons, but not necessarily on the same line.

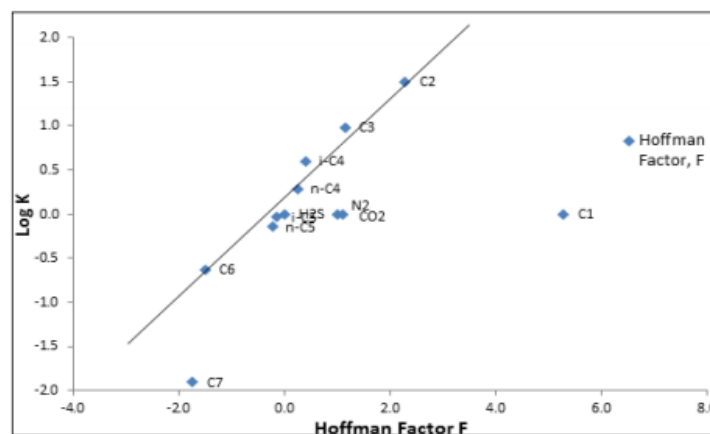


Figure 3.6: Hoffman plot (Akpabio, Isehunwa and Akinsete, 2015).

3.2.2.1.2 Buckley plot

The Buckley plot (Figure 3.7) is expressed by the semi logarithmic plot of k value versus the square of the critical temperature T_c of the reservoir fluid (Akpabio, Isehunwa and Akinsete, 2015). It gives a straight line with negative slope for the light hydrocarbon components and any significant deviation indicates possible non equilibrium separation or numerical errors in the data reporting (Akpabio, Udofia and Ogbu, 2014; Whitson and Brulé, 2000). As a component becomes less paraffinic then the deviation from the linearity becomes greater (Ganzer, n.d.).

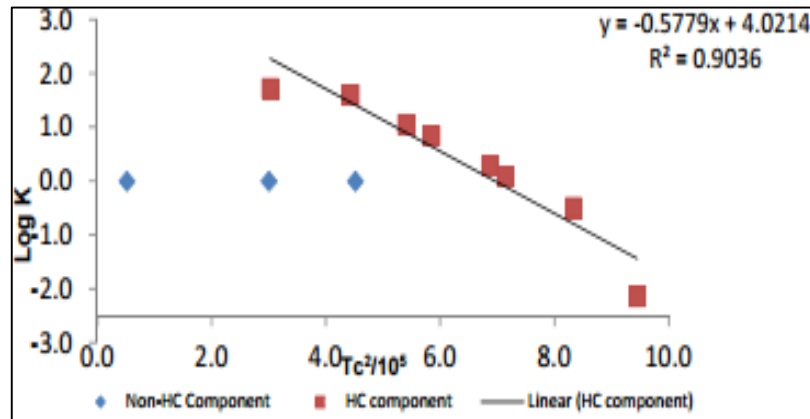


Figure 3.7: Buckley plot (Akpabio, Isehunwa and Akinsete, 2015).

3.2.2.1.3 Standing low pressure k values (Standing, 1979; Whitson and Brulé, 2000; Whitson, 1998)

Standing (1979) uses the Hoffman et al. method to generate a low-pressure k value equation for separator calculations.

$$\log(k_i \cdot P_{sp}) = a_1 \cdot F_i + a_o$$

$$a_o = 0.89 - 1.7 \cdot 10^{-4} \cdot P_{sp} - 3.5 \cdot 10^{-8} \cdot P_{sp}^2$$

$$a_1 = 1.20 + 4.5 \cdot 10^{-4} \cdot P_{sp} + 15.0 \cdot 10^{-8} \cdot P_{sp}^2$$

Where P_{sp} in psia.

The correlations for a_o and a_1 are valid for pressures up to 1,000 psia and temperatures from 500.7 to 662.7 Rankine.

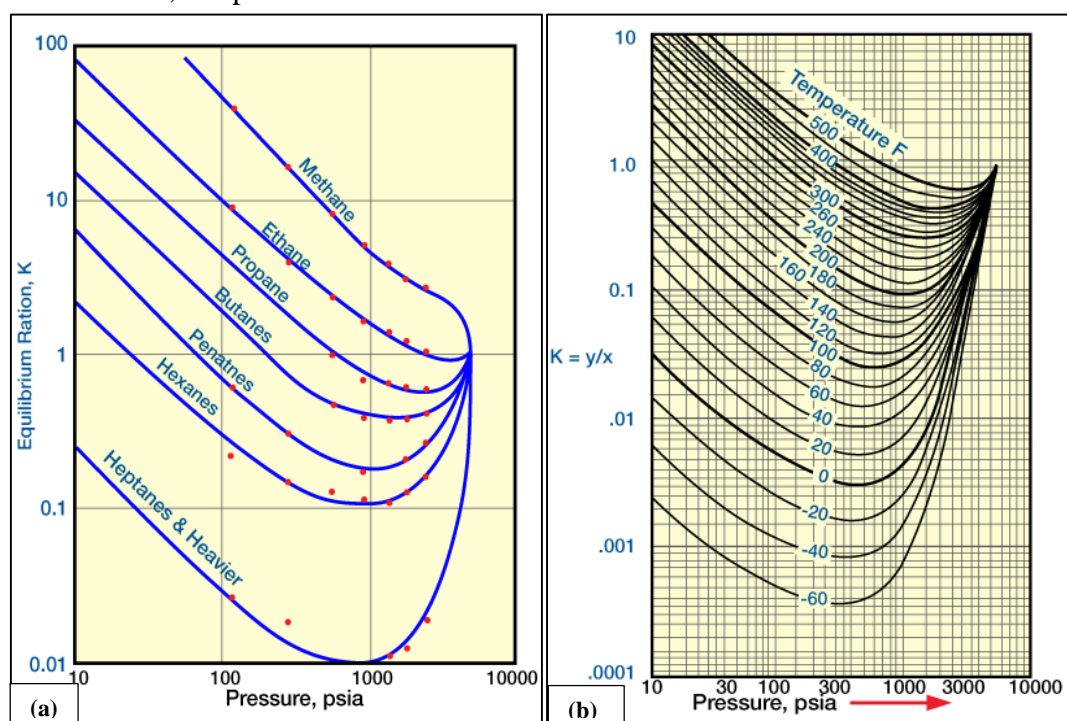
3.2.2.1.4 Galimberti Campbell method

Galimberti and Campbell (1969) suggested another useful approach for correlating k values for several simple mixtures containing hydrocarbons C_1 through C_{10} at pressures up to 3,000 psia and temperatures from 399.7 to 759.7 Rankine. The expression is stated as:

$$\log k_i = A_o + A_1 \cdot T_{c_i}^2.$$

3.2.2.1.5 Convergence pressure (Younger, 2004; Whitson and Brulé, 2000; Ahmed, 2007; Ahmed, 2010; Robinson, 1970; Nichita, Broseta and Montel, 2007; PETE 310, n.d.)

The convergence pressure (P_{conv}) is used as a variable to define the composition dependence of k values. It is a function of overall composition and temperature. When a hydrocarbon mixture of a fixed overall composition is held at a constant temperature as the pressure increases, the equilibrium values of all the components converge toward a common value of unity at certain pressure that is called convergence pressure (*Figure 3.8 (a)*). For a given component the convergence pressure depends only on temperature (*Figure 3.8 (b)*). For a more complex system only one graph of pressure versus $\log k_i$ exists for each component at a given temperature and convergence pressure. Black oils have convergence pressures of about 10,000 psia, volatile oils 7,000 psia and gas condensates 5,000 psia.



**Figure 3.8: (a) Equilibrium ratio for a low shrinkage oil at 200 °F.
(b) Equilibrium ratio for hexane at various temperatures and convergence pressure of 3,000psia.**

The convergence pressure is determined by taking a mixture of pure compounds, subject it to various pressures and temperatures in special cells and determine the composition in the liquid and gas phase. In the literature, several ways are found for the convergence pressure determination:

- Whitson and Michelsen (1989): prediction from EOS, negative flash
- Rzasz et al. (1952): empirical correlation as a function of temperature
- Rowe (1978): trial and error
- Hadden (1953): iterative method based on forming a binary system
- Nichita, Broseta and Montel (2007): negative flash

Working charts of Tables for k factors and convergence pressure are also available in many forms but the most systematic treatment for hydrocarbon systems is the one prepared by the Natural Gas Processors Suppliers Association (NGPSA). Sometimes, in order to find k values for heavy components, it is used an extrapolation to the T_b of the heavy component at a plot of $\log k$ versus $1/T_b$ for various components in the mixture at the system pressure (Whitson and Brulé, 2000).

3.2.2.1.6 Equation of state

Equations of state have appeal for predicting thermodynamic properties because they provide internally consistent values for all properties in convenient analytical forms (Almehaideb, Ashour and El-Fattah, 2003).

The following Table captures the applicability and the origin of some EOS models:

Table 3.2: Some models based on EOS and their applicability (Dahari, et al., 2006).

Model	Origin of model	Applicability of model
Soave Redlich Kwong (SRK)	Redlich Kwong	Vapor pressure curve can be reproduced well
Peng Robinson		Widely used in engineering thermodynamics
Peng Robinson Stryjek Vera	Peng Robinson	Give better predications of liquid densities
Lee Kesler Plocker	Benedict Webb Rubin	Accurate method for non polar substances and mixtures
Zundevitch Jofee	Redlich Kwong	Better prediction of vapor liquid equilibrium
Kabahi Danner	SRK	Improve vapor liquid liquid equilibrium calculations

The original *Benedict Webb and Rubin* equation (BWR) equation (1942) uses eight parameters for each component in a mixture plus a tabular temperature dependence for one of the parameters to improve the fit of vapor pressure data. The equation has difficulty with low temperatures, non-hydrocarbons, non-paraffins, heavy paraffins and in the critical region (Gas Processors Association, 1999; McFee, Mueller and Lielmezs, 1982).

Starling and Powers (1970) has included explicit parameter temperature dependence in a modified BWR equation which is capable of predicting light paraffin k values at cryogenic temperatures.

The **Redlich-Kwong** equation (1949) has the advantage of a simple analytical form which permits direct solution for density at specified pressure and temperature. The equation uses two parameters for each mixture component so they can be determined from critical properties. It is a useful way for predicting k values as far as temperature, acentric factor and the parameter which deals with the combination rule can be empirically varied (Wilson, 1969; Zudkevitch and Joffe, 1970; Spear, Robinson and Chao, 1969). Interaction parameters for non-hydrocarbons with hydrocarbon components are necessary in the Redlich-Kwong equation to predict the k values accurately when high concentrations of non-hydrocarbon components are present.

The **Chao-Seader** correlation (1961) uses the Redlich-Kwong equation for the vapor phase, the regular solution model for liquid mixture non-ideality and a pure liquid property correlation for effects of component identity, pressure and temperature in the liquid phase. The correlation has been applied to a broad spectrum of compositions at temperatures from 409.7 to 759.7 Rankine and pressures to 2,000 psia. The limitations of pressure and temperature have been reviewed by Lenoir and Koppany (1967).

Prausnitz and Chueh (1968) have developed a procedure for high pressure systems employing a modified Redlich-Kwong equation for the vapor and liquid-phase compressibility with a modified Wohl-equation model for liquid phase activity coefficients.

The **Soave Redlich-Kwong** (SRK) (1972) is a modified version of the Redlich-Kwong equation which transforms one of the parameters to a more temperature dependent term. The SRK correlation has improved the accuracy in predicting the saturation conditions of pure substances and mixtures, but it is weak when there is a hydrogen containing mixture (Gas Processors Association, 1999). Also, SRK can predict phase behavior in the critical region.

The **Kabadi-Danner** model (KD) (1985) is a modification of the original SRK equation, enhanced to improve the vapor-liquid-liquid equilibrium calculations for H₂O-hydrocarbon systems, particularly in the dilute regions. The modification is based on an asymmetric mixing rule, whereby the interaction in the water phase (with its strong hydrogen bonding) is calculated based on both the interaction between the hydrocarbons and H₂O, and on the perturbation by hydrocarbon on the H₂O-H₂O interaction (due to its structure).

Peng and Robinson developed a two-constant equation of state in 1976. In this equation, the attractive pressure term of the semi-empirical van der Waals equation has been modified. It accurately predicts the vapor pressures of pure substances and the liquid density (Twu, et al., 1994).

3.3 Empirical correlations (Whitson, 1998; Ahmed, 2007; Ahmed, 2010; Varotsis, 2014; Danesh, 1998; Whitson and Brulé, 2000; Lang and Donohue, 1985; Elmabrouk and Saskatchewan, 2012; Elmabrouk, et al., 2010; Nagi, et al., 2009; Velarde, Blasingame and McCain, 1999; Mignot, 2003; Dandekar, 2013; Archer and Wall, 1986)

In some cases in order to characterize a sample for its representativity, a prediction of some properties is acquired. The frequently used empirical correlations for the prediction of bubble point pressure, oil density, solution gas to oil ratio, oil formation volume factor (FVF) at bubble point, isothermal oil compressibility and viscosity are reviewed in the following sections. The ranges of the most common correlations are presented in the *Table 3.3*.

Table 3.3: Ranges of data in black oil correlations (Danesh, 1998; Mahmood and Al-Marhoun, 1996; Elsharkawy, Eligibaly and Alikhan, 1995).

Correlation	Standing	Lasater	Vasquez-Beggs	Glaso	Al-Marhoun
P_b (psia)	130-7,000	48 – 5,780	15 – 6,055	165 – 7,142	130 – 3,573
Temperature (°F)	100-258	82 - 272	162 – 180	80 - 280	74 - 240
R_s (scf/STB)	20 – 1,425	3 – 2,905	0 – 2,199	90 – 2,637	26 – 1,602
FVF (bbl/STB)	1.024 – 2.15	-	1.028 – 2.226	1.025 – 2.588	1.032 – 1.997
Tank oil gravity API	16.5 – 63.8	17.9 – 51.1	15.3 – 59.5	22.3 – 48.1	19.4 – 44.6
Gas specific gravity, γ_g	0.59 – 0.95	0.574 – 1.22	0.511 – 1.351	0.65 – 1.276	0.752 – 1.367
N₂ in surface (mole%)	0.0	0.0	-	-	0.0 – 3.89
CO₂ in surface (mole%)	<1.0	0.0	-	-	0.0 – 16.38
H₂S in surface (mole%)	0.0	0.0	-	-	0.0 – 16.3
Separator temperature (°F)	100 - 258	36 - 106	76 - 150	80 - 280	-
Separator pressure (psia)	265-465	15 - 605	60 - 565	415	-

3.3.1.1 Bubble point pressure

The bubble point pressure is required for most oil property calculations and can be estimated by the following correlations:

- *Standing (1947)*: It is based on 105 experimentally determined data points from 22 different California crude oil – gas mixtures. The correlation should be considered valid only for black oil systems with trace components of any non-hydrocarbon components.

$$P_b = 18.2 \cdot \left[\left(\frac{R_s}{\gamma_s} \right)^{0.83} \text{antilog}(0.00091 \cdot T - 0.125 \cdot ^\circ API) - 1.4 \right]$$

- *Lasater (1958)*: It is based on 158 experimentally determined data points from different crude oil systems.

$$P_b = P_f \cdot \frac{T + 459.67}{\gamma_g}$$

$$\gamma_g = \frac{\frac{R_s}{379.3}}{\frac{R_s}{379.3} + \frac{350\gamma_o}{M_o}}$$

Where P_f and M_o are found from figures.

- *Vazquez and Beggs (1980)*: They worked on a gas saturated crude based on 6,004 data points divided into two groups according to the relative volatility (API).

$$P_b = \left\{ \frac{C_1 \cdot R_s}{\gamma_{gs}} \text{antilog} \cdot \left[\frac{-C_3 \cdot ^\circ API}{T + 459.67} \right] \right\}^{1/C_2}$$

$$\gamma_{gs} = \gamma_{gp} [1.0 + 5.912 \cdot 10^{-5} \cdot ^\circ API \cdot T_{sp} \cdot \log(P_{sp}/114.7)]$$

Where the coefficients are found based on $^\circ API$

- *Glasø (1980)*: Glasø analyzed data from 26 different crude oil systems, primarily from the North Sea region with UOP characterization factors of about 11.9. The approach is based on the concept that the paraffinicity of the oil influences the gas - liquid equilibrium of black oil mixtures containing methane. Using graphical methods and regression analysis Glasø provided the relation presented below.

$$P_b = \text{antilog} \left\{ 1.7669 + 1.7447 \cdot \log \left[\left(\frac{R_s}{\gamma_s} \right)^{0.816} \frac{T^{0.172}}{^\circ API^{0.989}} \right] - 0.30218 \cdot \left[\log \left[\left(\frac{R_s}{\gamma_s} \right)^{0.816} \frac{T^{0.172}}{^\circ API^{0.989}} \right] \right]^2 \right\}$$

- *Al Mahroun (1988)*: He used nonlinear multiple regression analysis through 160 bubble point data from Middle East oil samples.

$$P_b = C_1 \cdot R_s^{C_2} \cdot \gamma_g^{C_3} \cdot \gamma_o^{C_4} \cdot (T + 459.67)^{C_5}$$

Where C_1, C_2, C_3, C_4 and C_5 are found through Tables.

In the literature, many scientists compare the available methods through average percent relative error (ARE), arithmetic average of the absolute values of the relative error (AARE), correlation determination (R^2) and root mean square error (E_{RMS}), as for *Figure 3.9*.

Model	ARE%	AARE%	R^2	E_{RMS}
Current study (2014)	-0.110	15.555	0.8787	418
Valkó and McCain (2003)	-0.909	16.968	0.8724	427
Arabloo et al. (2014)	4.662	17.977	0.8399	506
Al-Shammasi (2001)	-2.590	18.088	0.8520	472
Ikiensikimama and Ajienka (2012)	-3.168	18.928	0.8700	432
Standing (1947, 1981)	-3.389	19.053	0.8703	431
Velarde et al. (1999)	-2.613	19.173	0.8609	446
Nikpoor and Khanamiri (2001)	9.143	20.523	0.7669	610
Dindoruk and Christman (2004)	-2.679	21.739	0.8373	493
Vazquez and Beggs (1980)	-13.446	21.962	0.8718	465
Malallah et al. (2006)	3.828	22.559	0.8451	510
Kartoatmodjo and Schmidt (1994)	-11.187	23.040	0.8518	515
Riyahin et al. (2014)	10.445	23.553	0.8261	546
Asodeh and Kazemi (2013)	-10.940	23.702	0.8506	464
Al-Marhoun (1988)	-1.132	23.932	0.8187	595
Levitan and Murtha (1999)	1.933	24.584	0.7974	561
Lasater (1958) through Beggs (1987)	-17.336	24.763	0.8749	431
Dokla and Osman (1992)	-5.335	25.654	0.7258	627
Glaso (1980)	-15.401	25.696	0.8378	556
Boukadi et al. (2002)	8.145	26.304	0.7701	662
Almehaideb (2003)	-0.881	31.062	0.7877	582
Elsharkawy and Alikhan (1997)	18.133	32.156	0.7103	815
Khamehchi et al. (2009)	-27.713	33.013	0.8190	700
Khairy et al. (1998)	-12.434	34.622	0.7217	633
Macary and El-Batanoney (1993)	-22.435	38.134	0.7948	562
Obomanu and Okpobiri (1987)	-46.003	58.651	0.7720	1913
Patil et al. (2014)	31.826	60.719	0.4131	1442
Petrosky and Farshad (1998)	40.449	61.077	0.8695	597

Figure 3.9: Comparison of correlations for bubble point pressure prediction (Jarrahian, et al., 2014).

3.3.1.2 Oil density

Several reliable methods are available to determine the density of saturated crude oil mixtures from the compositions. The most widely used calculation methods are:

- *Standing and Katz (1942)* developed the correlation from evaluating experimental, compositional and density data on 15 crude oil samples containing up to 60 % mol methane. They correlated graphically the liquid density of methane and ethane with the density of the system. The crude oil density (ρ_o) is corrected for compressibility ($\Delta\rho_p$) and thermal expansion ($\Delta\rho_\tau$) as: $\rho_o = \rho_{sc} + \Delta\rho_p - \Delta\rho_\tau$
- *Alani – Kennedy 's method (1960)* developed an equation to determine the molar liquid volume, V_m , of pure hydrocarbons over a wide range of temperatures and pressures. Their equation is similar in form to the Van der Waals equation and has the form: $V_m^3 - \left[\frac{R \cdot T}{P} + b \right] \cdot V_m^2 + \frac{a \cdot V_m}{P} - \frac{a \cdot b}{P} = 0$
- Schlumberger chart that gives graphically the oil density given the R_s , B_o , γ_o and γ_g (Mignot, 2003).

3.3.1.3 Bubble point Oil Formation Volume Factor (B_{ob})

Correlations for the formation volume factor of a saturated crude oil at the bubble point have been developed by:

- *Standing (1947)*

$$B_{ob} = 0.972 + 1.47 \cdot 10^{-4} \cdot \left[R_s \cdot \left(\frac{\gamma_g}{\gamma_o} \right)^{0.5} + 1.25 \cdot T \right]^{1.175}$$

- *Vazquez and Beggs (1980):*

$$B_{ob} = 1.0 + C_1 \cdot R_s + C_2 \cdot \frac{^\circ API}{\gamma_{gs}} \cdot (T - 60) + C_3 \cdot \frac{^\circ API}{\gamma_{gs}} \cdot (T - 60) \cdot R_s$$

Where C_1 , C_2 and C_3 are found based on $^\circ API$.

- *Glasø (1980):*

$$B_{ob} = 1 + \text{antilog} \left\{ -6.58511 + 2.91329 \cdot \log \left[R_s \left(\frac{\gamma_g}{\gamma_o} \right)^{0.526} + 0.968 \cdot T \right] - 0.27683 \cdot \left(\log \left[R_s \left(\frac{\gamma_g}{\gamma_o} \right)^{0.526} + 0.968 \cdot T \right] \right)^2 \right\}$$

- *Al Mahroun (1996):* He updated his work by more data points from all over the world (4,012).

$$B_{ob} = 1.0 + C_1 \cdot R_s + C_2 \cdot R_s \cdot \frac{\gamma_{gs}}{\gamma_o} + C_3 \cdot (1 - \gamma_o) \cdot (T - 60) \cdot R_s + C_4 \cdot (T - 60)$$

3.3.1.4 Solution GOR

The solution GOR is the ratio of the volume of gas that comes out of solution to the volume of oil at standard conditions. The most well known correlations are:

- *Standing (1947):*

$$R_s = \gamma_g \cdot \left[\left(\frac{P_b}{18.2} + 1.4 \right) \cdot \text{antilog}(0.125 \cdot ^\circ API - 0.00091 \cdot T) \right]^{1.2048}$$

- *Lasater (1958):*

$$P_f = \frac{P_b \cdot \gamma_g}{T + 459.67} \text{ and } R_s = \frac{132,755 \cdot \gamma_o \cdot \gamma_g}{M_o \cdot (1 - \gamma_g)}$$

Where γ_g and M_o are determined from figures.

- *Vasquez and Beggs (1980)*

$$R_s = \frac{\gamma_{gs} \cdot P_b^{C_2}}{C_1} \text{antilog} \left[\frac{C_3 \cdot ^\circ API}{T + 459.67} \right]$$

Where the coefficients are found based on $^\circ API$

- *Glasø (1980):*

$$R_s = \gamma_g \left\{ \left[\text{antilog}(2.8869 - (14.1811 - 3.3093 \cdot \log P_b)^{0.5}) \right] \cdot \frac{^\circ API^{0.989}}{T^{0.172}} \right\}^{1.2255}$$

3.3.1.5 Isothermal compressibility

The isothermal compressibility of a single-phase fluid is defined as the volumetric change when pressure is changed and temperature held constant:

$$C_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$$

The partial of volume with respect to pressure is negative reflecting that an increment in pressure gives a decrease in volume. The magnitude of the isothermal compressibility increases with increasing temperature and diminishes with increasing pressure (Macias-Chapa, 1985). The applications that is mostly used are: instantaneous or tangent values from equations, extension of fluid properties from values higher than the bubble point, material balance equations and reservoir simulation (Spiney, Valko and McCain, 2007). The errors that may appear from wrong use of correlation can be as high as 25 % (Spiney, Valko and McCain, 2007). Different correlations for compressibility have been developed for gas, oil, water (brine) and multi-phase systems (Aseng, 2006). The expressions make use of: P (psi), T (°F), R_s (scf/STB), γ_{gs} (gas specific gravity that would result from separator conditions of 100 psi), γ_o (relative to water density) in order to calculate γ_{ob} (bubble point relative density) and isothermal oil compressibility C_o (psi^{-1}). The most basic techniques are presented below:

- *Calhoun (1947)*: There is a single value for the undersaturated isothermal oil compressibility for all pressures above the bubble point and is derived graphically.

$$\gamma_{ob} = \frac{\gamma_o + 2.18 \cdot 10^{-4} \cdot \gamma_g \cdot R_s}{B_o}$$

- *Trube (1957)* used pseudoreduced pressure and temperature to determine undersaturated oil compressibility graphically.

$$T_r = \frac{T+459.67}{T_c}, P_r = \frac{P}{P_c}, C_o = \frac{C_r}{P_c}$$

- *Vazquez and Beggs (1976)*:

$$C_o = \frac{-1433.0 + 5.0 \cdot R_s + 17.2 \cdot T - 1180.0 \cdot \gamma_{gs} + 12.61 \cdot ^\circ API}{P \cdot 10^5}$$

- *Al-Marhoun (2003)* presented a new correlation from middle East PVT reports.

$$C_o = -14.1042 + \frac{2.7314}{\gamma_{ob}} - \frac{56.0605 \cdot (P - P_b)}{\gamma_{ob}^3} - \frac{580.8778}{T + 459.67}$$

3.3.1.6 Oil viscosity

For the determination of oil viscosity, correlations are mostly used as far as EOS cannot predict viscosity well and PVT laboratories measure liquid viscosities to $\pm 5\%$ (Moffatt, n.d.). Oil viscosity is generally determined by first calculating the deal oil viscosity (no solution gas) and using that value to obtain the viscosity of the oil at the bubble point (Lang and Donohue, 1985). The *Figure 3.10* shows the Average Absolute Relative Deviations (AARD), R^2 (Squared correlation coefficients) and Root Mean Square Error (RMSE) for the most common correlations.

Author	AARD, %	R^2	RMSE
Beal [9]	891	0.1088	83.14
Beggs and Robinson [10]	217	0.0376	245.05
Glaso [11]	33.41	0.9270	3.84
Kaye [12]	52.05	0.2268	10.19
Al-Khafaji et al. [13]	29.97	0.7283	6.04
Petrosky [14]	41.62	0.8695	4.18
Egbogah and Ng [15]	55.60	0.9208	3.26
Labedi [16]	178	0.3910	14.95
Kartoatmodjo and Schmidt [17]	36.89	0.9065	4.50
Bennison [18]	70.97	0.6689	12.25
Elsharkawy and Alikhan [5]	72.92	0.9065	13.25
Hossain et al. [19]	68.92	0.6000	16.24
Naseri et al. [4]	27.57	0.8233	3.88
Alomair et al. [20]	72.42	0.8275	6.36
LSSVM Model (this study)	21.2	0.955	1.82

Figure 3.10: Comparison between the performances of common correlations for prediction of dead oil viscosity (Hemmati – Sarapardeh, et al., 2014).

Dead oil

- *Beal (1970)* $\mu_{od} = (0.32 + \frac{1.8 \cdot 10^7}{\text{°API}^{4.53}}) \cdot (\frac{360}{T+200})^a$

Where $a = \text{antilog}(0.43 + \frac{8.33}{\text{°API}})$

- *Glasø (1980)* $\mu_{od} = (3.141 \cdot 10^{10}) \cdot T^{-3.444} (\log \text{°API})^{10.313 \cdot \log T - 36.447}$

- *Beggs and Robinson (1975)* $\mu_{od} = 10^A - 1$

$A = B \cdot T^{-1.163}$, $B = 10^C$, $C = 3.0324 - 0.02023 \cdot \text{°API}$

At the bubble point

- *Beggs and Robinson (1975)* $\mu_{ob} = a \cdot (\mu_{od})^b$

Where: $a = 10.715 \cdot (R_s + 100)^{-0.515}$, $b = 5.44 \cdot (R_s + 150)^{-0.338}$

- *Chew and Connally (1959)* $\mu_{ob} = a \cdot (\mu_{od})^b$

Where: $a = 0.20 + 0.80 \cdot \text{antilog}(-0.00081 \cdot R_s)$

$b = 0.43 + 0.57 \cdot \text{antilog}(-0.00072 \cdot R_s)$

Undersaturated oil

- *Beal (1970)* $\mu_o = \mu_{ob} + 0.001 \cdot (P - P_b) \cdot (0.024 \cdot \mu_{ob}^{1.6} + 0.038 \cdot \mu_{ob}^{0.56})$

- *Vazquez and Beggs* $\mu_o = \mu_{ob} \cdot (\frac{P}{P_b})^m$

Where $m = 2.6 \cdot P^{1.187} \text{antilog}[(-3.9 \cdot 10^{-5}) \cdot P - 5.0]$

In the literature, several correlations were found for predicting viscosity based on the origin of the oil. For example, Alomair, et al. (2014) studied the Kuwaiti heavy crude oil, Mendoza de la Cruz, et al. (2013) the Mexican heavy dead crude oil, El-hoshoudy, et al. (2013) the Egyptian oil, Frashad, et al. (1996) the Colombian crude oil and Hemmati-Sarapardeh et al.. (2013) the Iranian oil. Also, many reports are found that compare the correlations for particular crude oils such as from the Middle East (Al-Mahroun, 2004), Kuwaiti (Elsharkawy, Eligibaly and Alikhan, 1995), Pakistani (Mahmood and Al-Marhoun, 1996), Iraqi (Hassan, 2011), Niger Delta (Ikiensikimama and Ajenka, 2012) and Illinois (Sim, 1993).

3.4 Conclusions

In order to obtain trustworthy fluid properties, the quality of the samples must be examined carefully. The validation process described at chapter 3 enhances the quality and confidence in PVT study data. Inadequate checking of sample quality or simple errors in recorded data can lead to PVT studies that are useless or even misleading, and this could have important financial penalties.

3.5 Bibliography

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4. Laboratory analysis of the recovered samples

The samples are taken to evaluate the properties of produced fluids at reservoir conditions, in the production tubing, surface separation facilities and in pipeline transportation after having been examined for their quality (Batzner, 2009). The analysis of reservoir fluids is conducted at specialized laboratories that have expensive equipment and well trained personnel. The study of the properties is called PVT study from the basic thermodynamic properties: Pressure, Volume and Temperature. The key properties to be determined for a reservoir fluid include (Whitson, 1998):

- Original reservoir composition(s)
- Saturation pressure at reservoir temperature
- Oil and gas densities
- Oil and gas viscosities
- Shrinkage (volume) factors of oil and gas from reservoir to surface conditions

The PVT measurement accuracy of some properties is presented at the *Figure 4.1*.

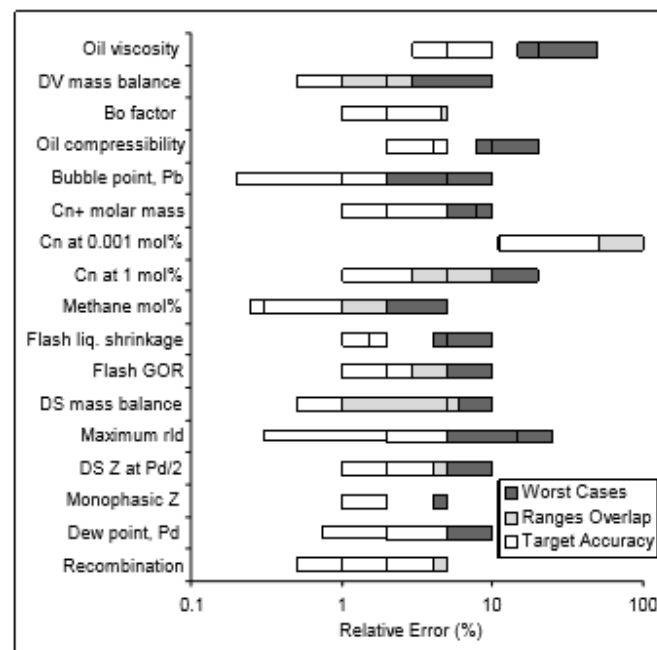


Figure 4.1: Commercial PVT measurement accuracy (Moffatt and Williams, 1998).

Depending on the nature of the sample the following laboratory analyses are recommended (S: Standard, P: Can be performed, N: Not performed):

Table 4.1: Laboratory analysis for oils and gas condensates (Whitson, 1998; Whitson and Brulé, 2000).

Laboratory Analysis	Oils	Gas Condensates
<i>Standard</i>		
Bottom hole Sample Composition	S	P
Recombined Separator Composition	P	S
C ₇₊ TBP Distillation	P	P
C ₇₊ Simulated Distillation (SIMDIS)	P	P
Constant Composition Expansion	S	S
Multistage Surface Separation	S	P
Differential Liberation	S	N
Constant Volume Depletion	P	S
<i>Special</i>		
Multicontact Gas Injection	P	P
Wax Point Determination	P	P
Asphaltene Precipitation	P	P
Slimtube Analysis (MMP / MME)	P	P
Water analysis (salinity, salt composition, solution gas ratio R _{sw} and solution gas composition, water FVF B _w , density)	P	P

The most usual reported properties found per PVT analysis can be summarized in the next Table:

Table 4.2: Properties per PVT analysis test.

PVT test Property	Multistage separator test	CCE	DV	CVD	Viscosity
Composition	x (gas)		x (gas)		
Bubble point pressure		x		x	
Density	x (tank, separator liquid, separator gas)	x	x (residual)	x (residual)	
Residual oil volume	x		x	x	
Isothermal oil compressibility		x (undersaturated)			
Specific gravity of removed gas	x		x		
GOR	x		x (solution GOR)		
B _o	x		x		
Gas formation volume factor B _g			x		
Gas z factor		x (undersaturated)	x	x	
Viscosity	x (gas)		x (gas)		x

4.1 Compositional Analysis

This section discusses how compositions are determined. The standard components quantified in petroleum reservoir fluids include (Whitson, 1998):

- Non-Hydrocarbons: N_2 , CO_2 , H_2S
- Hydrocarbons: C_1 , C_2 , C_3 , iC_4 , nC_4 , iC_5 , nC_5 , C_{6s} , C_n (n takes values from 7 to 35, depending on the instrument)

Compositional analysis of the reservoir sample, has several application in reservoir and production engineering (Freyss, et al., 1989; CoreLab, n.d.):

- Reservoir fluid behavior modelling and prediction of its physical properties
- The design of the refinery
- Existence of corrosive compounds such as H_2S
- Fingerprint analysis
- Contamination of reservoir fluid by drilling mud

The usual ways of determining composition is given at *subchapter 4.1.1* and *4.1.2* (chromatography and True Boiling Point distillation), while an overview of the compositional analysis for bottom hole, recombined and contaminated samples follows.

4.1.1 Chromatographic analysis

The composition of an oil sample is routinely determined by gas chromatography (GC). Nevertheless, it is limited when a complete analysis of stock tank oil that contain heavy alkanes (C_{20+}) and asphaltenes is desired (Freyss, et al., 1989). It is based on the selective separation of components as temperature is increased in a column. The sample is injected to the GC, is punctually vaporized in the injector and is driven by a carrier gas such as helium or nitrogen inside the chromatographic column. Due to the increase of temperature and the differential adsorption of the components on the stationary phase, the lighter components separate and move together with the carrier gas to a flame ionization detector (FID) or thermal conductivity detector (TCD) (Whitson, 1998). At the detectors, the eluted components are characterized for their concentration. The components are identified by comparing their retention time at the column with known previously analyzed components at the same GC conditions. The size of a chromatographic peak is proportional to the amount of material contributing to that peak, and is quantified by the measurement of the height of the peak or the measurement of the area under the detector response–retention time curve. The most usual way in determining the composition is the measurement of the area by computer or electronic integrators (Grob and Kaiser, 2004).

The analysis of the low boiling components is relatively straightforward because the majority of the components can be easily identified and analyzed by GC. However, other components are eluted as a continuous stream of overlapping peaks. The components detected by a GC between two neighboring normal alkanes are usually grouped together, measured and reported as a pseudo fraction or an SCN equal to that of a higher normal alkane. The molecular weight of the SCN group is found through material balances, while other properties from literature and TBP distillation (Dandekar, 2013).

As soon as the carbon number increases, many more isomers begin to appear on a chromatogram and the retention time is increased. Very heavy boiling-point components cannot be eluted; hence, they cannot be detected by GC. However, this amount of material remaining in the column must be accounted for to determine the overall composition of the fluid. The common method of estimating the non eluted fraction is to use an internal standard, where one or few fully detectable compounds, preferably not present in the oil, are added to the oil at a known mass ratio. The comparison of mass ratio as detected by GC with that of gravimetrically prepared mixture, gives an indication of the amount of non eluted fractions (Danesh, 1998). This method, known as spiking, relies on certain limiting assumptions which may lead to large deviations in measured concentration of non eluted fractions. To accurately quantify the non detectable heavy end, the following mass balance equation was proposed by Burke et al. (1991):

plus fraction = mass of sample injected – sum of mass of detectable components

Lastly, there is also the option of continuous function to describe the component molar distribution (exponential distribution or gamma distribution) and extending the measured concentration of eluted fractions to determine the non eluted part (Danesh, 1998). The characterization of the molecular weight and density of the heavier fraction is explained at *Subchapter 4.1.3*.

Nowadays, a more sophisticated gas chromatographic technique is the Capillary gas chromatography and is used to analyze petroleum fluids up to C₃₅. Capillary gas chromatography has high resolution and little flow resistance, so the column can be longer than the normal GC and identify more components (Pasadakis, 2015; Dandekar, 2013).

Also, GC with mass spectroscopy (GC – MS) has been widely practiced in the oil business. This technique helps to identify the amount and type of compounds present in an ionized sample by measuring the mass-to-charge ratio. Low fragmentation ionizing techniques are the key for producing molecular ion spectra. Also the Electrospray Ionization (ESI) has received particular interest in recent years (Zhan and Fenn, 2000) since ESI led to a Nobel award in 2002. At Electrospray Ionization, the ions are produced directly from sample solutions exposed to an electrical field and dispersed into tiny charged droplets.

High molecular weight and low volatility of the target compounds can make the use of GC difficult so, liquid chromatography may be preferred which uses instead of carrier gas, a carrier liquid. The High Performance Liquid Chromatography (HPLC) is very useful for the separation of oil fractions containing functionalized compounds (Pasadakis, 2015). In HPLC, the mobile phase is a liquid, and the compounds in a sample can be separated according to their affinity for the stationary phase (column material) and the liquid mobile phase (Borgund, 2007).

4.1.2 True boiling point distillation

The true boiling point (TBP) distillation separates an oil into cuts or fractions according to the range of boiling points used for separation. To avoid decomposition of the oil during distillation, vacuum is applied in four stages to reduce the distillation temperatures for heavier components (Whitson, 1998). The distillation usually proceeds from C₇ (or C₉) to about C₂₅, plus a residue (~C₂₆₊). Because the separation of components in a given distillation cut is only approximate, some overlap can be observed. It can be corrected though, to yield an ideal distillation curve.

After completion of the distillation process, sample vials are removed from the fraction collector and weighed to determine the mass of the distilled fractions. The mass of the residue is determined from the difference between the mass of the distillation flask containing the residue and mass of the empty distillation flask. The density can be measured using an oscillating tube densitometer while the molecular weight through a freezing point depression apparatus (Dandekar, 2013). The cryoscopic method of freezing point depression is sensitive to error and probably reliable at best to about ± 2 to 5% (Whitson, 1998). Average boiling points are taken from the Tables of Katz and Firoozabadi (1978) while the critical properties can be found from Tables in literature (Pedersen and Cristensen, 2007). Another way to determine the critical properties and acentric factors is to estimate them from correlation based on boiling points and measured specific gravities.

Other methods for compositional analysis that have been found in the literature are:

- Fractionation in a low or high temperature fractionating column and mass spectroscopy (Lang and Donohue, 1985)
- Simulated distillation technique (SIMDIS) that identifies hydrocarbon in the order of their boiling points (Hussein, et al., 2006). Simulated distillation results can be calibrated against TBP data, thus providing physical properties for the individual fractions.
- Microdistillation technique: Varotsis N. and Guieze P. have developed a fast and fully automated microdistillation technique (Freys, et al., 1989).

4.1.3 Determination of heavy end's properties (Hussein, et al., 2006; Freyss, et al., 1989; Lang and Donohue, 1985)

Before explaining the procedure of reporting the composition of various samples (bottom hole, recombined, contaminated) it is worth mentioning how the molecular weight and the specific gravity of the heavy end are quantified.

The density of the heavy end can be measured by a standard glass pycnometer or by a digital density meter. The standard glass pycnometer was suggested by Rogel and Carbognani (2003) for the density determination of a heavy end such as asphalt, bitumen and asphalt cement. The procedure is as follows. Firstly, a standard amount of the sample is placed at the pycnometer and a certain volume of the displacing fluid (usually n-Heptane) is added. By measuring the volume of the sample as the difference between the pycnometer volume and the n-heptane, the density can easily determined. On the other hand, Klug-Santner & Hold (2012) and Hookey (n.d.) proposed a digital density meter based on the ASTM method D4052 for heavy ends such as gasoline, diesel, jet fuel, waxes and lubricating oils. The density of the heavy end, for comparison reasons, can also be estimated by correlations. In more details, the specific gravity of the heavy end can be calculated from Soreide's correlation (1989) and Whitson's method (1980, 1984) (Whitson proposed a technique for characterizing the plus fraction that will estimate specific gravities for petroleum fractions using molecular weights and a correlation for the Watson characterization factor, K_w).

The molecular weight of the heavy end can be determined by:

- TBP data: requires large amounts of sample and long analysis responses
- Back-calculated if the molecular weight of surface oil is found. It is the most usual technique.
- Gas Chromatography Simulated Distillation (GCSD) (Carbognani, et al., 2012): A short column coated with an apolar stationary phase allows analytes to elute roughly based on their boiling points. Van der Waals are the main responsible forces retaining analytes over apolar stationary phases. The sample molecules are expected to elute roughly as a function of their molecular weights, since boiling point are a function of molecular weight. However, it has been proved that elution is affected also by other type of interactions, so, GCSD is not a very common technique.
- High Temperature Simulated Distillation (HTSD) (Carbognani, et al., 2012; Whitson and Brulé, 2000): HTSD report the distillation curve and other qualitative and quantitative outputs (*Figure 4.2*) such as qualitative chromatographic trace, distilled fractions cumulative report based on average carbon numbers assigned to the distillates and %wt determined for each carbon number interval (directly connected to molecular weight).

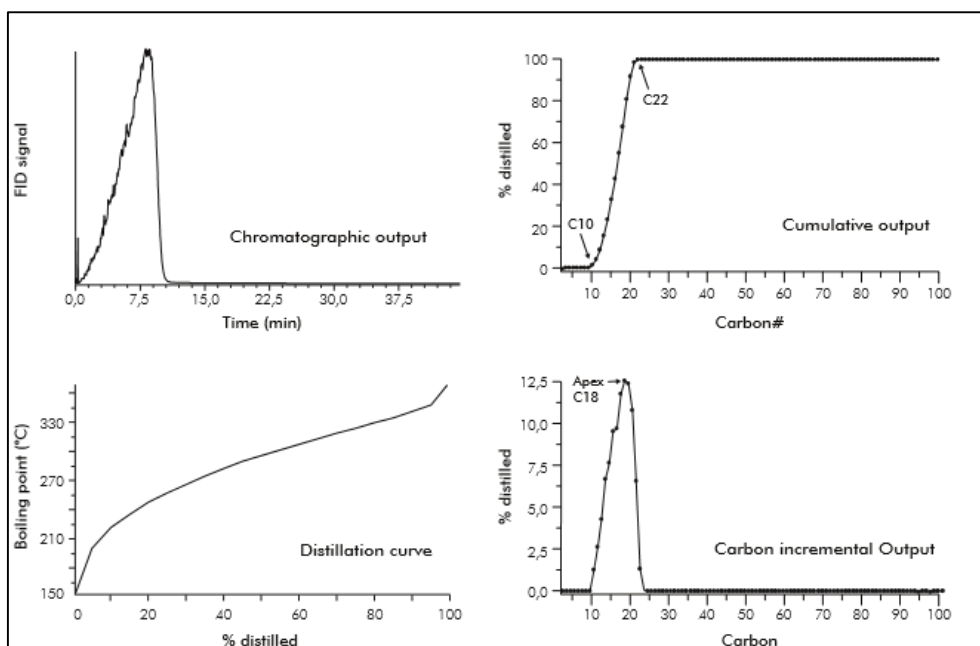


Figure 4.2: High Temperature Simulated Distillation Output.

The measured molecular weight for the plus fraction can have an error of as much as 20% (Al-Meshari, 2004) and its validity can be checked by correlations. The most usual ones are given below:

- Kesler and Lee (1976) introduced correlations for molecular weight, critical pressure, critical temperature and acentric factor to improve enthalpy predictions.
- Katz and Firoozabadi (1977) introduced generalized properties of SCN fractions, including molecular weights, specific gravities and normal boiling points.
- Whitson (1980) proposed a three parameter gamma probability distribution function to describe the relation between mole fraction and molecular weight of SCN components of the plus fraction.
- Whitson, Anderson & Soreide (1988) and Manafi, Mansoori & Ghotbi (1999) estimated the molecular weight after implementing a gamma function for the molecular weight distribution function.
- Ahmed, Cady and Story (1984) proposed a method of extending molar distribution.
- Riazi and Daubert (1987) developed a set of equations to evaluate properties (molecular weight, critical properties, acentric factor) by giving specific gravity and boiling point.
- Guo and Du (1989) introduced a molar distribution and compared critical properties.
- Riazi and Al-Sahhaf (1996) provided equations for calculating boiling point, molecular weight, density, specific gravity, critical properties, acentric factor, etc.
- Riazi (1997) developed a simple distribution function for the molecular weight distribution.
- Other correlations presented at Schneider (1998), Naji (2010), Whitson and Brulé (2000), etc.

4.1.4 Composition of bottom hole sample

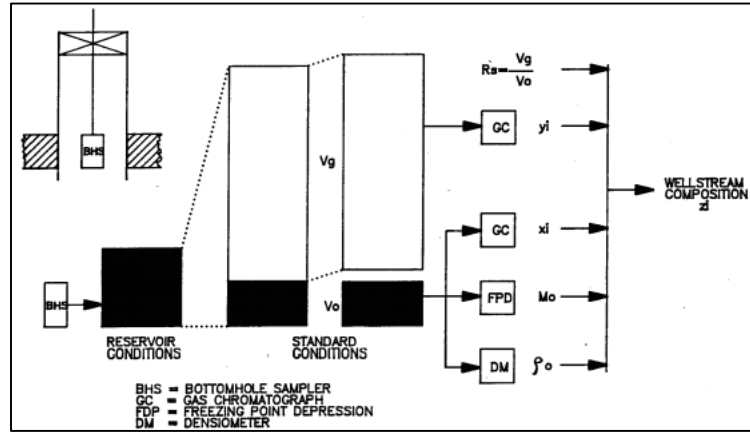


Figure 4.3: Bottom hole wellstream composition.

The procedure of determining the composition of bottom hole samples is expressed as (Whitson, 1998; Whitson and Brulé, 2000):

- Flashing the sample to atmospheric conditions
- Measuring the quantities of surface gas and oil
- Determining the normalized weight fractions (w_{gi} , w_{oi}) of surface samples by gas chromatography
- Measuring molecular weight (M_o) and specific gravity of the surface oil (γ_o)
- Converting weight fractions to normalized mole fractions (y_i , x_i)
- Recombining mathematically to the reservoir oil composition (z_i)

The composition of the reservoir oil can be expressed as:

$$\left. \begin{aligned} \text{mole reservoir} \cdot z_i &= \text{mole gas} \cdot y_i + \text{mole oil} \cdot x_i \\ \text{mole reservoir} &= \text{mole oil} + \text{mole gas} \end{aligned} \right\} \Rightarrow$$

$$z_i = \frac{\text{mole gas}}{\text{mole oil} + \text{mole gas}} \cdot y_i + \frac{\text{mole oil}}{\text{mole oil} + \text{mole gas}} \cdot x_i$$

By dividing with the term ‘mole oil’, it is derived

$$z_i = \frac{\frac{\text{mole gas}}{\text{mole oil}}}{1 + \frac{\text{mole gas}}{\text{mole oil}}} \cdot y_i + \frac{1}{1 + \frac{\text{mole gas}}{\text{mole oil}}} \cdot x_i$$

$$\text{Substituting: } F_g = \frac{\frac{\text{mole gas}}{\text{mole oil}}}{1 + \frac{\text{mole gas}}{\text{mole oil}}}, 1 - F_g = \frac{1}{1 + \frac{\text{mole gas}}{\text{mole oil}}}$$

So:

$$z_i = F_g y_i + (1 - F_g) x_i$$

In more details the following expressions are applied:

$$\begin{aligned} \text{mole gas} &= \frac{\text{gas volume}}{\text{molar gas volume}} = \frac{V_g (\text{scf})}{\frac{R (\frac{\text{psia} \cdot \text{ft}^3}{\text{Rankine} \cdot \text{lbmol}}) \cdot T_{sc} (\text{Rankine})}{P_{sc} (\text{psia})}} = \\ &= \frac{V_g (\text{scf})}{\frac{10.732 \frac{\text{psia} \cdot \text{ft}^3}{\text{Rankine} \cdot \text{lbmol}} \cdot 536.7 \text{ Rankine}}{14.7 \text{ psia}}} = 2.55 \cdot 10^{-3} (\frac{\text{lbmol}}{\text{ft}^3}) \cdot V_g (\text{scf}) \end{aligned}$$

$$\begin{aligned} \text{mole oil} &= \frac{\text{oil volume} \cdot \text{oil density}}{\text{average molecular weight}} = \frac{V_o (\text{STB}) \cdot 5.615 \frac{\text{ft}^3}{\text{STB}} \cdot \gamma_o \cdot 62.4 \frac{\text{lb}}{\text{ft}^3}}{M_o (\frac{\text{lb}}{\text{mol}})} = \\ &= 350.375 \frac{\text{lb}}{\text{STB}} V_o (\text{STB}) \cdot (\gamma/M)_o (\frac{\text{mol}}{\text{lb}}) \end{aligned}$$

$$\frac{\text{mole gas}}{\text{mole oil}} = \frac{2.55 \cdot 10^{-3} (\frac{\text{lbmol}}{\text{ft}^3}) \cdot V_g (\text{scf})}{350.375 \frac{\text{lb}}{\text{STB}} V_o (\text{STB}) \cdot (\gamma/M)_o (\frac{\text{mol}}{\text{lb}})} = \frac{7.3 \cdot 10^{-6} (\frac{\text{STB} \cdot \text{lbmol}}{\text{ft}^3 \cdot \text{lb}}) \cdot R_s (\frac{\text{scf}}{\text{STB}})}{(\gamma/M)_o (\frac{\text{mol}}{\text{lb}})}$$

$$\text{So } F_g \text{ can be expressed as: } F_g = \frac{1}{1 + [303.03 (\gamma/M)_o / R_s]}$$

Where: R_s is taken from the single stage flash (scf/STB) and M_o is given in $\frac{\text{lb}}{\text{mol}}$

$$y_i = \frac{w_{gi}/M_i}{\sum_{j \neq C_{7+}} (w_{gj}/M_j) + (w_{gC_{7+}}/M_{gC_{7+}})}$$

$$x_i = \frac{w_{oi}/M_i}{\sum_{j \neq C_{7+}} (w_{oj}/M_j) + (w_{oC_{7+}}/M_{oC_{7+}})}$$

$$M_{oC_{7+}} = \frac{w_{oC_{7+}}}{(1/M_o) - \sum_{j \neq C_{7+}} (w_{oj}/M_j)}$$

Usually $M_{gC_{7+}} = 105 \text{ lb/lbmol}$ is a good assumption!

The most probable source of error in composition of a bottom hole sample is the surface oil molecular weight which is usually accurate within ± 4 to 10% (Whitson, 1998; Whitson and Brulé, 2000; Moffatt, n.d.).

4.1.5 Composition of surface sample

The separator oil composition is obtained by flashing the separator oil to standard conditions, measuring properties and compositions of the resulting surface oil and gas and recombining these compositions to give the separator oil composition. The procedure is exactly the same as for the *Subchapter 4.1.4*.

The separator gas sample is introduced directly into a gas chromatograph. Weight fractions are converted to mole fractions using appropriate molecular weights. The molecular weight of the C_{7+} is determined from the molecular weight of the gas chromatographically determined. The specific gas gravity is obtained from gas chromatography (McDonough, 2002).

Following the same procedure as for *subchapter 4.1.4* it is derived that the wellstream composition is expressed as:

$$z_i = F_{gsp} y_i + (1 - F_{gsp}) x_i$$

$$F_{gsp} = \frac{\text{mole separator gas}}{\text{mole separator oil} + \text{mole separator gas}}$$

Where:

$$\text{mole separator oil} = \text{mole flashed liquid} + \text{mole flashed gas}$$

$$\text{mole flashed gas} = \frac{\text{gas volume}}{\text{molar gas volume}} = 2.55 \cdot 10^{-3} \left(\frac{\text{lbmol}}{\text{ft}^3} \right) \cdot V_g (\text{scf})$$

$$\text{mole oil} = \frac{\text{oil volume} \cdot \text{oil density}}{\text{average molecular weight}} = 350.375 \frac{\text{lb}}{\text{STB}} V_o (\text{STB}) \cdot (\gamma/M)_o \left(\frac{\text{mol}}{\text{lb}} \right)$$

$$\text{mole separator gas} = \frac{\text{gas volume}}{\text{molar gas volume}} = 2.55 \cdot 10^{-3} \left(\frac{\text{lbmol}}{\text{ft}^3} \right) \cdot V_g (\text{scf})$$

So, the F_{gsp} after some manipulation can be expressed as:

$$F_{gsp} = \frac{1}{1 + \frac{R_s \left(\frac{\text{scf}}{\text{STB}} \right) + 302.94 \cdot (\gamma/M)_o \left(\frac{\text{mol}}{\text{lb}} \right)}{(R_{sp})_{Lab} \left(\frac{\text{scf}}{\text{STB}} \right)}$$

The separator gas and oil samples will be recombined depending on the GOR value. The reported GOR has an accuracy of 5 to 15%, error occurred due to incorrect separator oil and gas rate (accuracy of separator gas and oil rates is typically 5% (Fevang and Whitson, 1994)), carry over of separator oil in separator gas stream and gas in the oil line.

It is very important to correct the test separator gas oil ratio for the measured gas rate as far as it usually incorporates errors (Whitson, 1998). The gas rate in the flowmeter is given by an expression $((z_g \cdot \gamma_g)^{-1/2})$ (Mignot, 2003), so, the solution GOR should be corrected by the following equation:

$$(R_{sp})_{Lab} = (R_{sp})_{field} \frac{\sqrt{(z_g)_{field}(\gamma_g)_{field}}}{\sqrt{(z_g)_{Lab}(\gamma_g)_{Lab}}}$$

Where:

$(R_{sp})_{field}$: separator gas oil ratio based on rates calculated in the field, $(\frac{scf}{STB})$

$(R_{sp})_{Lab}$: corrected separator gas oil ratio at laboratory conditions $(\frac{scf}{STB})$

$(z_g)_{field}$: separator gas Z-factor used in field calculation of gas rate

$(z_g)_{Lab}$: laboratory (true) separator gas Z-factor determined in the laboratory

$(\gamma_g)_{field}$: separator gas gravity used in field calculations of gas rate

$(\gamma_g)_{Lab}$: separator gas gravity based on measured composition or direct measurement

The recombination process of the recovered gas and oil samples starts with the selection of the preferred gas and liquid samples (Osfouri, et al., 2014). The appropriate volumes of separator gas and oil samples are transferred at high pressure vessels according to $(R_{sp})_{Lab}$ value and are homogenized (Nnabuo, et al., 2014). Pestak, Pande and Swanson (1989) give a formula for the reliability of the recombined composition.

4.1.6 Composition of open hole contaminated samples

Reservoir fluid samples are often contaminated by oil based drilling mud. The contaminate is usually consisted of C_{11} – C_{29} components and dominated by paraffinic C_{14} – C_{18} components (Pedersen and Christensen, 2007). Dybdahl (2006) states that the OBM contamination in the sample increases with the tightness of the formation. In order to get a true picture of the reservoir fluid in a field, the contaminated reservoir fluid composition must be numerically cleaned. The cleaning procedure depends on which is the plus fraction defined at the compositional analysis. In other words, the applied method of cleaning is relevant of whether the components of mud belong partially or totally to the plus fraction of the compositional analysis (Thomas, Shtepani and Bennion, 2002). The method of subtraction and the skimming technique are proposed by Gozalpour et al (2002), Smellie (2010), Samir (n.d) and Ezekwe (2011) as the methods for determining the true oil reservoir composition.

4.2 Constant Composition Expansion (Whitson, 1998; Whitson and Brulé, 2000; Lang and Donohue, 1985; Varotsis, 2014)

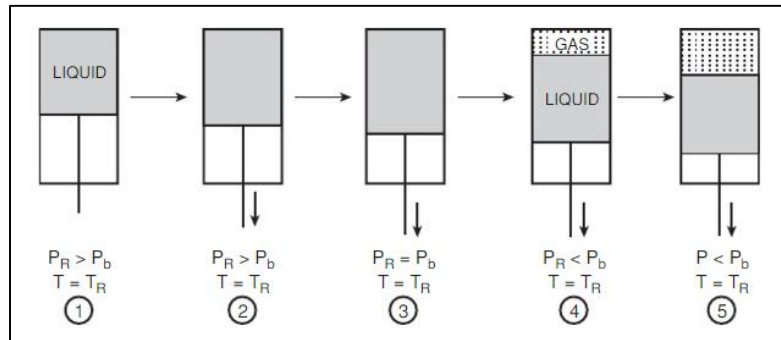


Figure 4.4: Scheme of constant composition expansion.

The Constant Composition Expansion (CCE) is the most commonly performed PVT experiment and is carried out for both oils and gases. It is also called constant mass expansion or flash vaporization. A cell is filled with a known mass of reservoir fluid. Visual cells are the most common cells, as far as gas can be seen at the top of the visual cell and the liquid shrinkage below the bubble point can be measured (Ahmed, 2007; Shariati and Peters, 2002). The sample is brought to reservoir temperature and held constant, while the pressure is above the initial reservoir pressure, ensuring that the fluid is in single phase. The pressure is lowered stepwise and equilibrium is obtained at each new pressure. The cell contents are agitated at each pressure to aid the equilibration process and avoid the phenomenon of supersaturation or metastable equilibrium (Kennedy and Olson, 1952). The oil expands and its volume is recorded. Just below the bubble point, the measured volume will increase more rapidly because gas evolves from the oil, yielding a higher fluid compressibility. The CCE is used to determine the following:

Bubble point pressure: Other ways of measuring the bubble point pressure include analytical (~40%) and synthetic (~60%) approaches (Dohm, et al., 2012). Synthetic-nonvisual experimental methods make use of acoustics (Reis, et al., 2006; Galipeau, et al., 1995), quartz sensors (Oag, et al., 2003; Ziegler and Rolf, 1987; Joung and Kim, 2006) and infrared spectroscopy (Novitskiy, et al., 2011). A new synthetic-nonvisual approach is presented by Bao et al. (2014) which exploits the principle of thin-film interference on reflection-based optical fiber sensors.

Undersaturated oil density: For the bubble point pressure the oil volume is recorded (V_{ob}) so by knowing the initial mass of the sample, the bubble point density can be easily calculated.

Isothermal oil compressibility: $C_o = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$

4.3 Multistage Separator Test (Whitson, 1998; Whitson and Brulé, 2000; Lang and Donohue, 1985; Varotsis, 2014; Nnabuo, Okafor and Ubani, 2014)

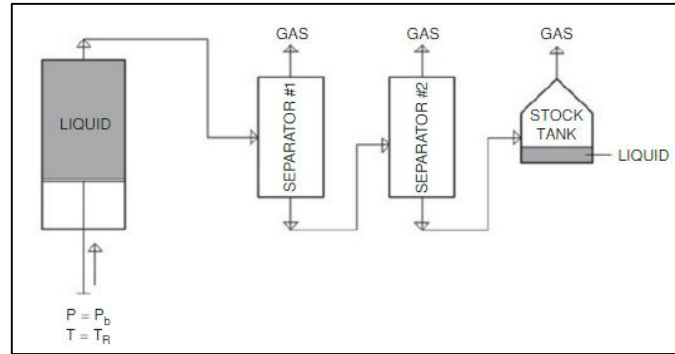


Figure 4.5: Scheme of multistage separator test.

The multistage separator test is performed on oil samples primarily to provide a basis for converting differential - liberation data from a residual oil to a stock-tank oil basis and to determine the number of separators and the conditions that maximize stock-tank oil production. In fact, by considering the degrees of freedom, there is only one variable to be optimized, the pressure. Usually two or three stages of separation are used, with the last stage being at atmospheric pressure and near-ambient temperature (tank). Measured properties include initial volume at saturation pressure, separator oil volume at each stage and residual oil volume, density and composition (Imo-Jack and Emelle, 2013).

Figure 4.5 illustrates how the separator test is performed. Initially, the reservoir sample is brought to saturation conditions and the volume is measured. Then, it is brought to the pressure and temperature of the first-stage separator. All of the gas is removed and the oil volume at the separator stage is noted, as well as the volume, number of moles, and specific gravity of the removed gas. If requested, the composition of gas samples can be measured by gas chromatography. The oil remaining after gas removal is brought to the conditions of the next separator stage. The gas is again removed and quantified. Oil volume is noted, and the process is repeated until stock-tank conditions are reached. The final oil volume and specific gravity are measured at standard conditions. Gas removed at each stage is quantified as standard gas volume $((V_g)_{sc} \text{ (scf)})$ per volume of stock-tank oil $((V_o)_{sc} \text{ (STB)})$: $R_s = \frac{(V_g)_{sc}}{(V_o)_{sc}}$

Sometimes an additional column of data is reported, giving standard gas volume per volume of separator oil.

4.4 Differential Liberation Expansion (Whitson, 1998; Whitson and Brulé, 2000; Lang and Donohue, 1985; Varotsis, 2014; Nnabuo, Okafor and Ubani, 2014)

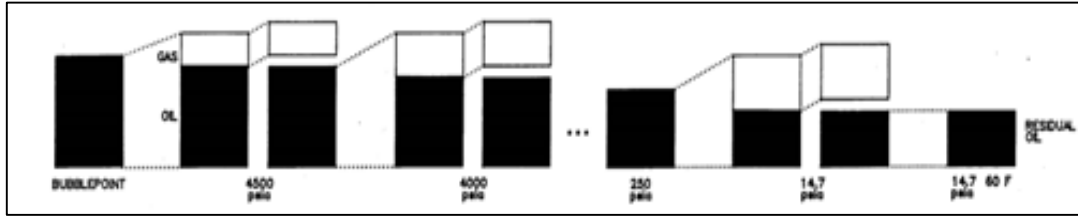


Figure 4.6: Scheme of differential liberation expansion.

The differential liberation experiment (DLE) is also referred to as differential vaporization (DV) or differential expansion and is designed to approximate the depletion process of an oil reservoir, and thereby provide suitable PVT data for calculating reservoir performance (Dake, 1978).

The pressure is decreased below the bubble point and the cell is agitated until equilibrium is reached. All gas is removed at constant pressure, and the volume (ΔV_g), moles (Δn_g), and specific gravity of the removed gas (γ_g) are recorded. This procedure is repeated 10 to 15 times at decreasing pressures, and finally at atmospheric pressure. The final residual oil is cooled, where the resulting residual oil volume and specific gravity are measured at ambient temperature. Based on measured data (P (cell pressure, psia), T (temperature °R)), other properties are calculated, such as:

$$\text{Differential oil FVF: } B_{od} = \frac{V_o}{V_{or}} \text{ (scf/residual barrel or } \text{sm}^3/\text{sm}^3\text{)}$$

$$\text{Gas specific gravity: } \gamma_g = \frac{M_{gas}}{M_{air}} = \frac{M_{gas}}{28.964 \frac{\text{lb}}{\text{lbmol}}}$$

Where M_{gas} : molecular weight of gas

$$\text{Gas Z-factor: } Z = \frac{V_R \cdot P_R}{T_R} \frac{T_{sc}}{V_{sc} P_{sc}}$$

$$\text{Gas formation volume factor: } B_g = \frac{V_{g,cell}}{V_{g,sc}}$$

$$\text{Where: } V_{g,cell} = \frac{Z \cdot n \cdot R \cdot T_R}{P_R}$$

$$V_{g,sc} = \frac{Z_{sc} \cdot n \cdot R \cdot T_{sc}}{P_{sc}}$$

Ideal gas: $z_{sc} = 1$

$$T_{sc} = 519.7 \text{ Rankine, } P_{sc} = 14.7 \text{ psia}$$

$$B_g \left(\frac{\text{ft}^3}{\text{scf}} \right) = \frac{0.02819 \cdot Z \cdot T_R (\text{Rankine})}{P_R (\text{psia})}$$

4.4.1 Conversion of differential volumetrics

For engineering calculations, volume factors R_s and B_o are used to relate reservoir oil volumes (V_o) to produced surface volumes ($V_{\bar{g}}$ and $V_{\bar{o}}$).

$$R_s = \frac{V_{\bar{g}}}{V_{\bar{o}}} \text{ (scf/STB)}$$

$$B_o = \frac{V_o}{V_{\bar{o}}} \text{ (bbl/STB)}$$

Differential properties R_{sd} and B_{od} are relative to residual oil volume.

$$R_{sd} = \frac{V_{\bar{g}}}{V_{\bar{o}r}} \text{ (scf/residual bbl)}$$

$$B_{od} = \frac{V_o}{V_{\bar{o}r}} \text{ (bbl/residual bbl)}$$

The conversion of differential solution gas-oil ratio (R_{sd}) and differential oil FVF (B_{od}) to a stock-tank oil basis must be applied (Standing, 1977). It is expected that the differential value of solution GOR will be higher than the R_s from the separation test as DV is accomplished at higher temperature so more intense vaporization of liquid is expected and thus more gas to be produced. The equations traditionally used to convert differential volume factors to a stock-tank basis are (Lyons, 2010; Dake, 1978):

$$R_s = R_{sb} - (R_{sdb} - R_{sd}) \frac{B_{ob}}{B_{odb}}$$

$$B_o = B_{od} \frac{B_{ob}}{B_{odb}}$$

Where:

B_{ob} : the bubble point oil FVF (bbl/STB)

R_{sb} : solution GOR from a multistage separator flash (scf/STB)

R_{sdb} (scf/residual bbl) and B_{odb} (bbl/residual bbl) are differential volume factors at the bubble point pressure.

The term (B_{ob}/B_{odb}) represents the volume ratio ($V_{\bar{o}r}/V_{\bar{o}}$) and is used to eliminate the residual oil volume ($V_{\bar{o}r}$) from the R_{sd} and B_{od} data. Note that the conversion from differential to flash data depends on the separator conditions (B_{ob} and R_{sb} depend on separator conditions).

The conversions given by the previous equations are only approximate. A more accurate method was suggested by Dodson et al. (Whitson and Brulé, 2000). Their method is called composite liberation and requires that some of the equilibrium oil is taken at each stage of the DV experiment and flashed through a multistage separator to give the volume ratios R_s and B_o directly. This laboratory procedure is costly and time-consuming, and therefore is seldom used.

4.5 Constant Volume Depletion (Whitson, 1998; Whitson and Brulé, 2000; Lang and Donohue, 1985; Varotsis, 2014)

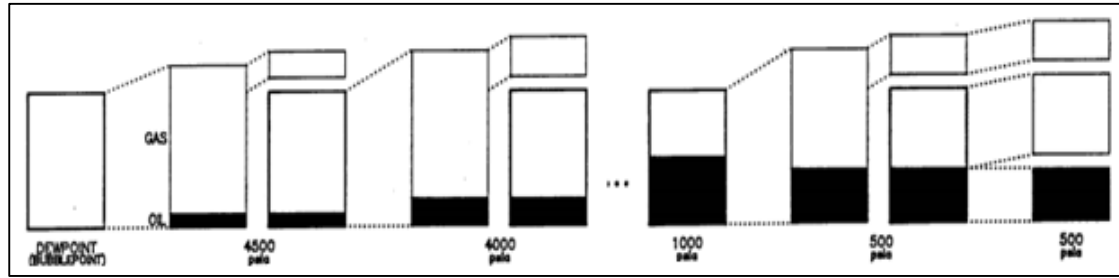


Figure 4.7: Scheme of constant volume depletion.

The constant volume depletion (CVD) experiment is designed to provide volumetric and compositional data mostly for gas condensates. It is rarely used for volatile oil reservoirs producing by pressure depletion. The CVD experiment provides data that can be used directly in reservoir engineering calculations, including:

- Reservoir material balance giving recovery of total well stream (wet gas recovery) versus average reservoir pressure
- Average oil saturation in the reservoir (liquid dropout and re-vaporization) that occurs during pressure depletion

Initially, the bubble point pressure, P_b , of the reservoir sample is established visually and the cell volume, V_{cell} , at saturated conditions is recorded. The pressure is then reduced just below the saturation pressure. The cell is agitated until equilibrium is achieved and volume that occupies each phase is measured. At constant pressure, sufficient gas is removed to return the cell volume to the original saturated volume. In the laboratory, the removed gas is brought to atmospheric conditions, where the compressibility is measured. Surface compositions $y_{\bar{g}}$ and $x_{\bar{o}}$ of the produced surface volumes from the reservoir sample are measured, as also the volumes $\Delta V_{\bar{g}}$ and $\Delta V_{\bar{o}}$, densities $\rho_{\bar{g}}$ and $\rho_{\bar{o}}$ and oil molecular weight $M_{\bar{o}}$. From these quantities, it can be calculated the moles of gas removed, Δn_g .

$$\Delta n_g = \frac{\Delta V_{\bar{o}} \cdot \rho_{\bar{o}}}{M_{\bar{o}}} + \frac{\Delta V_{\bar{g}}}{379}$$

Then the equilibrium gas factor can be calculated as: $Z = \frac{P \cdot \Delta V_g}{\Delta n_g \cdot R \cdot T}$

4.6 Fluid viscosity

Knowledge of viscosity throughout the reservoir is vital for modeling production and predicting reserves recovery. Firstly, some methods of measuring viscosity will be presented and then others than are in research. At the end of the subchapter differences in heavy oils viscosity measurements will be summarized.

Nowadays, the most usual way to measure viscosity is by the Cambridge viscometer for Newtonian and non-Newtonian liquids (Kasameyer, Airey and Cole, 2010). This test method covers the measurement of dynamic viscosity and derivation of kinematic viscosity of liquids by means of an oscillating piston viscometer. Two coils move a piston back and forth magnetically at a constant force and circuitries analyze the piston's two-way travel time to measure the viscosity (Cambridgeviscosity, n.d.). The Cambridge viscometers are also consisted of a temperature detector to monitor real time temperature, a deflector to guide fluid into the measurement chamber and self cleaning technology.

Other viscosity measurement methods that have been proposed in the past, are the rolling ball viscometer (Heidaryan, et al., 2011), falling-body viscometer (Boned, et al., 2003; Monsalvo, et al., 2005), vibrating wire viscometer (Meng, et al., 2008; Diogo, et al., 2013) and capillary tube viscometer (Abdulagatov and Azizov, 2006; Deng, et al., 2012; Tate, et al., 2006). The rolling ball viscometer measures the time required for a steel ball to toll a given distance through a tube filled with the fluid to be tested (Varotsis, 2014; Lang and Donohue, 1985). The falling body viscometer relies on gravity to provide the external force in which an object is allowed to descend freely (Schaschke, 2010). The capillary method measures the time taken for a define quantity of fluid to flow through a capillary with known diameter and length. The capillary method is a low cost but with high accuracy method; a measurement error of viscosity on the order of 5% is found in the literature (Hussein, et al., 2006). The capillary method also has the ability to achieve very high shear rates, even with high viscosity samples (Zhuqiang, et al. 2015). Large range of viscosity has also the electromagnetic viscometer, while it has more accurate viscosity measurement (VinciTechnologies, n.d.).

The ranges of the previously mentioned viscometers are presented in the *Table 4.3*:

Table 4.3: Capabilities of viscometers (Kasameyer, Airey and Cole, 2010).

	Oscillating piston	Capillary tubes	Rolling ball	Vibrational
Accuracy	± 1 %	± 1 %	± 1- 2 %	Not available
Sample per test (mL)	5	25 - 100	500	50
Max. Pressure rating (psi)	20,000	15,000	10,000	Atmospheric
Mercury free	Yes	No	Yes	Yes
Clean in place	Yes	No	No	No
Measures gas viscosity	Yes	No	No	No
Temperature range (°C)	-20 to 190			-40 to 150

The Cambridge viscometer is developed with ASTM Standard D7483-08 (Cambridge viscosity, n.d.) while the other methods as follows:

Method No.	Title of Method	Type of Viscometer/Geometry
D 88	Saybolt Viscosity	short capillary
D 445	Kinematic Viscosity of Transparent and Opaque Liquids (and the Calculation of Dynamic Viscosity)	capillary low shear
D 1092	Measuring Apparent Viscosity of Lubricating Greases	capillary high shear
D 2162	Basic Calibration of Master Viscometers and Viscosity	capillary low shear
D 2532	Viscosity and Viscosity Change After Standing at Low Temperature of Aircraft Turbine Lubricants	capillary low shear
D 2669	Apparent Viscosity of Petroleum Waxes Compounded with Additives (Hot Melts)	rotational coaxial cylinder
D 2983	Low-Temperature Viscosity of Automotive Fluid Lubricants Measured by Brookfield Viscometer	rotational coaxial cylinder
D 3236	Apparent Viscosity of Hot Melts Adhesives and Coating Materials	rotational coaxial cylinder
D 3245	Pumpability of Industrial Fuel Oils	rotational coaxial cylinder
D 3829	Predicting the Borderline Pumping Temperature of Engine Oil	rotational coaxial cylinder
D 4486	Kinematic Viscosity of Volatile and Reactive Liquids	capillary low shear
D 4624	Measuring Apparent Viscosity by Capillary Viscometer At High-Temperature and High-Shear Rates	capillary high shear
D 4683	Measuring Viscosity at High Shear Rate and High Temperature by Tapered Bearing Simulator	rotational tapered cylinder
D 4684	Determination of Yield Stress and Apparent Viscosity of Engine Oils at Low Temperature	rotational coaxial cylinder
D 4741	Measuring Viscosity at High Temperature and High Shear Rate by Tapered-Plug Viscometer	rotational tapered cylinder
D 5018	Shear Viscosity of Coal-Tar and Petroleum Pitches	rotational coaxial cylinder
D 5133	Low Temperature, Low Shear Rate, Viscosity/Temperature Dependence of Lubricating Oils Using a Temperature- Scanning Technique	rotational tapered cylinder
D 5293	Apparent Viscosity of Engine Oils Between -5 and -30°C Using the Cold-Cranking Simulator	rotational coaxial cylinder
D 5481	Measuring Apparent Viscosity at High-Temperature and High-Shear Rate by Multicell Capillary Viscometer	high shear capillary
D 5967	Evaluation of Diesel Engine Oils in the T8 Diesel Engine	capillary low shear
D 6080	Defining the Viscosity Characteristics of Hydraulic Fluids	capillary low shear

Figure 4.8: Methods and type of viscometer for viscosity determination (Manning and Hoover, 2003).

4.6.1 Methods in research for viscosity measurement

In the following paragraphs there are presented modern methods in research for viscosity measurement:

Khan, et al. (2013) presented a suspended microchannel resonator (SMR) which measures the density of the sample with a resolution of 0.01 kg/m^3 and viscosity with an accuracy of 0.025 mPa s . The SMR is transparent, facilitating visual inspection of the microchannel content and belongs to a system which contains packaging and tubing to deliver samples to the resonator. The system can easily handle multiple viscous fluids and have presented promising results. The complicated fabrication and the need of new sensor for every sample makes them expensive at a commercial scale.

The case for using NMR as a method to provide viscosity for oils ranging from 10cp to 3,000,000cP is presented by Bryan et al. (2005, 2002). Hydrogen protons have a property known as spin, which causes the protons to act as small bar magnets. In the presence of an external magnetic field, the protons will therefore tend to line up either parallel or anti-parallel to the external field lines. A pulse sequence is then applied to the protons, giving them energy and causing them to tip onto another plane, called the transverse plane. As they give off their energy, they return back to their equilibrium position. Samples with high viscosity have molecules that cannot move by one another as easily as samples with low viscosity. This lack of mobility in high viscosity samples leads to more frequent exchange of energy between protons of these samples, allowing

energy to be dissipated more rapidly (Jones, and Taylor, 2015). The viscosity is measured by recording the strength of the signal, the characteristic relaxation time and the NMR amplitude index. The characteristic relaxation time could either be the time for the signal to reappear in the direction of the external field lines or the time for the signal to disappear in the transverse plane (faster way). The strength of the magnetic signal is directly proportional to the number of hydrogen protons in the fluid, which is a measure of fluid volume. The NMR amplitude index is defined to relate NMR amplitude to amount of fluid.

There are also patents for the determination of viscosity, such as the viscometer module with crystal resonator-type sensor (Smith and Lovik, 2000).

4.6.2 Dependence of viscosity on asphaltene content, shear rate and temperature

The asphaltene content, shear rate, temperature and pressure will be examined for the effect on the viscosity value.

Two concentrations regimes have been identified in crude oils: a diluted regime where viscosity increases linearly with asphaltene content (eg. Einstein linear relation) and a concentrated regime where viscosity is strongly dependent on asphaltene content (Goual, n.d.). Ghanavati, Ramazani. and Sarapardeh (2014) identified three regimes, the diluted (same characteristics as Goual's paper), the intermediate (intermediate characteristics of diluted and concentrated regime) and the concentrated (same characteristics as Goual's paper).

As it can be derived from *Figure 4.9* the viscosity for small asphaltene volume is linearly dependent on asphaltene volume and almost independent on temperature. As the asphaltene content is increased, the viscosity deviates from the linear behavior to asphaltene content and depends strongly on temperature. As far as the shear rate is concerned, it is concluded that for the same content of asphaltene and temperature, the viscosity is increased with decreasing shear rate, proving a shear thinning behavior. Endokimov, Eliseev and Eliseev (2001) found that when asphaltene suspension is present in sufficiently high concentrations, asphaltene microparticles change the flow properties to viscoelastic non-Newtonian behaviour with an apparent yield stress and a shear-rate exponent depending on the temperature. The change in viscosity with frequency (shear rate) is explained through the power law, also known as Ostwald model (Akeredolu, n.d.):

$$\nu = K \cdot \dot{\gamma}^{n-1}$$

Where:

ν : viscosity

K: consistency coefficient

$\dot{\gamma}$: shear rate or frequency

n: power law index (the term (n-1) takes values smaller than 1 for shear thinning fluids)

For the same concentration of asphaltene, the increase of the temperature decreases the viscosity (shear thinning non Newtonian behavior) (Ghannam, et al., 2011). The relationship specifying the viscosity behavior can be either the Arrhenious model (Akeredolu, n.d.; Abivin, et al., 2011) or the Williams Landel Ferry for low temperature (glass transition zone) (Abivin, et al., 2011).

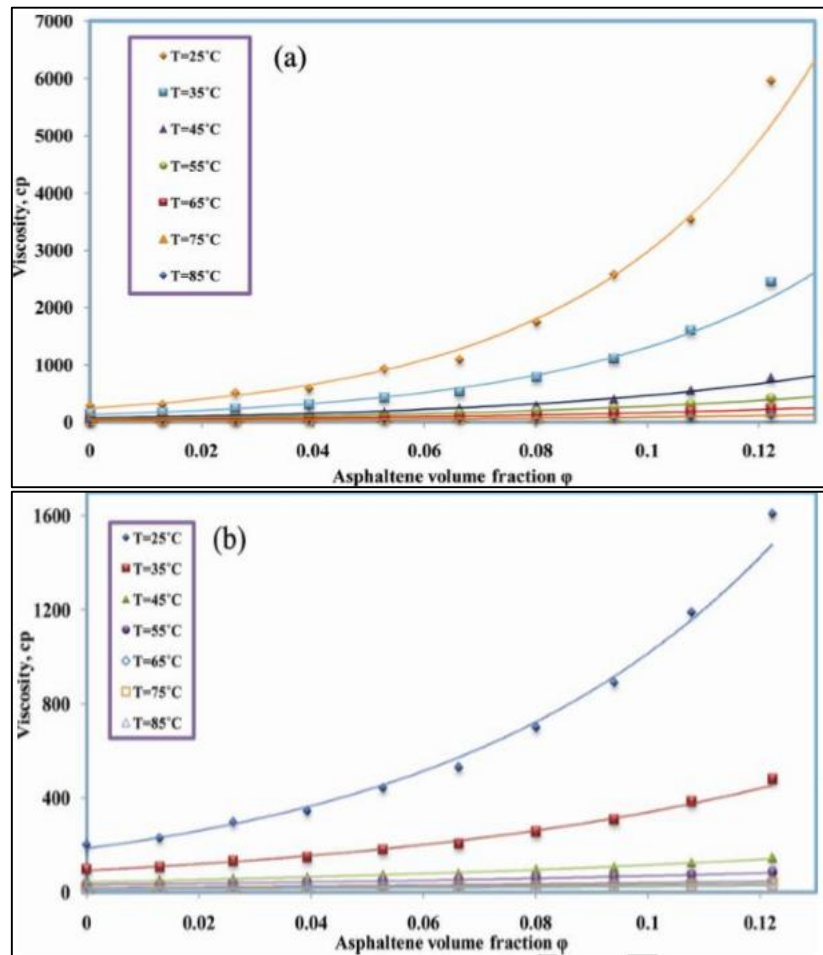


Figure 4.9: Measured viscosity versus the asphaltene volume fraction at various temperatures at: (a) low shear rate, (b) high shear rate (Ghanavati, Ramazani. and Sarapardeh 2014).

4.7 Special Laboratory PVT studies

There are special tests that examine more sophisticated properties. Less frequently conducted PVT analysis include:

- Analysis of produced water, including salinity and brine composition
- Flow assurance studies
- Studies for the miscibility pressure

4.7.1 Formation water composition (Abdou, et al., 2011)

In the case of produced formation water in the wells, many oil and gas producers react with alarm. The formation water properties contain wealth of information that can be used to impact field economics. Quantifying water chemistry aids in the understanding of reservoir connectivity and in characterizing transition zones in carbonates.

Water composition depends on a number of parameters, including depositional environment, mineralogy of the formation, its pressure and temperature history and the influx or migration of fluids. Early in field life, analysis of formation water establishes the salinity and resistivity of the water for petrophysical evaluation (Warren and Salley, 1994). The water pH and salinity values are used in metallurgical calculations for selection of tubulars (Wiliford, et al., 1999).

The formation water may have a considerable content of inorganic mineral components of water (salts, metals and complex salts of iron) (Pedersen and Christensen, 2007; Marinakis, 2015). Salt deposition is often referred to as scaling and is a potential problem in pipelines. Scale can also be formed when water of different composition gets mixed (Mackay and Sorbie, 2000). The *Figure 4.10* gives a summary of the most important factors that affect the scale precipitation.

Scales	Temperature Effects	Pressure Effects	pH Value Effects	Dissolved Solids Effects
	Less soluble with increased temperature.	Less soluble with reduced pressure.	Less soluble with increased pH value.	Less soluble with reduced total dissolved solids in water.
Calcium Carbonate	More likely scale will form with hotter water.	If waters go through the bubble point, CO ₂ would evolve from solution and scale likely to form.		Adding salts into distilled water can increase the solubility.
Barium Sulfate	For common temperature range, solubility increase with increased temperature.	Less soluble with reduced pressure.	Little impact.	More soluble with increased dissolved salt.
Strontium Sulfate	Less soluble with increased temperature.	Less soluble in NaCl brines with reduced pressure.	Little impact.	More soluble with increased NaCl content.
Calcium Sulfate	Less soluble with increased temperature for the common reservoir temperature range.	Less soluble with reduced pressure.	Little impact.	More soluble with increased water salinity.

Figure 4.10: Summary of major factors impacting scale precipitation (Guo, et al., 2005).

4.7.2 Studies for the miscibility pressure (Stepani, et al., n.d.; Ahmed, 2007)

A key parameter in the design of a gas injection project is the minimum miscibility pressure (MMP), the pressure at which the local displacement efficiency approaches 100%. To determine accurately the MMP, it is in general necessary to perform six displacements at six different pressures. The MMP is usually taken to be the intersection point between the line of high recovery and the line of low recovery after 1.2 pore volume of solvent injection. The thermodynamic conditions required for dynamic miscibility with injection gas, as well as the gas composition are best determined by laboratory experiments. The most common experiments conducted to determine the miscibility conditions are shown schematically in the following figure:

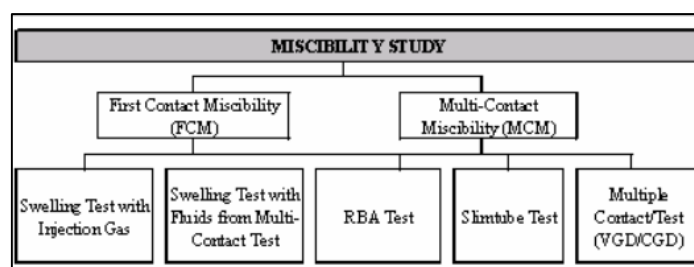


Figure 4.11: Miscibility study (Stepani, et al., n.d).

4.7.2.1 Swelling Test (P-x) with Injection Gas

The swelling test is the most common PVT experiment for first contact miscibility studies. During a swelling test, gas with a known composition is added to the original reservoir oil at varying proportions in a series of steps. After each addition of certain measured volume of gas, the overall mixture is quantified in terms of the molar percentage of the injection gas. The gas addition starts at the saturation pressure of the reservoir fluid and continues up to about 80% mol injected gas in the fluid sample. When a gas is injected into a reservoir, it can go into solution and swell the oil; so the volume of the oil becomes larger. The data are presented in a pressure – composition (P-x) and main PVT single-phase property versus injection gas addition diagram.

4.7.2.2 Rising Bubble Apparatus Experiment (RBA)

The Rising Bubble Apparatus (RBA) miscibility test is a rapid and cost effective technique to provide approximate miscibility pressures for oil - injection gas mixtures. In this method, the MMP is determined from the visual observations of changes in the shape and appearance of bubbles of injected gas as they rise through a visual high-pressure cell filled with the reservoir crude oil. A series of tests are conducted at different pressures or enrichment levels of the injected gas, and the bubble shape is continuously monitored to determine miscibility.

4.7.2.3 Slim tube Experiment

The MMP determined by slim tube tests has been accepted by the oil industry as the target reservoir pressure for designing a miscible process. In order to reduce the runs for the MMP determination for the slim tube experiment, the MMP value from rising bubble apparatus experiment is set as starting pressure. The displacement of oil by gas is conducted in a long and narrow sand pack to examine the flushing efficiency and fluid mixing during a miscible displacement process. The purpose of the experiment is solely to examine the phase behavior properties for a given gas displacement by eliminating reservoir heterogeneities, water, and gravity. However, slim tubes have a porous medium which bears little resemblance to reservoir rocks and water is not present during the test. Therefore, routine core analysis (RCAL) and special core analysis (SCAL) are complementing the above studies to guide the reservoir engineer in assessing the reservoir performance.

4.7.2.4 Multiple Contact Experiment

Multiple Contact experiments are performed to generate quasistatically the complete range of compositions and interfacial tensions that will be generated in the reservoir under injection conditions. For a better understanding of phase behavior and miscibility conditions, multiple contacts at different pressures are recommended. The multi-contact test procedure starts by mixing the original injection gas and original reservoir oil at operating pressure. Then, three forward contacts (vaporizing gas drive) and three reverse contacts (condense gas drive) are sufficient to determine the type of mechanism (vaporizing, condensing or condensing / vaporizing). The experimental data include interfacial tension (IFT), viscosity, fluid formation volume factors, gas-oil ratio, k values and the compositions of each phase at each contact. Jaubert, et al. (2001) concluded that when the injected gas is not pure CO₂ (and probably not pure N₂ or pure H₂S), it is enough to fit only two parameters of the equation of state on data, including classical PVT data & swelling data & MCT data, and then predict the MMP.

In the following Table a comparison between the methods of determining MMP is conducted:

Table 4.4: Comparison between swelling test, slim tube test and multiple contact experiment.

Characterization	Price	Time	Difficulty
Swelling test	Cheap	quick	Easy
Slim tube	Expensive, time consuming	Time consuming	More difficult than the other two
Multiple contact	cheap	Quick	Easy

4.7.3 Flow assurance studies

The flow assurance design process involves fluid properties characterization and thermal - hydraulic calculations, for the development of operation strategies that prevent problems such as solid blockages, severe slugging, sand erosion and corrosion. Four issues have been identified in the flow assurance design process (Bai and Bai, 2005):

- Fluid characterization
- Steady-state thermal-hydraulic calculations
- Transient flow thermal-hydraulic calculations
- Final system design and operation procedures for flow assurance

Only the first point is in the context of this master thesis and can be divided in (Texas OilTech Laboratories, Inc, n.d.):

- Asphaltenes in Heavy Oil
- Wax in Heavy Oil
- Scaling Formation
- Hydrate Formation
- Emulsion Analysis

In *Figure 4.12* is presented the phase transitions for flow assurance:

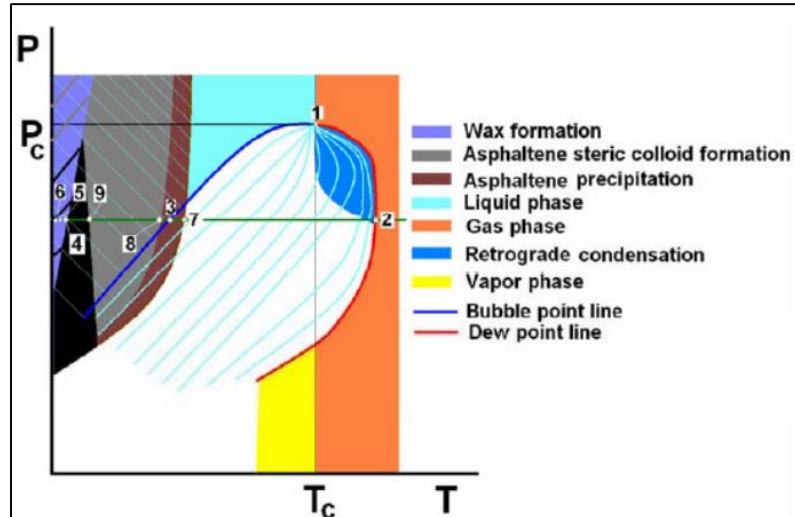


Figure 4.12: Relevant phase transitions for flow assurance (Time, 2011).

4.7.3.1 Wax

Wax is the name given to heavy components of crude oil that consist of linear n-paraffins and branched iso-paraffins with a carbon number from C₂₀ to C₇₀ (Sarica and Panacharoensawad, 2012). Wax precipitation is generally problematic as they plug the production tubing, surface separation facilities and pipelines (Dandekar, 2013). To determine the amount of wax in a crude oil, a compositional analysis is required. High temperature gas chromatography (HTGC) detects heavy components in the oil as high as C₁₀₀ (Alboudwarej et al., 2006; Geochemical services, n.d). During high temperature gas chromatography, compounds of high boiling point are kept mobile as the column is heated at temperature 500 °C (Geochemical services, n.d). Elselike, Supercritical fluid chromatography (SFC) must be applied. SFC involves dissolving the sample in a medium which is held at supercritical temperature and pressure in a holding cell. Then the pressurised sample is transferred to the GC where it is depressurised and fed onto the analytical column. This avoids using the very high temperatures of HTGC which incurs less risk of sample decomposition.

A key parameter used to determine problems of wax deposition is the crude cloud point or wax appearance temperature (WAT). As the temperature of a liquid solution is lowered to the wax appearance temperature, the wax molecules form clusters. Wax molecules continue to attach and detach from these clusters until they reach a critical size and become stable. These clusters are called nuclei and the process of cluster formation is called nucleation. Once the nuclei are formed and the temperature remains below the WAT, the crystal-growth process occurs as further molecules are laid down in a lamellar or plate-like structure (Petrowiki, n.d.). The WAT is measured using microscopy, differential scanning calorimetry (DSC) and viscometer (Pedersen and Christensen, 2007). In microscopy technique as wax appearance temperature is taken the highest temperature which crystals could be observed in a microscope (Ronningsen, et al., 1991). The DSC is associated with the release and requirement of heat when crystallization is taking place. The viscometer takes the advantage that when wax precipitation occurs, the viscosity is increased so the WAT can be determined by a plot of viscosity versus temperature.

The wax deposition can be treated by heating, pigging and inhibitors (Marinakis, 2015). Wax inhibitors may be added to waxy crude oils to facilitate transport in undersea pipelines. The most commonly used inhibitors lower the apparent viscosity and the pour point. The pour point is the temperature at which the oil phase solidifies due to formation of a gel network of precipitated wax crystals. Three groups of wax inhibitor are found in the literature: wax crystal modifiers, detergents and dispersants.

4.7.3.2 Asphaltenes

Asphaltenes are large polar molecules primarily formed by carbon and hydrogen, with one to three heteroatoms (nitrogen, oxygen or sulfur) per molecule (McCain, 1990; Mansoori, 2009). The heteroatoms can be part of aromatic rings clusters or can be in the links between the rings. Asphaltenes are petroleum fractions that are defined by a solubility classification, soluble in aromatic solvents (e.g., toluene and benzene), but are insoluble in light aliphatic solvents (e.g., pentane and heptane) (Mitchell and Speight, 1973). They influence the viscosity and stabilize oil-water emulsions (Akbarzadeh, et al., 2007). Petroleum heavy crudes / residues have been repeatedly verified as suspensions of asphaltene colloids stabilized by resins (Endokimov, Eliseev and Eliseev, 2001; Zerpa, 2013). It is a fact that asphaltenes tend to interact between them and form asphaltene colloids or micelles (Rodrgues, n.d.; Mousavi-Dehghani, et al., 2004) which are the heaviest components in crude oil with by far the lowest solubility (Mullins, et al., 2007).

There are efforts underway to characterize asphaltenes in terms of their chemical structure, elemental analysis and carbonaceous sources. Andrews et al, (2015) defined the C:H ratio (1:1.1) with 40% C aromatic and 90% H on saturated C while their molecular weight is 500 – 1,000 amu and their diameter 21Å (Mullins, and Groenzin, 1999; Mullins, n.d.). The following figure depicts some methods that were used to determine the molecular weight of the asphaltenes:




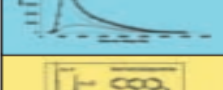

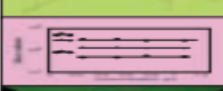

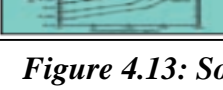

Graphic icon	Method name	Brief description	Molecular weight or molecular size
	Field-ionization mass spectrometry (FI-MS)	Probe-vaporized asphaltenes passing through a high-energy electric field are ionized. Their mass-to-charge ratio is used to generate a mass spectrum.	800 g/mol
	Electrospray ionization, Fourier transform ion cyclotron resonance mass spectrometry (ESI FT-ICR MS)	This Nobel Prize-winning ionization method evaporates solvent from solute, allowing very large molecules to go into the vapor phase.	Most between 400 and 800 g/mol, with a range of 300 to 1,400 g/mol.
	Atmospheric pressure photoionization mass spectrometry (APPI MS)	Gas-nebulized samples are ionized by light to measure the mass-to-charge ratio of the asphaltenes.	750 g/mol, with a range of 400 to 1,200 g/mol
	Field-desorption/field-ionization mass spectrometry (FD-FI MS)	An asphaltene sample deposited on a needle-like surface is desorbed and ionized when heat and a high electric field are applied. The ion mass-to-charge ratio is used to generate the mass spectrum.	~ 1,000 g/mol with a broad distribution
	Laser desorption ionization (LDI)	A laser pulse on a solid asphaltene sample creates a gas plume. Low laser power and low gas densities are required for accuracy.	800 to 1,000 g/mol
	Time-resolved fluorescence depolarization (TRFD)	Rotational diffusion constants of asphaltene molecules in solution are measured by detecting the rate of decay of induced polarization.	~ 2 nm diameter corresponding to 750 g/mol with a range between 500 and 1,000 g/mol
	Nuclear magnetic diffusion	Asphaltene molecules diffuse in an NMR field. Diffusion time is related to molecular size.	~ 2.6 nm diameter. Some dimers, or pairs of molecules, yield the larger size.
	Fluorescence correlation spectroscopy (FCS)	Translational diffusion coefficients of fluorescing molecules lead to a length scale corresponding to a sphere-equivalent hydrodynamic radius.	~ 2.4 nm diameter corresponding to 750 g/mol. Smaller for coal asphaltenes.
	Taylor dispersion diffusion	The translational diffusion coefficient of molecules in laminar flow is related to molecular size.	~ 1.4 nm diameter for coal asphaltenes (same as Groenzin and Mullins, reference 5)

Figure 4.13: Some of the techniques that yield consistent results for asphaltene molecular weight and size (Akbarzadeh, et al., 2007).

Typically, two different laboratory tests are conducted for asphaltenes:

- Determination of total asphaltenes in the oil, based on standardized ASTM method, expressed as grams of solids per 100 mL
- Oil stability tests that involve flocculation onset titration of the oil with a precipitant such as n-heptane (Dandekar, 2013). The oil stability test is based on the insolubility of asphaltenes to low molecular weight paraffins (Guo et al., 2005).

The SARA analysis gives an indication of fluid stability with respect to asphaltene precipitation for conventional oils (not for heavy oils) (Hussein, et al., 2006). The SARA analysis fractionates stock tank oil into weight percent saturate, aromatic, resin and asphaltene (Alboudwarej, et al., 2002).

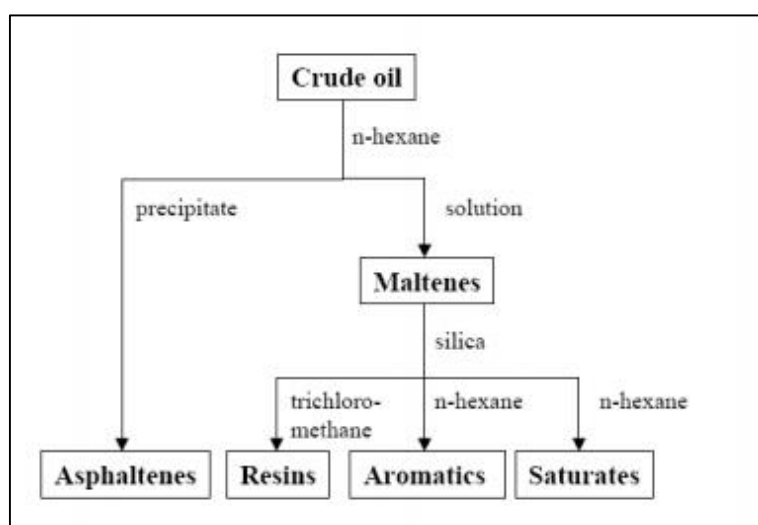


Figure 4.14: SARA fractionation scheme (Aske, et al., 2001).

Asphaltene precipitation may occur in the reservoir, in the production well, during pipeline transportation and in process plants. A simple method to determine the asphaltene precipitation tendency of a reservoir oil is the de Boer plot (de Boer et al., 1995), which identifies three regions (severe, slight and no problem) based on the difference of reservoir pressure and bubble point pressure as function of oil density at in-situ conditions (Wang et al., 2006). The asphaltene precipitation potential increases with increasing pressure above the bubble point pressure. The higher the pressure, the more asphaltenes can be kept in solution in the oil. Also, the asphaltene precipitation is more likely to take place from a reservoir fluid of low density (dominated by paraffins) than from a reservoir fluid of high density (dominated by aromatics).

4.7.3.3 Gas hydrates

Gas hydrates are crystalline compounds formed by cages of hydrogen-bonded water molecules (host) stabilized by encapsulation of small gas molecules (guest), such as methane, ethane, propane or carbon dioxide (Sloan and Koh, 2008). The physical properties of hydrates are similar to those of ice (Guo, et al., 2015). The hydrate formation may lead to plugging of pipelines and ultimately shutdown of production. The gas hydrate phase envelope, defined by equilibrium pressure and temperature conditions, can be determined by thermodynamic flash calculations based on the van der Waals and Platteeuw model with excellent engineering accuracy (Ballard and Sloan, 2004b). Several commercial thermodynamic programs are developed for the prediction of gas hydrate (Multiflash R from Infochem Computer Services, PVTsim R from Calsep, CSMGem from the Colorado School of Mines, based on the Gibbs energy minimization method (Ballard and Sloan, 2004a)) (Sloan and Koh, 2008). The composition of hydrocarbon fluids and produced water, obtained during the fluids characterization, are used as input to these programs to obtain the hydrate equilibrium curve. The treatment of the gas hydrates is accomplished through pigging, blowdown, heating and thermodynamic or kinetic inhibitors (Marinakis, 2015).

4.7.3.4 Emulsions

Exporting oil not fulfilling the quality criteria of emulsion quantity ($<0.5\% \text{ w/o}$), results in large economic penalties (Silset, 2008). In the petroleum industry, two types of emulsions are frequently encountered: water-in-oil (W/O) and oil-in-water (O/W) emulsions. Emulsions are defined as thermodynamically unstable systems in which one liquid is dispersed, in the form of droplets, in another immiscible liquid (Gutierrez, et al., 2008; Meleson, Graves and Mason, 2004). During crude oil production, there are several sources of forming emulsions including flow through reservoir rock, tubing, flow lines, and production headers as well as at pump, valves, fittings, chokes and surface equipment.

Crude oils have to be tested for emulsion forming tendency. Several correlations can be used to predict the formation of emulsions (Fingas, 2005). The test procedure for emulsion tendency is called Mackay and Zagorski Test (Mackay and Nowak, 1984).

Characterizing emulsions of the petroleum industry is a crucial problem. The most important measurement to characterize emulsions is forced oscillation rheometry study to evaluate the stability of the emulsion (Fingas, 2005). The presence of significant elasticity clearly defines whether a stable emulsion has been formed. It is a fact that most researchers studied the stability of emulsions by measuring the amount of water resolved with time, as far as it is a very simple test (Fingas, 2014). Jiang, et al. (2007) have demonstrated the use of NMR to investigate time-dependent stability properties of water-in-oil emulsions under different conditions. The NMR technique was compared to optical microscopy by Fingas (2005) and showed good correlation over several experiments involving ageing and breaking of the emulsions.

In addition, the viscosity of the emulsion can be an indicator of the stability of the dispersion. The emulsion viscosity must be calculated as far as viscosity affects the rheology behavior. The NMR method described earlier, is applicable to predict viscosity of crude oil emulsions. It can also be determined through empirical correlations given by Pal & Rhodes (1989) and Bullard et al (2009). Pal (2000) studied several oil / water emulsions by using a controlled-stress rheometer and found that at low to moderate values of water cut, the emulsions could exhibit Newtonian behavior while at higher values of water cuts, emulsions exhibited shear-thinning behavior strongly influenced by the droplet size. For water / oil emulsions, Abivin et al. (2009) found that the viscosity versus shear rate curves exhibited a Newtonian behavior for low shear rates. Sandoval – Rodrigues, Canas-Marin and Martinez-Rey (2014) concluded that whatever the emulsion, the viscosity is decreased for high shear rates (Non Newtonian behavior).

The use of Differential Scanning Calorimetry has permitted to get important information about the morphology of emulsions. Furthermore, it has been also possible to evidence the formation of gaseous hydrates within emulsions and solid products that can block the flowing of petroleum fluids in the conduits (Clausse, et al., 2005). Calorimetry may provide useful qualitative information about the granulometry of emulsions. It is also possible to characterize the degree of polydispersity of an emulsion. As a result, the study of emulsion aging is possible by thermal analysis. The comparison of thermograms can give information about the stability. Quantitative information on the granulometry of emulsions may also be deduced from data obtained during crystallization (Clausse, et al., 2005).

The droplet-size distribution for oilfield emulsions is determined by the following methods (Schramm, 1992):

- Microscopy and image analysis
- Use of electrical properties such as conductivity and dielectric constants (connection between viscosity and dielectric properties of the emulsions (Fingas, 2005))
- A limited number of studies have included the use of NMR to investigate heavy oil and bitumen emulsions. Paso, et al. (2008) used PGSE NMR (pulse gradient spin-echo) to estimate the droplet size distribution of a water in heavy oil emulsion at three temperatures while Achiele et al. (2009) a pulse field gradient with diffusion editing (PEG-DE) with average measured droplet at 12 – 30 μm .
- Physical separation including chromatographic techniques, sedimentation techniques and field-flow fractionation.
- Scattering techniques such as light scattering, neutron scattering and X-ray scattering cover droplet sizes from 0.4 nm to more than 100 μm .
- Turbiscan LAB Expert equipment uses multiple light scattering techniques to detect and determine the destabilizing phenomena suffered by the dispersed systems as they age. With this technology, the destabilizing phenomena of the dispersed systems are detected around 50 times more quickly than by simple observation. The Turbiscan equipment allows emulsion concentration systems of up to 95% to be studied without the need for dilution. This is very important, as diluting the sample itself means variations in the stability of the dispersed systems (Buron, et al., 2004). The particle size measurement range is from 0.05 μm to 1,000 μm while the repeatability of the measurement can be as high as 0.05 % (Turbiscan Lab, n.d.).

4.8 Conclusions

PVT experimental measurements provide key data for reservoir engineering and production applications. Depending on the nature and the volume of the sample, different analysis can be accomplished. The results of the PVT analysis are essential for proper field development, accurate reserve estimation, reservoir simulation studies, material balance calculation, optimum fluid recovery plans, etc. Accurate analysis does not necessarily demonstrate the validity of the properties. Poor quality of PVT data will impact fluid characterization and equation of state modelling, so the samples must be checked further for their validity and accuracy (chapter 5).

4.9 Bibliography

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5. Quality control of the PVT report data

The accurate analysis of the PVT data will enhance the effective management of reservoirs, determine the quantity and the quality of produced fluids and assure correct design of surface facilities. So, the PVT data from the laboratory must be checked for accuracy, consistency and validity.

The errors of PVT according to Moffatt (n.d.) arise from the issues depicted in the figure:

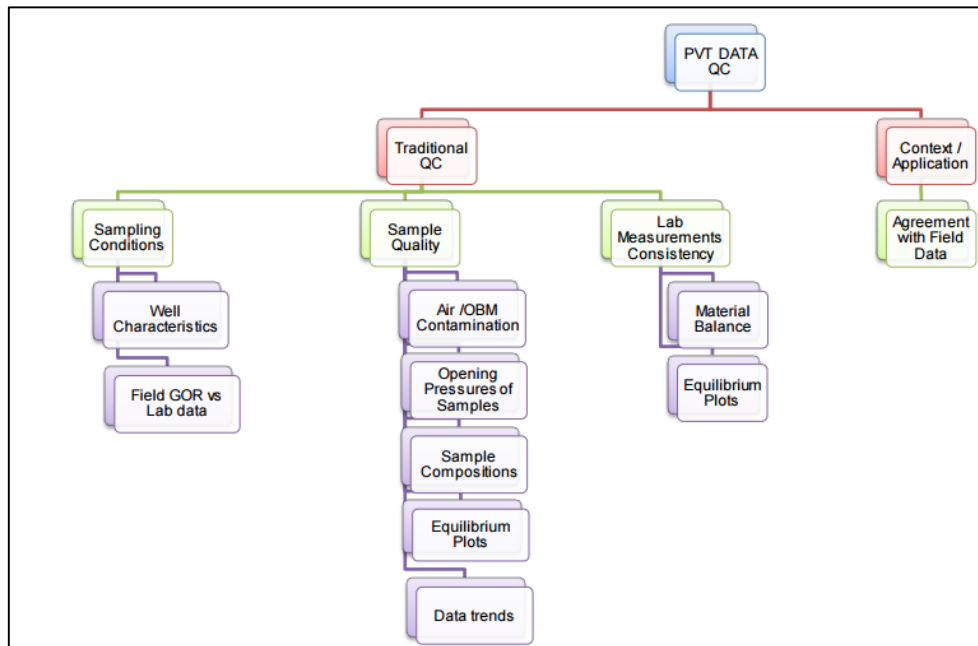


Figure 5.1: PVT data Quality control (Moffatt, n.d).

In order to have high quality of data the Abu Dhabi Company for Onshore Oil Operations (ADCO) has automated the PVT workflow as:

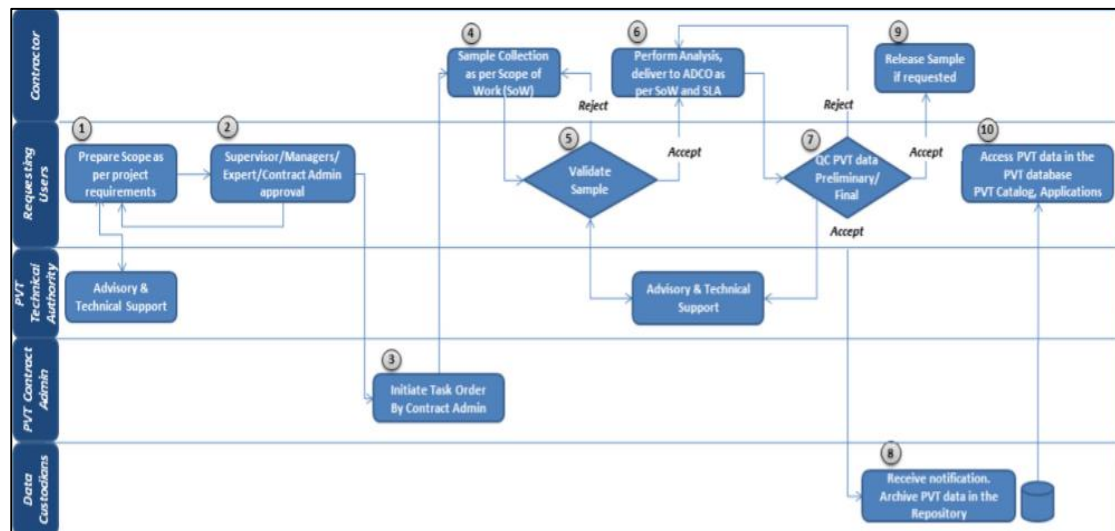


Figure 5.2: Automated Workflow for ADCO (Mawlod and David, 2015).

The steps of PVT data control are (Khan, et al., 2012; Akpabio, Udofia and Ogbu, 2014; Imo-Jack and Emelle 2013; Moffat and Williams, 1998; Lawrence and Gupta, 2009; Osfour, et al., 2014; Whitson, 1998):

- Implementation of Quality Assurance / Quality Control procedures to ensure data quality and consistency:
 - ✓ Material balance checks to assess consistency of composition and flash data
 - ✓ Graphical techniques to compare data
 - ✓ Comparison with equation of state or k value prediction
- Development of mathematical model to capture fluid property changes accurately as functions of pressure, temperature and composition

Samaniego, et al. (2004) describe the validation process of correcting inconsistencies manually (KVALCO), semi-automatically (VALCO) and automatically (AUTOVAL).

5.1 Mass balance (Whitson, 1998; Varotsis, 2014; Danesh, 1998; Whitson and Brulé, 2000; Akpabio, Udofia and Ogbu, 2014; Osfour, et al., 2014; Imo-Jack and Emelle 2013; Lawrence and Gupta, 2009; Akpabio, Isehunwa, and Akinsete, 2015; Nnabuo, Okafor and Ubani, 2014)

The mass balance is a rigorous test that should be applied in order to verify the consistency of composition. It can be used for analyzing results from separator test, constant volume depletion data and differential liberation data. A simple and major consistency test is to sum up the composition and ensure that they add up to 100%. Nevertheless discrepancies in composition from modern PVT reports are usually very small (Imo-Jack and Emelle 2013). Material balance can be conducted as forward and backward process. In the forward material balance, the starting fluid is the original sample and gases are removed in a stepwise process aligned to the laboratory pressure drop steps. The densities of the fluid are calculated at each pressure step and compared with the laboratory report. In the case of the backward material balance, the residual oil is the starting fluid and released gases are added back to the oil until the initial composition is constructed. Pestak, Pande and Swanson (1989) suggest the definition of % error as the percent difference between mass of fluid recovered and mass of starting fluid to confirm the quality of the data.

One mole of fluid of composition z is considered at a certain temperature and pressure (T, P) and is split into L moles of liquid and V moles of vapor composition. The mass balance is based on the following general flash equation describing the individual component material balance around a flash separation stage:

$$L \cdot x_i + V \cdot y_i = F \cdot z_i$$

$$\left(\frac{y_i}{z_i}\right) = \left(-\frac{L}{V}\right) \frac{x_i}{z_i} + F/V$$

By plotting y_i/z_i versus x_i/z_i a straight line equation is obtained with an intercept at F/V and negative slope (L/V). Any deviation from the straight line indicates mass balance inconsistency. The R^2 (Squared correlation coefficient) of the equation value must tend towards unity. The reciprocal of the slope may be used to compute GOR and thereafter compare with the measured GOR. The conversion from mole to barrels is necessary when the values of the liquid density and molecular weight are provided.

5.2 Thermodynamic consistency of the gas and liquid phase during DV and separator test

The k values for the gaseous and liquid phase are computed in order to assess their thermodynamic consistency during the PVT tests. The PVT data that have inconsistencies such as negative equilibrium constants and crossing of the equilibrium constants curves, must be corrected (Samaniego, et al., 2004). According to Brinkman and Sicking (1960) a graph of $\log k_i$ versus the boiling temperature T_{bi} of the different components of the hydrocarbon mixture must follow a straight line. Also, the Hoffman plot and Buckley plot are qualitative assessment of data quality (Akpabio, Udofia and Ogbu, 2014).

5.3 Graphical techniques

Plotting reported properties as a function of pressure is a simple first step in assessing oil data quality. Properties for undersaturated oils should exhibit smooth monotonic trends with pressure (Lawrence and Gupta, 2009; Imo-Jack and Emelle, 2013). When plotting properties for undersaturated oils, compressibility should decrease with increasing pressure, while density and viscosity should increase with increasing pressure. Samaniego et al. (2004) provide another useful plot, the logarithm of the liquid or gas composition versus pressure, where no humps or cross of lines must be observed.

A cross plot is another way to judge the quality of the PVT properties by correlating the found properties with ones predicted by correlations (*Chapter 3.3*). The graph demonstrates the degree of agreement between the experimental and predicted values. If the points lie on the 45° line it indicates that the measured properties are accurate.

A very simple qualitative test for oil data consistency is to compare the residual oil API gravity from the differential liberation with the stock tank API gravity from the separator test (Lawrence and Gupta, 2009). Typically, the oil remaining from the DV test will be denser (lower API gravity) than the stock tank oil from the separator test as the DV test is conducted at higher temperature. While this test is not completely rigorous, it can be very useful for identifying inconsistent data. In the same concept, Imo-Jack and Emelle (2013) suggest the comparison of the density of the separator test and differential liberation. Finally, the calculated from mass balance molar mass of the residual oil can be compared to the molar mass of the stock tank oil and must have larger value.

Some compositional PVT reports include the analysis of the liquid remaining in the cell at the end of the last depletion stage. That residual composition can be compared against the tank composition (Samaniego, et al., 2004).

5.3.1 Watson characterization Factor (Whitson, 1998; Whitson and Brulé, 2000)

The C_{7+} molecular weight ($M_{C_{7+}}$) is highly susceptible to error, with an accuracy ranging from 2 to 10% (Whitson, 1998). The Watson characterization factor K_w describes the relative paraffinicity of a petroleum product and is defined from the normal boiling point (T_b (° R)) and the specific gravity relative to water (γ) as: $K_w = \frac{T_b^{1/3}}{\gamma}$

An approximate relation for the Watson factor based on molecular weight and specific gravity is: $K_w = 4.5579 \cdot M^{0.15178} \cdot \gamma^{-0.84573}$

A plot of $M_{C_{7+}}$ versus $\gamma_{C_{7+}}$ can be updated with each new sample, where a line of constant $K_{w,C_{7+}}$ is drawn (Figure 5.3). Deviation of ± 0.03 in $K_{w,C_{7+}}$ is acceptable while larger errors indicate possible errors in reported molar composition (Whitson, 1998).

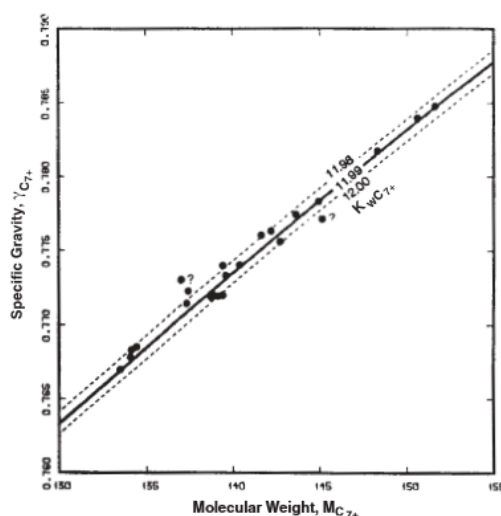


Figure 5.3: Specific gravity versus molecular weight for C_{7+} (Whitson and Brulé, 2000).

5.3.2 Y - function

The Y-function is linear with pressure and is related to the two phase volume (V_p (scf)), bubble-point volume (V_b (scf)), bubble-point pressure (P_b (psia)) and pressure (P (psia)) as follows: (Whitson, 1998; Hosein, Mayrhoo. and McCain, 2014; Nnabuo, Okafor and Ubani, 2014):
$$Y = \frac{P_b - P}{P \cdot (V_p/V_b - 1)}$$

The Y - function, which is dimensionless, is applied to CCE data below the bubble-point from black oil PVT studies (Standing, 1952) but has also been extended to determine the bubble-point pressures for black oils and volatile oils (Hosein, Mayrhoo. and McCain, 2014).

5.4 Building an EOS PVT model (Osfour, et al., 2014; Akpabio, Udofia and Ogbu, 2014; Akpabio, Isehunwa and Akinsete, 2015; Lawrence and Gupta, 2009)

Reservoir and production engineers require PVT measurements to predict reservoir performance and future processing needs. PVT models are usually generated with the aid of mathematical algorithms expressed as Equation of State (EOS) (Schebetov, Rimoldi and Piana, 2010).

EOS can be modeled with the following general procedure:

- Selection of an appropriate EOS expression that can represent the reservoir fluid well (Akpabio, Udofia and Ogbu, 2014; Wang and Pope, 2001; Nagarajan, Honarpour and Sampath, 2007). For particular oils, specialized EOS have been generated such as for the Egyptian crude oils (Mansour, et al., 2013) and for heavy hydrocarbons (Mohesen – Nia, 2014; Samaniego, et al., 2004).
- Experimental data such as composition at reference pressure, temperature and depth, are entered to the EOS model. It is worth mentioning that special care must be given at the selected experimental data as far as they must be under thermodynamic equilibrium with approved material balance.
- The deviation between the calculated from EOS model and experimental properties is checked.
- If GOR and density do not match, then the molecular weight or specific gravity of the pseudo component is changed by 5-10%.
- Binary Interaction Parameters (BIP) are used to match saturation pressure while the Pseudo components are split.
- The BIPs and critical properties of pseudo components are regressed if a large deviation is noticed.
- After regression, the EOS model can be lumped for use in simulation model to reduce the simulation time (compositional simulators).

Equation of state parameters can sometimes be tuned beyond reasonable bounds to match PVT measurements that are not physically sound. When an equation of state is overly tuned to bad data then the ability to predict properties outside the range of the measurements is compromised (Akpabio, Udofia and Ogbu, 2014).

A comparison of three different prediction models is presented in *Table 5.1* where the error in bubble point pressure is calculated.

Table 5.1: Comparison of results for three prediction models with measured bubble point Pressure (McCain, et al., 1998).

	Average Error in P_b %	Average Absolute Error in P_b %
<i>Non linear regression</i>	0.6	11.4
<i>Non parametric regression</i>	3.1	11.8
<i>Neural network</i>	-0.3	6.0

5.5 Conclusions

High quality, accurate PVT data can reduce uncertainty in reservoir fluid properties, provide a sound foundation for reservoir engineering studies and improve investment efficiency. While acquiring sufficient volumes of representative reservoir fluid samples is the first step in obtaining reliable PVT data (chapter 3), understanding and identifying the quality of the PVT data (chapter 5) is essential.

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6. Application of PVT quality control methods on oil PVT lab reports

In this Chapter, the quality of PVT reports for samples coming from Tunisia, Congo and other unknown locations will be examined. For the fluids of unknown origin were given the names 'Unknown 9' and 'Unknown X'. An excel file called '*name of oil.xlsx*' was built in order to check:

- Quality of separator samples
 - ✓ P_{bubble} of the liquid samples versus the separator pressure
 - ✓ P_{opening} of the gas samples versus the separator pressure
 - ✓ Comparison of composition between separator gas samples
 - ✓ Thermodynamic consistency of the separator phases
 - ✓ Recombination process for the reservoir fluid
- Quality of bottom hole samples
 - ✓ P_{bubble} versus the bubble point pressure from CCE
 - ✓ Composition of flashed phases
- CCE test
 - ✓ Y function
 - ✓ Isothermal oil compressibility
- Differential vaporization test
 - ✓ Material balance for each pressure step
 - ✓ Thermodynamic consistency of the phases at each pressure step
 - ✓ Comparison of composition of residual oil and stock tank oil
 - ✓ Comparison of molar mass between residual oil and stock tank oil
- Laboratory separator tests
 - ✓ Material balance for each pressure step
 - ✓ Optimization of separator pressure through the plot of the reported GOR values of the separator tests versus pressure
- Comparison of differential and laboratory separator tests data
 - ✓ Conversion of differential liberation data to stock tank oil basis
 - ✓ Comparison of molar mass between residual oil and stock tank oil
 - ✓ Comparison of solution gas to oil ratio
- Viscosity
 - ✓ Viscosity distribution

As far as the material balance is concerned for the differential vaporization and the laboratory separator tests, the basis of the computations is 1 m³ of residual oil. For the DV test, the mass of the residual oil can be calculated based on its density. The mass of the bubble point fluid can be represented by the summation of all the masses of the gas removed at each pressure step and the mass of the residual oil. The molar mass of the reservoir fluid is known, so the moles of the reservoir fluid are obtained.

For the laboratory separator test, the same procedure is used.

In the following subchapters, the results of the PVT experiments and the quality control study will be given for each oil and test separately.

6.1 Tunisian oil 1

A PVT report for a Tunisian oil is tested with respect to the sample representativity and PVT report accuracy.

6.1.1 Quality control of the analyzed samples

Separator samples were used for the study. Firstly, a comparison of opening and bubble point pressure, air content, carry over and BS&W is held. At the PVT laboratory sheet the carry over for the gas phase is examined by checking the liquid hydrocarbon, water and mud content. In *Table 6.1*, the recorded conditions of separator and well head are presented:

Table 6.1: Conditions of separator and well head.

Separator pressure (psia)	Separator temperature (°F)	Well head pressure (psia)	Well head temperature (°F)
63	90	1,135	174

The following Table depicts the results of checking each sample taken.

Table 6.2: Separator samples for Tunisian oil 1.

Gas				
#	Time	Opening pressure (psia) at 68 °F	Carry over	Air (mole %)
SG 01	10:05	75	0	0
SG 02	10:30	85	0	0
SG 03	11:00	85	0	0
SG 04	11:25	85	0	0
Liquid				
#	Time	Bubble point pressure (psia) at 90 °F	BS&W	
SLS01	10:05	60	0	
SLS02	10:55	65	2cm ³ water	

From the liquid samples, the SLS01 seems to be the best choice because it does not contain water. As far as the bubble point pressure is concerned, both liquid samples have acceptable values, since the separator pressure is 63 psia.

None of the gas samples, contain air, liquid hydrocarbons, water, mud and sediments so the opening pressure and the composition will be used for their evaluation. The opening pressure of the gaseous phase must be checked versus separator pressure. The following expression can be used for the conversion of separator pressure to opening pressure: $P_{opening} = P_{sp} \cdot \frac{T_{opening}}{T_{sp}}$

Despite the fact that three gas samples have the same opening pressure, the SG01 seems to be the best sample as it has the closest value of opening pressure to the converted opening pressure from separator pressure. Furthermore, the sample SG01 was taken at the same time with SLS01, so, if they are recombined, they have better chances of being thermodynamically consistent.

The compositions of the gas samples are presented in the following Table:

Table 6.3: Compositions of the gas field separator samples for Tunisian oil 1.

	SG01	SG02	SG03	SG04
N₂ (%mol)	24.70	24.96	24.12	24.05
CO₂ (%mol)	37.47	37.31	37.90	37.58
H₂S (%mol)	0.00	0.00	0.00	0.00
CH₄ (%mol)	20.33	20.38	20.51	20.49
C₂H₆ (%mol)	4.67	4.59	4.64	4.78
C₃H₈ (%mol)	5.34	5.18	5.31	5.51
iso C₄H₁₀ (%mol)	1.56	1.59	1.58	1.62
nC₄H₁₀ (%mol)	2.60	2.64	2.62	2.70
iso C₅H₁₂ (%mol)	1.07	1.09	1.09	1.09
n C₅H₁₂ (%mol)	0.98	0.99	0.97	0.97
pseudo C₆ (%mol)	0.74	0.75	0.74	0.72
C₇₊ (%mol)	0.54	0.52	0.52	0.49
Molar mass (g/mol)	35.53	35.49	35.57	35.56

All of the gas samples have similar composition distribution and molar masses.

Finally, the samples SG01 and SLS01 seem to be the best samples to be recombined, so their thermodynamic consistency (their composition is presented in *Table 6.5*) is tested by Hoffman plot (*Figure 6.1*) and Buckley plot (*Figure 6.2*), as follows:

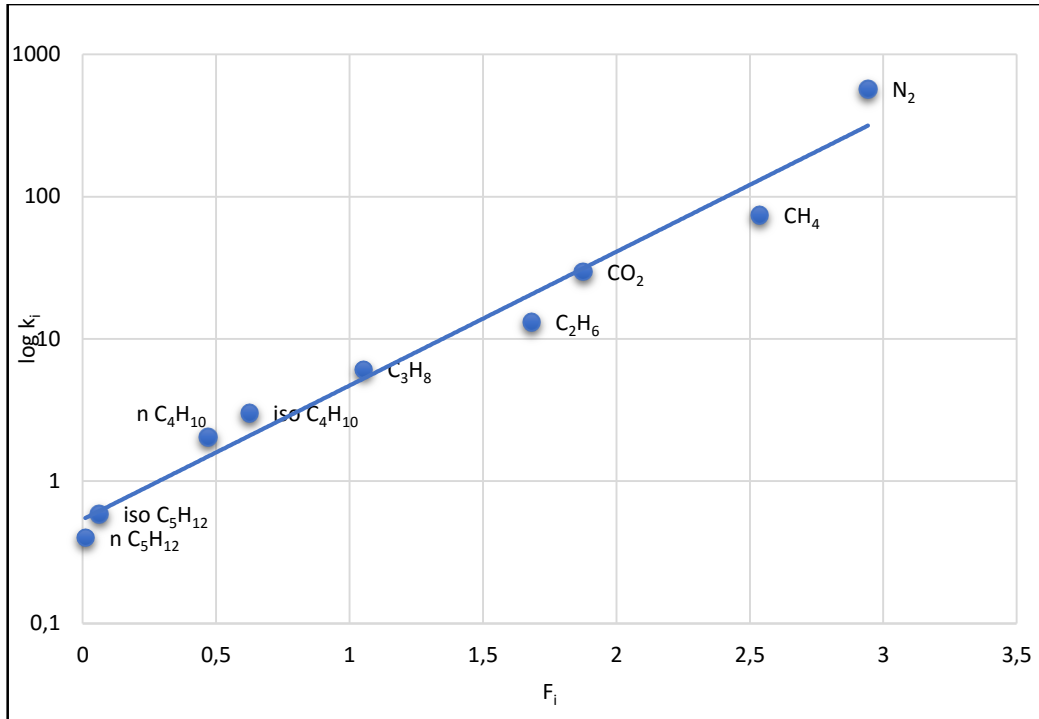


Figure 6.1: Hoffman plot for Tunisian oil 1 - SG01 and SLS01.

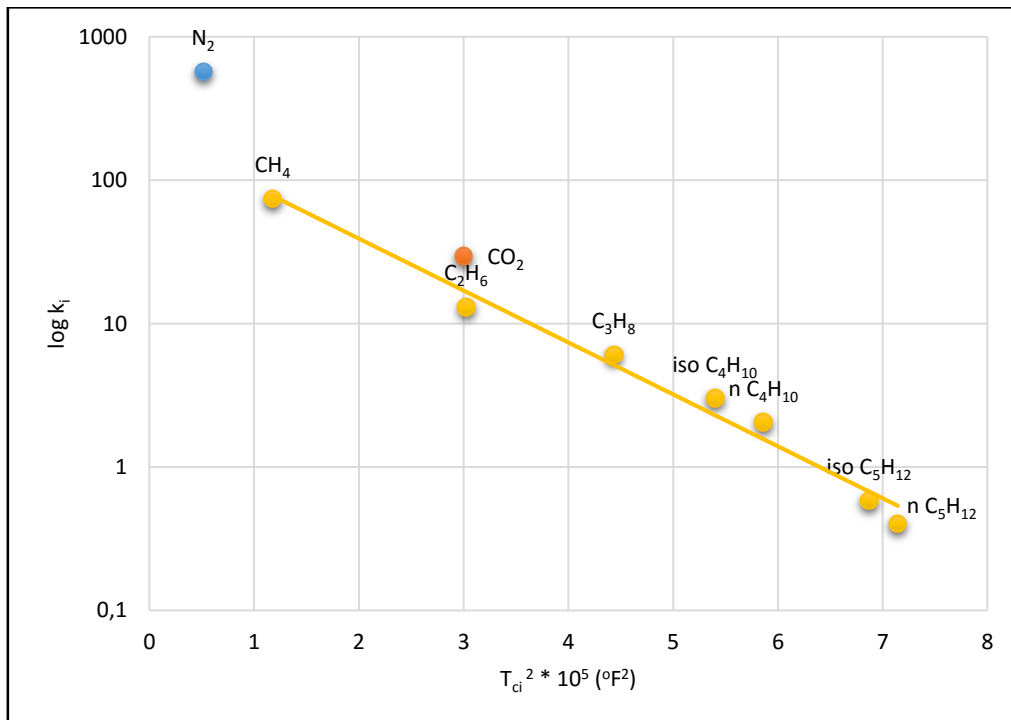


Figure 6.2: Buckley plot for Tunisian oil 1 - SG01 and SLS01.

As can be derived from the previous plots, the behavior of the components is the anticipated one; linearity in the Hoffman plot and line with negative slope in the Buckley plot. So, the gas and liquid phases are in thermodynamic equilibrium and the separator gas and liquid samples have been correctly selected for the recombination process.

The recombination process for the reservoir fluid took place with molar ratio according to the corrected gas to oil ratio. The obtained data for the field and laboratory data are presented in the following Table:

Table 6.4: Correction of gas to oil ratio.

	Z	Specific gravity	R_{sp} (scf/bbl)
Field	0.957	1.255	580
Laboratory	0.989	1.226	$\frac{580 \text{ scf/bbl}}{\frac{\sqrt{0.957 \cdot 1.255}}{\sqrt{0.989 \cdot 1.226}}} = 577 \text{ scf/bbl}$

The chromatographically obtained compositions of the separator gas, separator liquid and recombined fluid are presented in Table 6.5. It is worth mentioning that the composition of separator liquid was obtained after flashing and recombining it mathematically to the separator liquid.

Table 6.5: Compositions and molar masses of the separator liquid, separator gas and recombined reservoir fluid.

	Separator liquid	Separator gas	Recombined fluid
N₂ (%mol)	0.04	24.70	11.66
CO₂ (%mol)	1.30	37.47	18.34
H₂S (%mol)	0.01	0.00	0.00
CH₄ (%mol)	0.28	20.33	9.72
C₂H₆ (%mol)	0.36	4.67	2.39
C₃H₈ (%mol)	0.90	5.34	2.99
iso C₄H₁₀ (%mol)	0.52	1.56	1.01
nC₄H₁₀ (%mol)	1.28	2.60	1.90
iso C₅H₁₂ (%mol)	1.83	1.07	1.47
n C₅H₁₂ (%mol)	2.43	0.98	1.75
pseudo C₆ (%mol)	6.94	0.74	4.02
pseudo C₇ (%mol)	11.27	0.39	6.14
pseudo C₈ (%mol)	13.41	0.13	7.16
pseudo C₉ (%mol)	10.56	0.02	5.60
pseudo C₁₀ (%mol)	9.20	0.00	4.87
pseudo C₁₁ (%mol)	6.67	0.00	3.53
C₁₂₊ (%mol)	33.00	0.00	17.45
Molar mass (g/mol)	164.4	35.53	103.7

The composition of the reservoir oil has typical values of a black oil. As expected, the separator liquid is heavier than the recombined reservoir fluid.

6.1.2 CCE test

The CCE test provides the relative volume according to *Table 6.6*:

Table 6.6: CCE data for Tunisian oil 1.

Pressure (psia)	Relative volume
5,015	0.9708
4,763	0.9746
4,492	0.9790
4,253	0.9828
4,000	0.9872
3,770	0.9914
3,567	0.9952
3,400	0.9986
3,332 = P_b	1.0000
3,282	1.0036
3,172	1.0129
2,980	1.0318
2,744	1.0604
2,439	1.1085
2,022	1.2063
1,746	1.3048
1,393	1.5030
1,088	1.8018
808	2.3078

At pressure equal to bubble point pressure, the relative volume equals to unity.

Laboratory inaccuracies in measuring the total hydrocarbon volume just below the saturation pressure frequently require correction by smoothing the relative volume data. The Y - function is used to smooth the values of the relative volume by plotting the Y-function as a function of pressure on a Cartesian scale and by using the coefficients of it to correct the relative volume. The whole procedure is described by Ahmed (2007). Generally, the Y - function when plotted, forms a straight line and has only a small curvature at pressures close to the bubble point pressure, as in *Figure 6.3*:

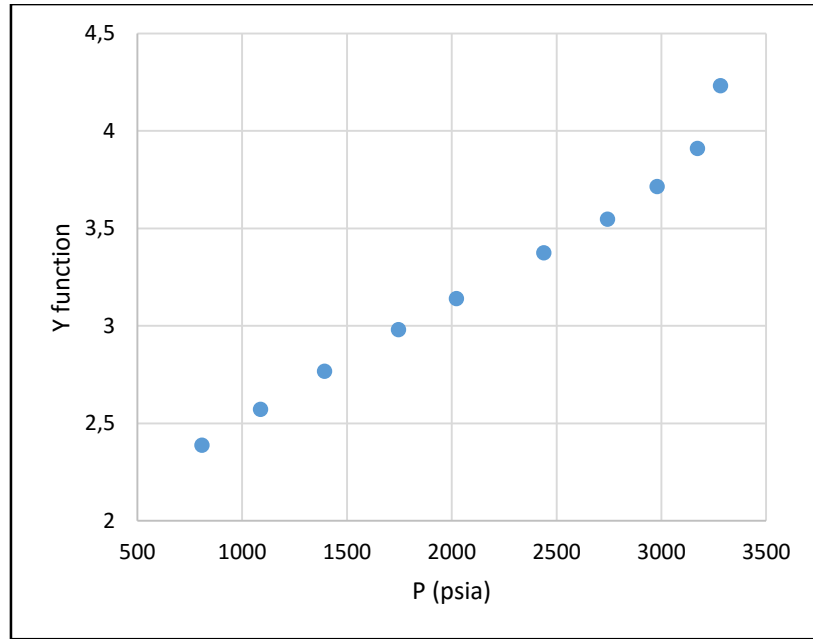


Figure 6.3: Y function.

As far as the oil compressibility is concerned, its value for pressures above bubble point can be derived from CCE by counting the derivative of volume to the pressure change. It is expected that, as pressure decreases, the oil compressibility increases linearly (Figure 6.4). A small error in relative volume leads to huge deviation of the derivative of the volume, so the isothermal compressibility would deviate from linearity with pressure. The values of isothermal oil compressibility were found with respect to the given relative volume (Table 6.6). The Figure 6.4 presents the isothermal oil compressibility versus pressure:

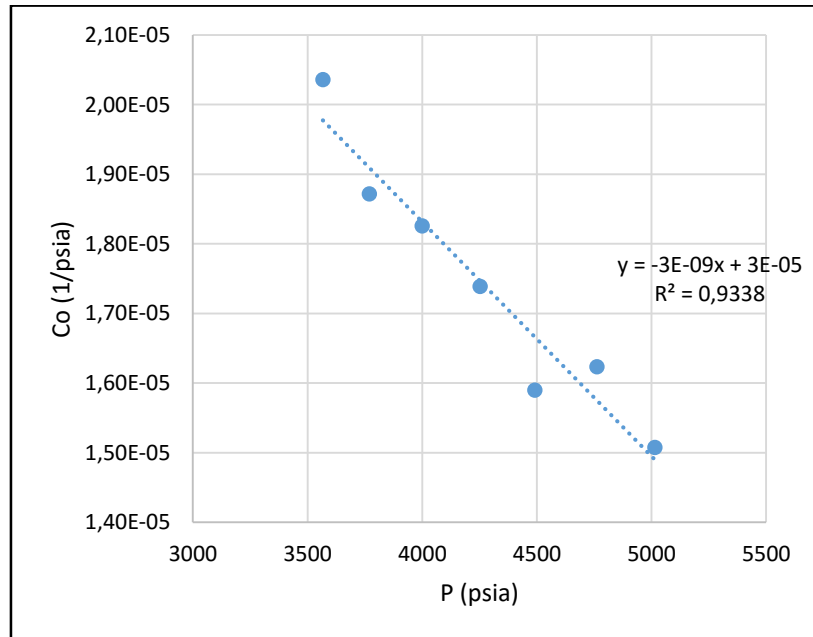


Figure 6.4: Isothermal oil compressibility for pressures above bubble point.

In Figure 6.4, the points lie on the line $y = -3 \cdot 10^{-9} \cdot x + 3 \cdot 10^{-5}$ in a satisfying manner.

6.1.3 Differential vaporization test

For the differential vaporization test, a material balance will be held in order to find the k values and the compositions of the gaseous and liquid phases at each pressure step, and the molar mass of the residual oil.

The mass of removed gas at each pressure step is calculated based on the solution GOR (*Table 6.7*).

Table 6.7: Mass of removed gas at each pressure step at DV for Tunisian oil 1.

Pressure (psia)	R_s (sm ³ /sm ³)	Moles of gas (moles)	Moles of removed gas	Molar mass of gas (g/mol)	Mass of removed gas (kg)
3,332	165.6	6,990.3	-	-	-
2,821	148.3	6,260.0	730.3	33.8	24.683
2,200	125.8	5,310.3	949.8	33.43	31.751
1,420	95.3	4,022.8	1,287.5	34.16	43.980
702	64.8	2,735.3	1,287.5	36.51	47.005
226	38.8	1,637.8	1,097.5	42.95	47.138
15	0	0.0	1,637.8	73.77	120.822

For example, for $p = 2,821$ psia:

$$R_s = 148.3 \text{ sm}^3/\text{sm}^3$$

$$\text{moles of gas} = \frac{R_s}{0.02369 \text{ m}^3/\text{mol}} = 6,260.0 \text{ mol}$$

$$\text{moles of removed gas} = 6,990.3 \text{ mole} - 6,260.0 \text{ mole} = 730.3 \text{ mole}$$

$$MW_{\text{gas}} = 33.8 \text{ g/mol}$$

$$\text{So: mass of removed gas} = 730.3 \text{ mole} \cdot 33.8 \frac{\text{g}}{\text{mole}} = 24.683 \text{ kg}$$

The mass of the residual oil is found from the tank density for 1 sm³ of residual oil. The mass of the bubble point fluid is calculated by adding the masses of the gases removed at each pressure step (*Table 6.7*) plus the mass of the residual oil. The molar mass of the reservoir fluid is known, so the moles of the bubble point fluid are obtained. The following Table summarizes the results.

Table 6.8: Mass of residual oil and moles of bubble point fluid.

Residual oil relative density	Mass of residual oil(kg)	Mass of bubble point fluid (kg)	Molar mass of reservoir fluid (g/mol)	Moles of bubble point fluid
0.838	838	1,153.379	103.7	11,122.3

From the number of moles of gas removed at each pressure step, the moles of liquid and the molar ratios of each phase are found. Then, since the gas compositions are given at each pressure step, the liquid phase compositions can be obtained. In more details, the moles of liquid phase are found from the simple material balance:

$$\text{moles of inlet stream} = \text{moles of gas} + \text{moles of liquid}$$

The inlet stream is always the liquid phase from the previous pressure step.

The compositions of the liquid and the gas phase for each pressure step are given in the following Tables:

Table 6.9: Gas compositions at different pressure steps.

Pressure Composition	2,821psia	2,200 psia	1,420 psia	702 psia	226 psia	15 psia
N₂ (%mol)	36.40	36.84	30.50	18.88	6.24	0.52
CO₂ (%mol)	30.65	30.02	33.62	40.23	42.56	11.52
H₂S (%mol)	0.00	0.00	0.00	0.00	0.00	0.00
CH₄ (%mol)	20.88	21.32	22.41	22.19	14.65	2.83
C₂H₆ (%mol)	2.97	3.01	3.49	4.79	7.01	3.43
C₃H₈ (%mol)	3.02	3.00	3.57	5.11	10.05	9.57
iso C₄H₁₀ (%mol)	0.90	0.92	1.07	1.54	3.38	5.04
nC₄H₁₀ (%mol)	1.58	1.56	1.86	2.59	6.10	10.98
iso C₅H₁₂ (%mol)	0.82	0.82	0.90	1.26	2.99	8.44
n C₅H₁₂ (%mol)	0.83	0.81	0.89	1.23	2.87	9.07
pseudo C₆ (%mol)	0.88	0.84	0.88	1.16	2.60	12.63
C₇₊ (%mol)	1.07	0.86	0.81	1.02	1.55	25.99
Molar mass (g/mol)	33.80	33.43	34.16	36.51	42.95	73.77

Table 6.10: Liquid compositions at different pressure steps.

Pressure	2,821psia	2,200 psia	1,420 psia	702 psia	226 psia	15 psia
Composition						
N₂ (%mol)	9.92	7.21	3.54	0.66	-0.40	-0.76
CO₂ (%mol)	17.47	16.21	13.46	8.45	1.96	-1.83
H₂S (%mol)	0.00	0.00	0.00	0.00	0.00	0.00
CH₄ (%mol)	8.94	7.69	5.37	2.21	-0.15	-1.34
C₂H₆ (%mol)	2.35	2.28	2.09	1.59	0.55	-0.58
C₃H₈ (%mol)	2.99	2.99	2.89	2.48	1.04	-2.34
iso C₄H₁₀ (%mol)	1.02	1.03	1.02	0.92	0.46	-1.36
nC₄H₁₀ (%mol)	1.92	1.96	1.97	1.86	1.05	-2.88
iso C₅H₁₂ (%mol)	1.52	1.59	1.69	1.78	1.54	-1.19
n C₅H₁₂ (%mol)	1.81	1.92	2.08	2.24	2.12	-0.64
pseudo C₆ (%mol)	4.24	4.58	5.17	5.92	6.55	4.14
C₇₊ (%mol)	47.82	52.54	60.71	71.90	85.28	108.79
Molar mass (g/mol)	108.61	116.17	129.12	146.49	166.18	202.81

Negative compositions and compositions above 100% are indications of errors occurred during DV. Such unrealistic results are attributed to errors during the analysis of the gas compositions by chromatography. As a result, the light components appear to exhibit higher concentrations than they should have had, while exactly the opposite applies for the heavy components. So, the residual oil has negative compositions for light components and >100 % for the heavy end. The gas chromatograph may cannot track correctly the traces of the compounds, so perhaps, a cold trap would help to avoid this situation.

The values of the liquid molar mass appear to be reasonable since at each pressure step the remaining oil becomes heavier. It is worth mentioning that the calculation of the molar mass of the residual oil does not take into account its composition as it is computed from the overall material balance.

The semi logarithmic plot of k values at each pressure step and per component is made and the results are presented in the following Figure. It must be pointed out that due to negative compositions of some components, the logarithmic k values of some components for pressure 226 psia and 15 psia can not be computed and are not depicted in the following Figure.

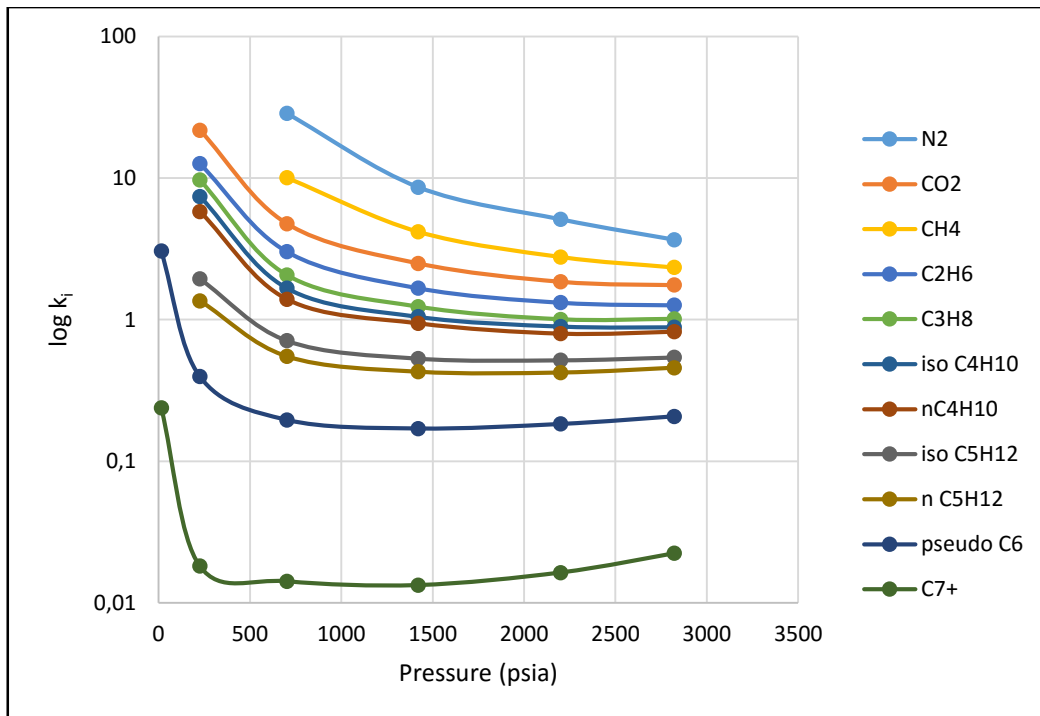


Figure 6.5: Semi logarithmic plot of k versus pressure for each component at DV test.

If the above curves are extrapolated, the convergence pressure of the system could be determined.

In Figures 6.6 and 6.7, the compositions of the gas and the liquid phases for all the pressure steps are presented.

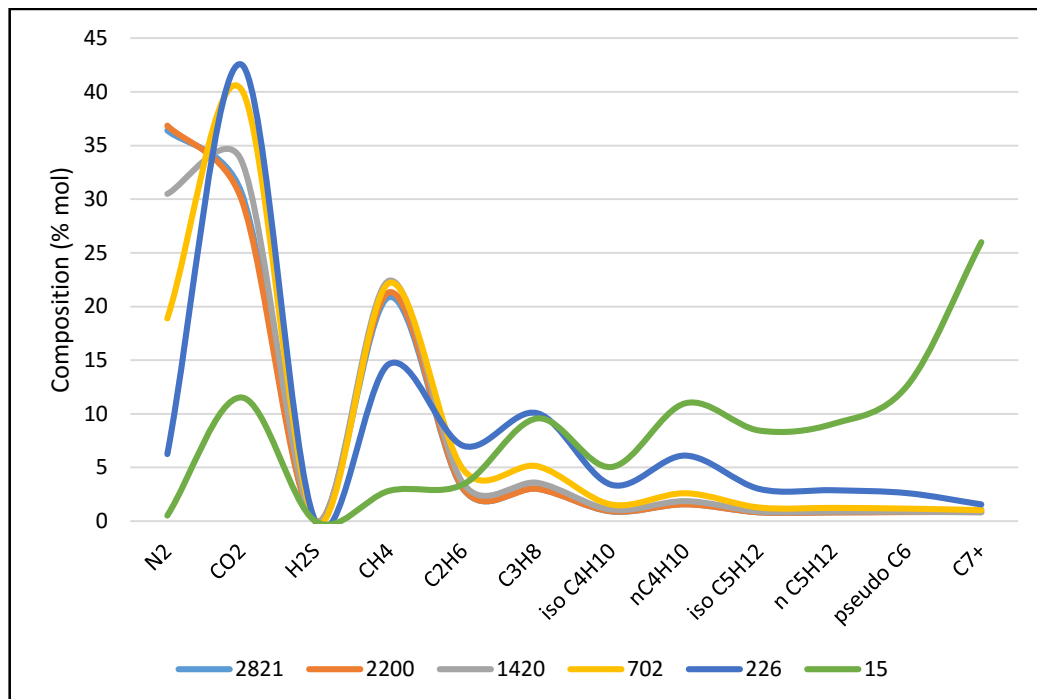


Figure 6.6: DV gas compositions for all the components and pressure steps.

The DV gas compositions have exactly the same distributions for pressure steps 2,821 and 2,200 psia. As pressure decreases down to 702 psia, small deviation in the gas compositions is observed, with the decrease in nitrogen and the increase in carbon dioxide being more obvious. As expected, as pressure decreases, the composition of the evaporated gas is slightly richer in heavy compounds. For pressure of 226psia, a decrease in nitrogen and methane is observed, while the components heavier than ethane have almost doubled their % mol composition from the previous pressure step, except of the C_{7+} one that it is not increased. Finally, at 15 psia the composition in nitrogen, carbon dioxide, methane and ethane decreases while the propane is not influenced. All the other components increased their composition drastically, with the C_{7+} occupying sixteen times higher % mol composition than the previous pressure steps.

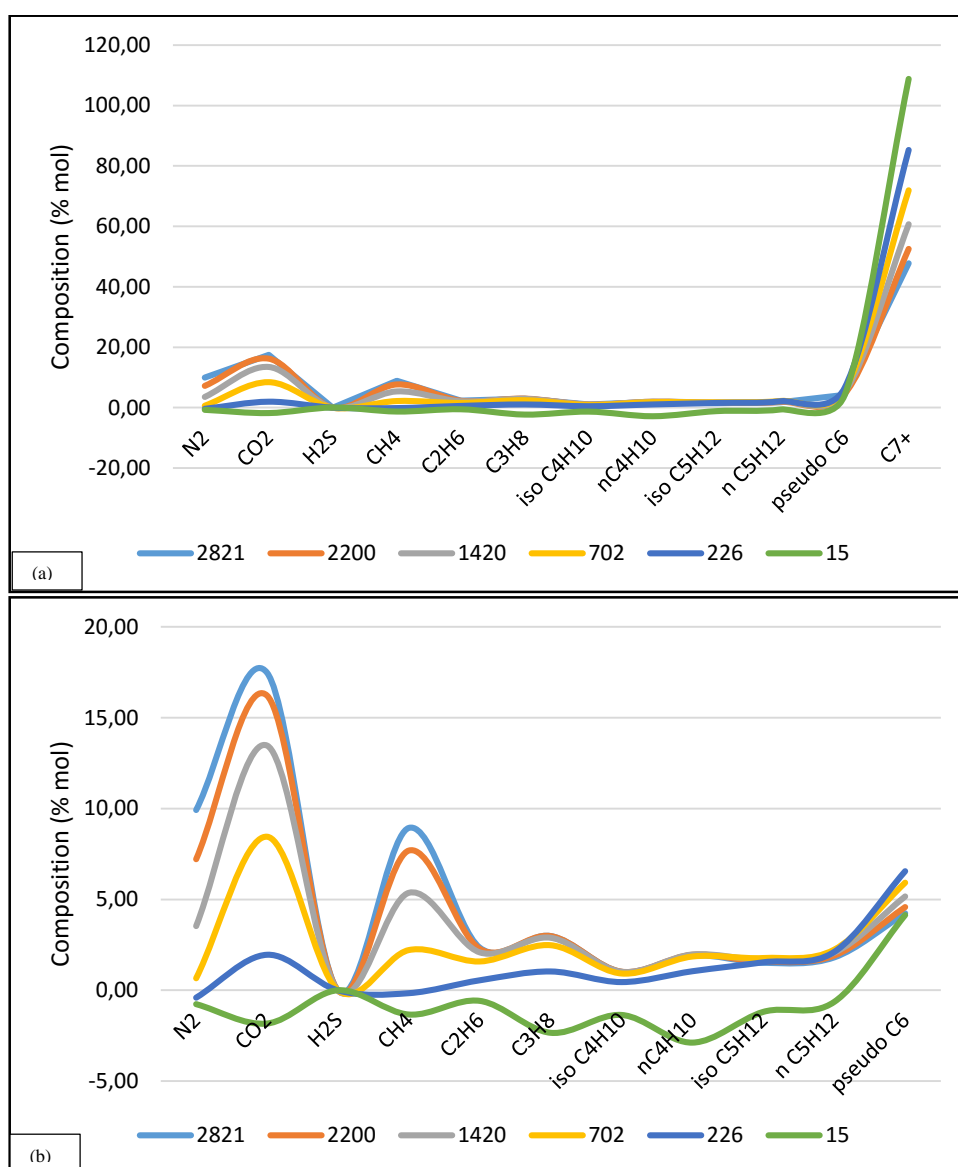


Figure 6.7: DV liquid compositions for all the components and pressure steps:
(a) original plot, (b) zoom in without C_{7+} composition.

The DV liquid compositions for components lighter than C_2H_6 and at pressures down to 702 psia have almost the same distributions with values of composition that decrease, while components heavier than C_2H_6 are slightly affected. At pressure of 226 psia and 15 psia, the results are not realistic ($<0\%$ and $>100\%$).

As far as the material balance is concerned the terms y_i/z_i and x_i/z_i are computed for each pressure step in order to construct the following plots:

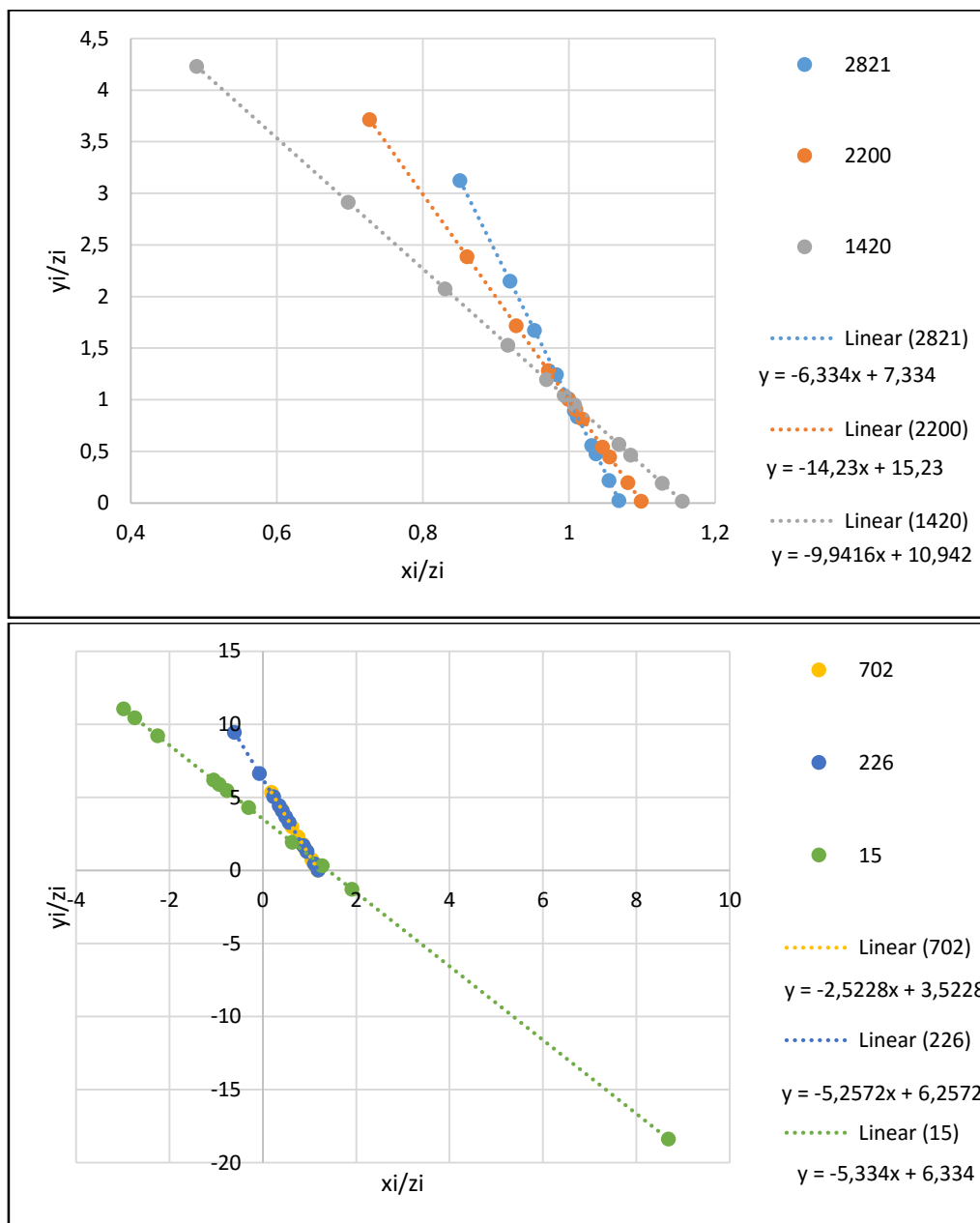


Figure 6.8: Material balance for each pressure step at DV test.

In Figure 6.8 is observed perfect linearity for each pressure step. So, the material balance at each pressure step is satisfied, despite the fact that the composition exhibits unrealistic values (negative) for some components. In the case of plotting the material balance per component, the following figures will result:

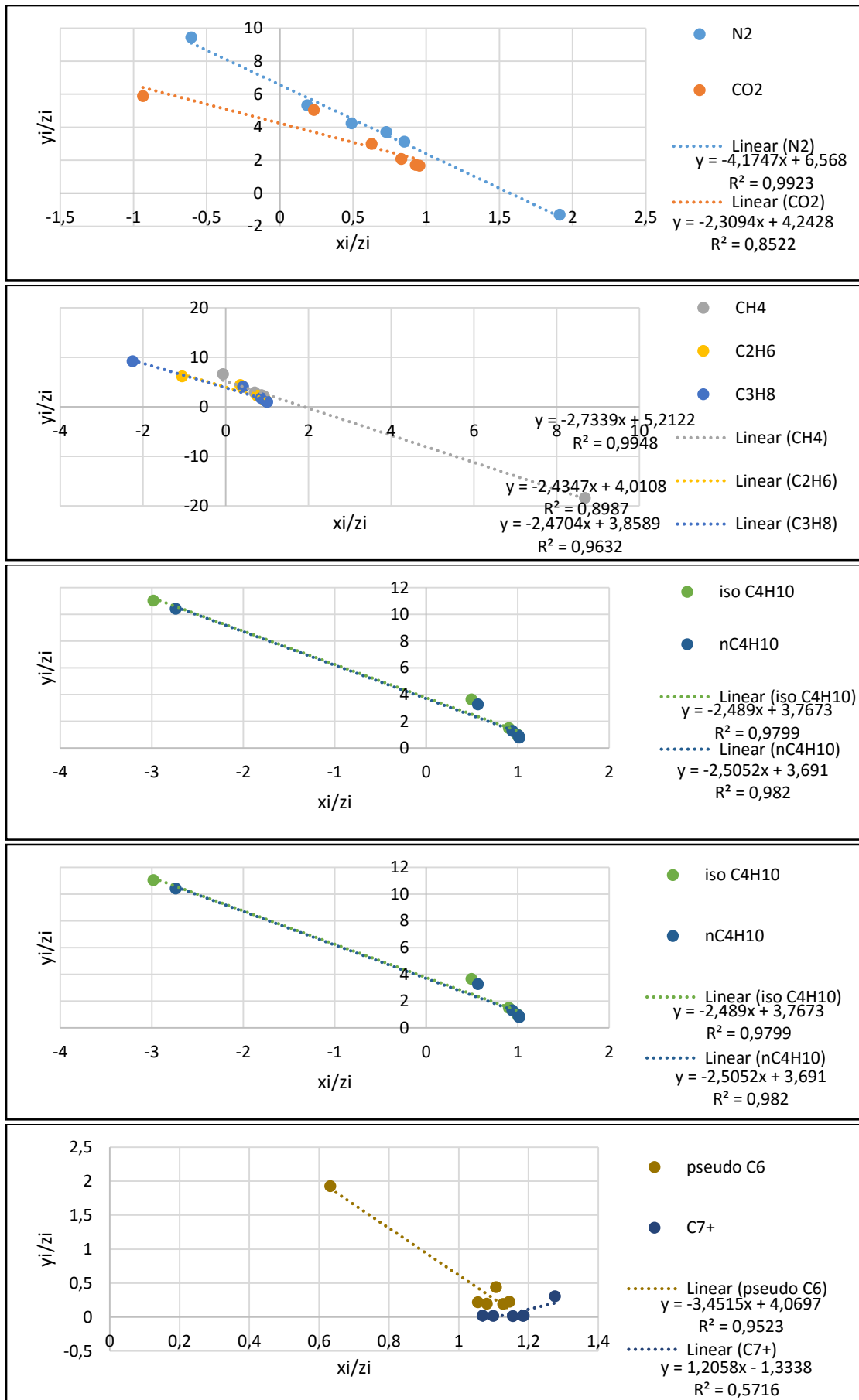


Figure 6.9: Material balance for each component at DV test.

In *Figure 6.9* the CO_2 and C_2H_6 have the anticipated behavior (line with negative slope) but some points abstain from the line (the squared correlation coefficient does not tend towards units). On the other hand, the C_{7+} has line with positive slope, indication of error.

It is worth mentioning that only the forward material balance could be accomplished because the data needed to proceed with the backward material balance were unavailable (the liquid composition of the residual oil was not recorded in the PVT spreadsheet).

Finally, the calculated composition and the molar mass of the residual oil are compared to the stock tank oil ones (*Table 6.11*).

Table 6.11: Comparison of the back calculated residual oil and the measured stock tank oil compositions.

Composition	Residual oil from DV	Stock tank oil
N_2 (%mol)	-0.76	0.04
CO_2 (%mol)	-1.83	1.30
H_2S (%mol)	0.00	0.01
CH_4 (%mol)	-1.34	0.28
C_2H_6 (%mol)	-0.58	0.36
C_3H_8 (%mol)	-2.34	0.90
iso C_4H_{10} (%mol)	-1.36	0.52
n C_4H_{10} (%mol)	-2.88	1.28
iso C_5H_{12} (%mol)	-1.19	1.83
n C_5H_{12} (%mol)	-0.64	2.43
pseudo C_6 (%mol)	4.14	6.94
C_{7+} (%mol)	108.79	84.11
Molar mass (g/mol)	202.8	164.4

The back calculated residual oil from DV data is heavier than the measured stock tank oil. The two compositions cannot be compared due to the negative values of the residual oil composition. Nevertheless, it is observed, that the residual oil from DV is poorer at all the components except from the heavy end, when compared to the stock tank oil. Except from possible errors occurred during gas analysis of the liberated gas, the possible erratic values of molar mass of the gas phase and / or the reservoir fluid, may burden furthermore the calculations during material balance. The molar mass of the reservoir fluid is prone to errors, so if the calculations were based only on mol composition, the results could be potentially physical sound.

Despite the fact that the DV study concluded to errors in % mol composition of the residual oil, the volumetric DV data B_o , B_g and R_s are the most important variables from the test and have physically sound values.

6.1.4 Laboratory separator tests

Material balance is also held for the laboratory separator tests. In more details, the mass of removed gas at each pressure step is calculated according to the Gas liquid ratio (Table 6.12). The basis of the calculations is 1 sm³ of stock tank oil.

Table 6.12: Mass of removed gas at each pressure step for the laboratory separator tests.

p=500 psia				
	Gas liquid ratio (sm ³ /sm ³)	Moles of removed gas (moles)	Molar mass of removed gas (g/mole)	Mass of removed gas (kg)
Separator	70.9	2,992.8	32.34	96.788
Tank	34.2	1,443.6	43.77	63.188
p=265 psia				
	Gas liquid ratio (sm ³ /sm ³)	Moles of removed gas (moles)	Molar mass of removed gas (g/mole)	Mass of removed gas (kg)
Separator	80.1	3,381.2	33.28	112.525
Tank	23.3	983.5	44.82	44.082
p=115 psia				
	Gas liquid ratio (sm ³ /sm ³)	Moles of removed gas (moles)	Molar mass of removed gas (g/mole)	Mass of removed gas (kg)
Separator	92.1	3,887.7	34.63	134.632
Tank	10.8	455.9	46.19	21.057
p=15 psia				
	Gas liquid ratio (sm ³ /sm ³)	Moles of removed gas (moles)	Molar mass of removed gas (g/mol)	Mass of removed gas (kg)
Separator	120.0	5,065.4	38.38	194.411

For example, for p = 500 psia at separator:

$$GOR = 70.9 \text{ sm}^3/\text{sm}^3$$

$$\text{moles of removed gas} = \frac{GOR}{0.02369 \text{ m}^3/\text{mol}} = 2,992.8 \text{ mole}$$

$$MW_{\text{gas}} = 32.34 \text{ g/mole}$$

$$\text{So: mass of removed gas} = 2,992.8 \text{ mole} \cdot 32.34 \frac{\text{g}}{\text{mol}} = 96.788 \text{ kg}$$

The mass of the stock tank oil is found through the tank density for 1sm³ stock tank oil:

Table 6.13: Mass of stock tank oil at each pressure step.

p (psia)	Tank density (g/cm³)	Mass of stock tank oil (kg)
500	0.815	815
265	0.814	814
115	0.814	814
15	0.820	820

The mass of the reservoir oil for each flash test is calculated by adding the masses of the gas removed at separator and tank at each pressure step, plus the mass of the stock tank oil at each pressure step. The molar mass of the reservoir fluid is known, so the moles of the reservoir fluid at each pressure step are obtained.

Table 6.14: Moles of reservoir fluid for the laboratory separator tests.

p (psia)	Mass of removed gas from separator (kg)	Mass of removed gas from tank (kg)	Mass of stock tank oil (kg)	Mass of reservoir fluid (kg)	Molar mass of reservoir fluid (g/mol)	Mol of reservoir fluid (mol)
500	96.788	63.188	815	974.976	103.7	9,401.9
265	112.525	44.082	814	970.608		9,359.8
115	134.632	21.057	814	969.689		9,350.9
15	194.411	0.000	820	1,014.411		9,782.2

From the number of moles of gas removed at each step, the liquid phase composition is calculated at each pressure step by material balance. The liquid compositions for p = 115 psia are given in the following Table:

Table 6.15: Compositions of laboratory separator test at p = 115 psia.

	Separator gas	Separator liquid	Tank gas	Tank liquid
N₂	24.28	2.68	1.98	2.74
CO₂	38.74	3.82	33.73	1.10
CH₄	21.72	1.18	8.53	0.51
C₂H₆	4.80	0.67	8.10	0.00
C₃H₈	4.97	1.58	19.11	0.00
iso C₄H₁₀	1.32	0.79	6.91	0.23
nC₄H₁₀	2.00	1.83	11.36	0.96
iso C₅H₁₂	0.74	1.99	4.31	1.78
n C₅H₁₂	0.64	2.54	3.36	2.47
pseudo C₆	0.45	6.56	1.73	7.00
C₇₊	0.33	76.36	0.88	82.23
Molar mass (g/mol)	34.6	152.85	46.19	162.56
Moles	3,887.7	5,463.2	455.9	5,007.3

The material balance for $p = 115$ psia of the separator is presented in the following figure:

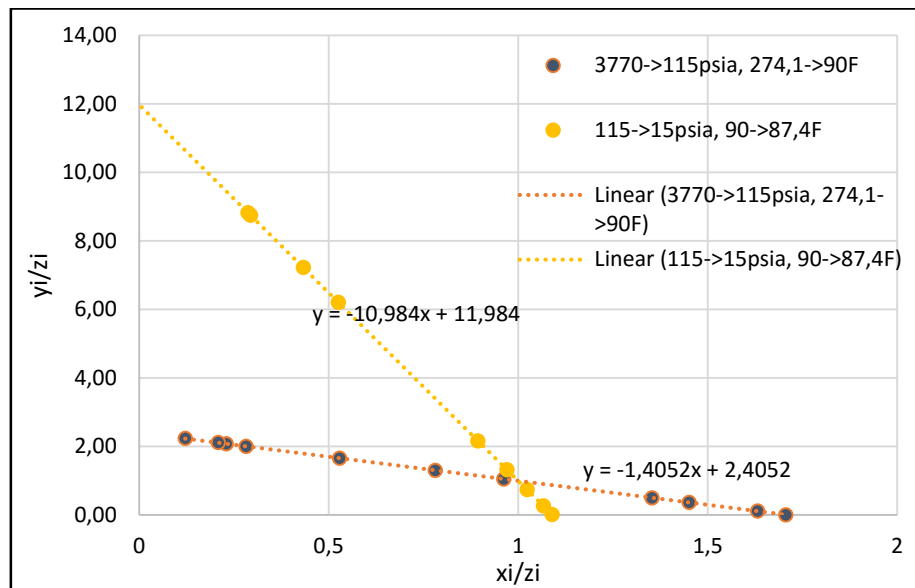


Figure 6.10: Material balance for the separator tests for $p=115$ psia.

The optimum pressure for the separator test is selected from *Figure 6.11*. The optimum pressure is the pressure at which the GOR has the minimum value, so the liquid product is maximized. The *Figure 6.11* was constructed by adding the gas liquid ratio from separator and tank (*Table 6.12*) to make the total gas liquid ratio at each pressure step.

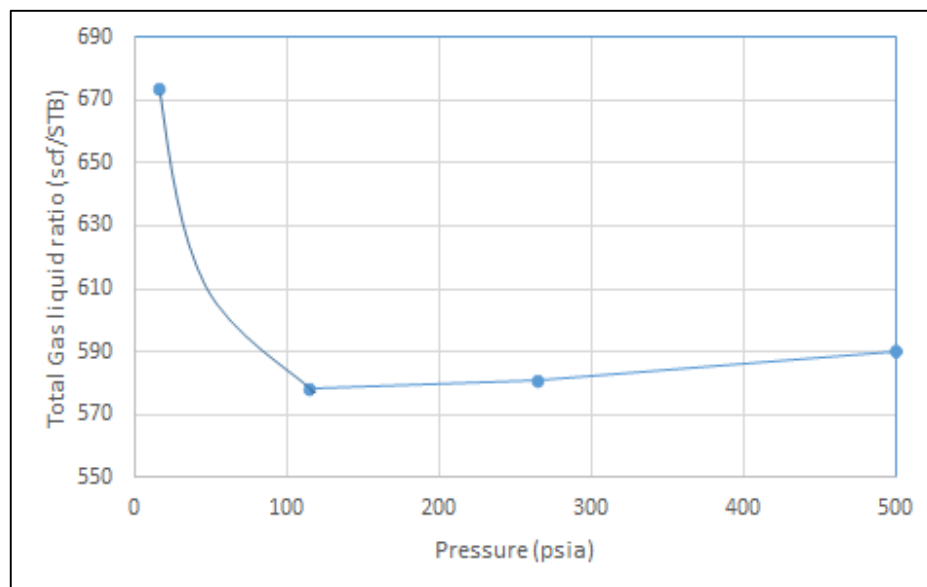


Figure 6.11: Optimization of the separator pressure.

The pressure $p = 115$ psia is the optimum pressure, where $B_{ob} = 1.436$ bbl/STB and $R_{sb}=578$ scf/STB.

6.1.5 Comparison of differential liberation and laboratory separator test data

The solution GOR and the formation volume factor from the differential liberation test and the optimum separator test are compared in the next Table:

Table 6.16: Comparison of volumetric output from differential liberation and laboratory separator tests.

	R_{sb} (scf/STB)	B_{ob} (barrel/STB)
Laboratory separation	578	1.436
Differential liberation	930	1.690

In Table 6.16, the differential liberation test exhibits higher value of solution GOR at bubble point pressure than the laboratory separator tests as the DV occurs at higher temperature and therefore more gas is released. When the molar mass, density and API gravity of the residual oil and stock tank oil are compared (Table 6.15), it is concluded that the DV data lead to a heavier residual oil than the stock tank oil from the laboratory separator tests.

Table 6.17: Comparison of API gravity, density and molar mass between differential liberation and laboratory separator test.

	Residual oil from DV	Stock tank oil from laboratory test
API gravity	37.3	42.3
Density (g/cm³)	0.838	0.814
Molar mass (g/mol)	202.8	162.56

The differential vaporization test gives results on a residual tank basis, so in order to convert those to stock tank oil basis, data from the optimum pressure separator test are used. By applying the conversion described in the subchapter 4.4.1 the volumetrics of the differential vaporization are recalculated on a stock tank oil basis (Table 6.18):

Table 6.18: Conversion of differential volumetrics to stock tank oil basis.

Pressure (psia)	R_{sd} (scf/barrel residual)	R_s (scf/STB)	B_{od} (barrel/barrel residual)	B_o (barrel/STB)
3,332	930	578	1.690	1.463
2,821	833	496	1.644	1.397
2,200	706	388	1.588	1.349
1,420	535	242	1.510	1.283
702	364	97	1.421	1.207
226	218	-27	1.329	1.129
15	0	-212	1.108	0.941

The negative values in *Table 6.18* for the R_s and the $B_o < 1$ are not physically sound. This indicates the weakness of the method to convert differential volumetric values to stock tank oil basis at low pressures. The incorrect values occur because the method does not take into account the required adjustment in gas and oil relative densities (Al-Marhoun, 2003).

6.1.6 Viscosity test

Finally, the viscosity of the reservoir fluid versus the pressure is studied.

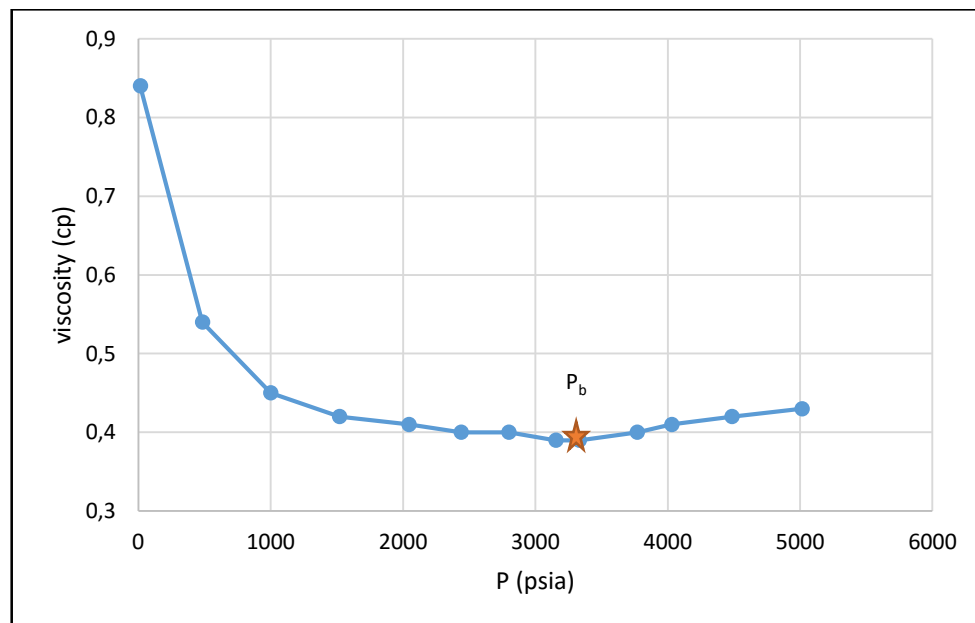


Figure 6.12: Viscosity experiment.

For pressures lower than the saturation pressure, the viscosity of the oil increases as pressure decreases due to the evaporation of the volatile components. On the other hand, the viscosity increases almost linearly as pressure increases for $p > P_b$.

6.1.7 Results for Tunisian oil 1

It is concluded that the Tunisian oil 1 PVT report has shown some problems during the experimentation. The following Table summarizes the results of the quality control check in more details:

Table 6.19: Summary of the PVT quality control test for Tunisian oil 1.

	Comments	Acceptability
Quality control of the recorded samples	Confirmation of the selected samples, thermodynamic consistency of liquid and gas phase, acceptable compositions	Yes
CCE test	Linearity for isothermal compressibility, linearity for Y function	Yes
DV	Material balance is satisfied for each pressure step, material balance for each component is not satisfied, % mol concentration < 0 and >100	Yes / No
Laboratory separator tests	Material balance for each pressure step is satisfied, logical values of % mol concentration	Yes
Viscosity	Logical behavior	Yes

6.2 Tunisian oil 2

As for the Tunisian oil 1, a quality control of the samples and the PVT test for another oil from Tunisia was performed. The process that was followed was exactly the same as before, so only the inputs and the results will be included at the subchapter.

6.2.1 Quality control of the analyzed samples

In *Table 6.20*, the recorded conditions of separator and well head are presented:

Table 6.20: Conditions of separator and well head.

Date	Separator pressure (psia)	Separator temperature (°F)	Well head pressure (psia)	Well head temperature (°F)
2 April	135	87	553	102
2 April	145	93	554	104
4 April	127	96	595	107
4 April	127	96	600	107
5 April	130	100	530	104
5 April	130	100	530	114

It is observed that the conditions of the separator were not stable on 2 April. In order to take valid samples it is preferred to have stable separator conditions, as for 4 and 5 April.

The following Table depicts the results of checking each sample taken.

Table 6.21: Separator samples for Tunisian oil 2.

Gas				
#	Date, time	Opening pressure (psia) at 75.2 F	Carry over	Air (mole %)
SG01	2 April, 22:40	175	0	0
SG02	2 April, 23:50	175	0	0
SG03	4 April, 22:20	165	0	0
SG04	4 April, 23:50	165	0	0
SG05	5 April, 6:15	175	0	0
SG06	5 April, 5:00	165	0	0
Liquid				
#	Time	Bubble point pressure (psia)	BS&W	
SLS01	2 April, 22:20	131 at 87 F	0	
SLS02	2 April, 23:45	143 at 93 F	0	
SLS03	4 April, 22:40	114 at 96 F	0	
SLS04	4 April, 23:55	128 at 96 F	0	
SLS05	5 April, 6:00	125 at 100 F	0	
SLS06	5 April, 5:00	125 at 100 F	0	

The separator conditions on 2 April were not stable, so the samples taken on that date will may not be representative of the reservoir fluid. It is worth mentioning that none of the gas samples contain air and carry over and none of the liquid samples BS&W. The opening pressures of the gas samples taken on 4 April are the same and closer to the converted separator pressure to opening pressure, so they are preferred from the ones taken on 5 April. As far as the liquid sample is concerned the SLS04 has the same bubble point pressure as the separator pressure so it seems to be the best liquid sample. If SLS04 is selected, then the SG04 must be used for the recombination process due to the time constraint (the gas and liquid sample must have been taken at almost the same time).

The compositions of the gas samples are presented in the following Table:

Table 6.22: Compositions of the gas field separator samples for Tunisian oil 2.

	SG01	SG02	SG03	SG04	SG05	SG06
N₂ (%mol)	10.82	10.82	10.60	10.55	10.35	9.93
CO₂ (%mol)	8.26	8.16	7.95	7.96	7.83	7.77
H₂S (%mol)	0.00	0.00	0.00	0.00	0.00	0.00
CH₄ (%mol)	60.32	60.13	59.71	59.52	58.22	58.97
C₂H₆ (%mol)	7.92	7.87	8.16	8.19	8.38	8.33
C₃H₈ (%mol)	6.15	6.26	6.61	6.64	7.19	7.07
iso C₄H₁₀ (%mol)	2.06	2.11	2.22	2.25	2.53	2.50
nC₄H₁₀ (%mol)	2.28	2.34	2.45	2.50	2.85	2.79
iso C₅H₁₂ (%mol)	0.79	0.82	0.84	0.87	1.00	0.99
n C₅H₁₂ (%mol)	0.64	0.66	0.67	0.70	0.80	0.78
pseudo C₆ (%mol)	0.41	0.44	0.43	0.45	0.48	0.50
pseudo C₇ (%mol)	0.26	0.28	0.26	0.27	0.27	0.28
pseudo C₈ (%mol)	0.08	0.10	0.09	0.09	0.08	0.08
pseudo C₉ (%mol)	0.01	0.01	0.01	0.01	0.01	0.01
pseudo C₁₀ (%mol)	0.00	0.00	0.00	0.00	0.00	0.00
pseudo C₁₁ (%mol)	0.00	0.00	0.00	0.00	0.00	0.00
C₁₂₊ (%mol)	0.00	0.00	0.00	0.00	0.00	0.00
Molar mass (g/mol)	25.71	25.84	25.97	26.07	26.59	26.45

All gas samples have similar composition distribution and molar masses.

Finally, the samples SG04 and SLS04 seem to be the best samples to be recombined, so their k values are tested by Hoffman plot (*Figure 6.13*) and Buckley plot (*Figure 6.14*), as follows:

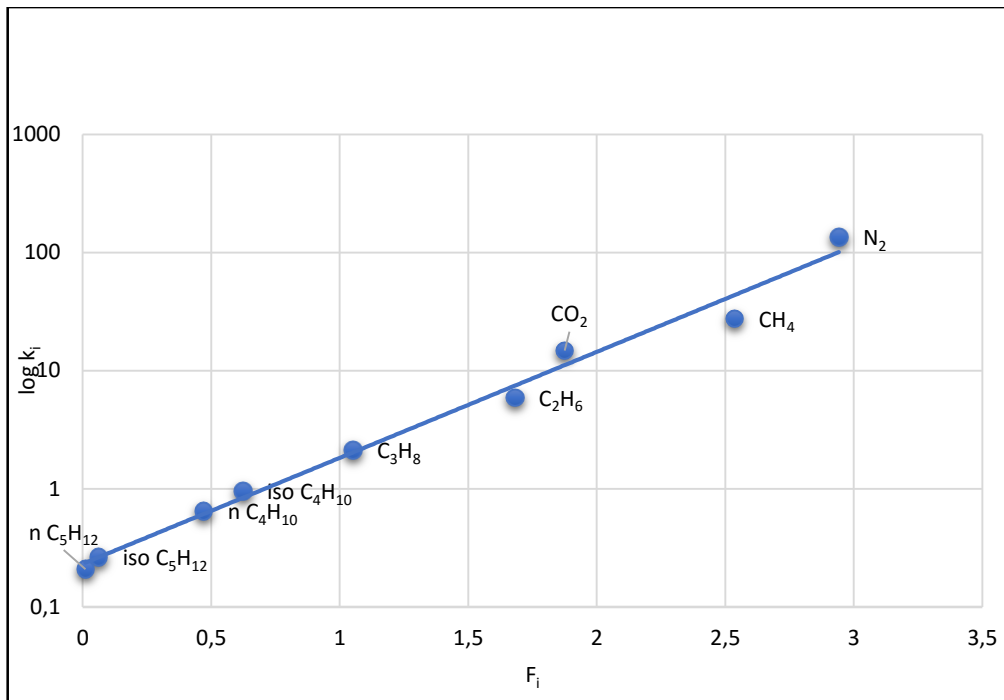


Figure 6.13: Hoffman plot for Tunisian oil 2 – SG04 and SLS04.

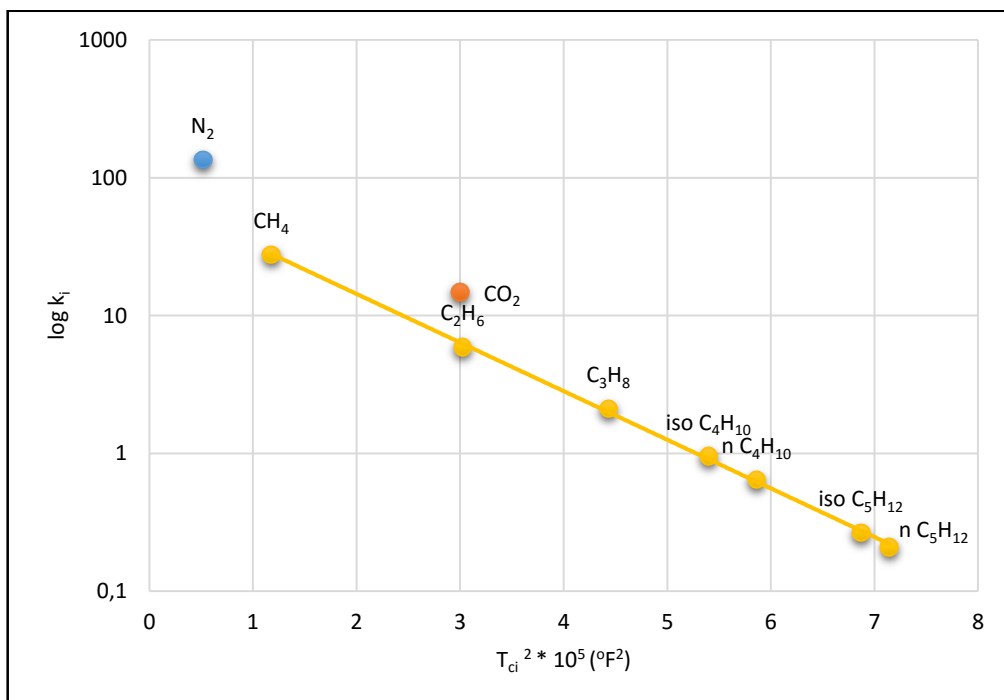


Figure 6.14: Buckley plot for Tunisian oil 2 – SG04 and SLS04.

The gas and liquid phases are in thermodynamic equilibrium as there is linearity in Hoffman plot and a line with negative slope in the Buckley plot. It can also be derived, that the nitrogen and the carbon dioxide are very close to the line at both plots. So, the separator gas and liquid samples have been correctly selected for the recombination process.

The recombination process for the reservoir fluid took place with molar ratio according to the corrected gas to oil ratio. The obtained data for the field and laboratory data are presented in the following Table:

Table 6.23: Correction of gas to oil ratio.

	Z	Specific gravity	R_{sp} (scf/bbl)
Field	0.965	0.920	116
Laboratory	0.979	0.899	116

The gas to oil ratio has exactly the same value at field and laboratory measurements.

The chromatographically obtained compositions of the separator gas, separator liquid and recombined fluid are presented in Table 6.24.

Table 6.24: Compositions and molar masses of the separator liquid, separator gas and recombined reservoir fluid.

	Separator liquid	Separator gas	Recombined fluid
N₂ (%mol)	0.08	10.55	1.72
CO₂ (%mol)	0.56	7.96	1.72
H₂S (%mol)	0.00	0.00	0.00
CH₄ (%mol)	2.23	59.52	11.20
C₂H₆ (%mol)	1.42	8.19	2.48
C₃H₈ (%mol)	3.19	6.64	3.73
iso C₄H₁₀ (%mol)	2.37	2.25	2.35
nC₄H₁₀ (%mol)	3.89	2.50	3.67
iso C₅H₁₂ (%mol)	3.28	0.87	2.90
n C₅H₁₂ (%mol)	3.36	0.70	2.94
pseudo C₆ (%mol)	6.23	0.45	5.33
pseudo C₇ (%mol)	7.97	0.27	6.76
pseudo C₈ (%mol)	9.25	0.09	7.81
pseudo C₉ (%mol)	6.81	0.01	5.75
pseudo C₁₀ (%mol)	6.09	0.00	5.14
pseudo C₁₁ (%mol)	4.99	0.00	4.21
C₁₂₊ (%mol)	38.29	0.00	32.29
Molar mass (g/mol)	166.8	26.07	144.8

The composition of the reservoir oil has typical values of a black oil.

6.2.2 CCE test

The CCE test provides the relative volume according to *Table 6.25*:

Table 6.25: CCE data for Tunisian oil 2.

Pressure (psia)	Relative volume
3,000	0.9800
2,325	0.9863
2,000	0.9894
1,490	0.9946
1,200	0.9977
1,100	0.9988
996 = P_b	1.000
980	1.0045
962	1.0101
944	1.0158
913	1.0275
860	1.0505
792	1.0853
707	1.1430
590	1.2588
455	1.4910
346	1.8405
252	2.4309

The Y-function in *Figure 6.15* forms almost a straight line versus pressure:

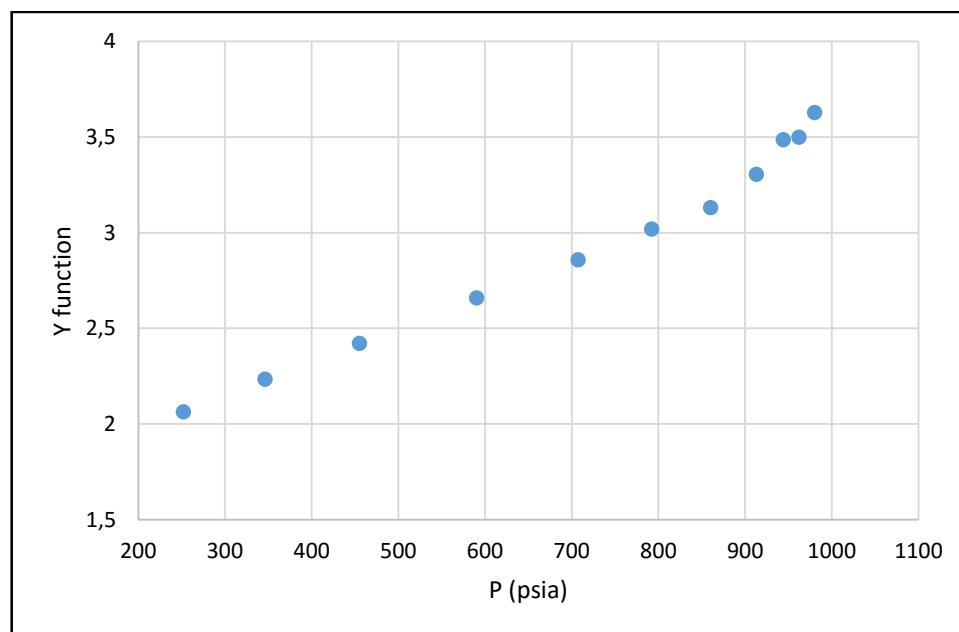


Figure 6.15: Y function.

The isothermal oil compressibility increases linearly as pressure decreases. In *Figure 6.16*, the points lie on the line $y = -10^{-9} \cdot x + 10^{-5}$ in a satisfying manner.

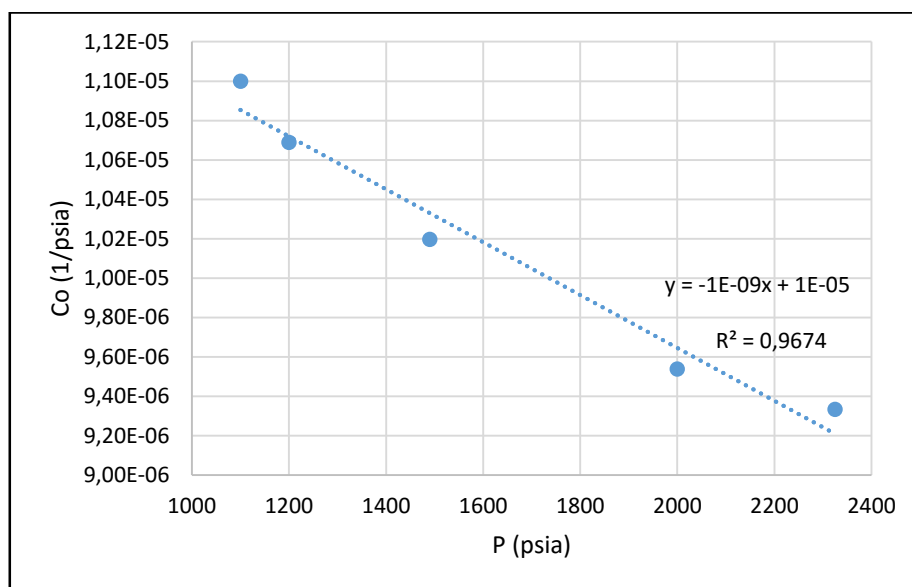


Figure 6.16: Isothermal oil compressibility for pressures above bubble point.

6.2.3 Differential vaporization test

For the differential vaporization test, a material balance is held. The mass of removed gas at each pressure step is calculated based on the solution GOR (*Table 6.26*).

Table 6.26: Mass of removed gas at each pressure step at DV for Tunisian oil 2.

Pressure (psia)	R_s (sm ³ /sm ³)	Moles of gas (moles)	Moles of removed gas	Molar mass of gas (g/mol)	Mass of removed gas (kg)
996	43.8	1,848.9			
819	39.7	1,675.8	173.1	24.03	4.159
652	34.6	1,460.5	215.3	24.07	5.182
479	29.3	1,236.8	223.7	24.56	5.495
332	24.1	1,017.3	219.5	25.73	5.648
163	16.1	679.6	337.7	30.50	10.300
15	0	0.0	679.6	61.19	41.585

The calculation of the moles of the bubble point fluid is presented in *Table 6.27*.

Table 6.27: Mass of residual oil and moles of bubble point fluid.

Residual oil relative density	Mass of residual oil(kg)	Mass of bubble point fluid (kg)	Molar mass of reservoir fluid (g/mol)	Moles of bubble point fluid
0.832	832	904.368	144.8	6,245.6

The compositions of the liquid and the gas phase for each pressure step are given in the following Tables:

Table 6.28: Gas compositions at different pressure steps.

Pressure Composition	819 psia	652 psia	479 psia	332 psia	163 psia	15 psia
N ₂ (%mol)	21.39	17.33	12.24	7.53	2.78	0.23
CO ₂ (%mol)	5.67	6.27	7.13	8.20	9.30	3.12
H ₂ S (%mol)	0.00	0.00	0.00	0.00	0.00	0.00
CH ₄ (%mol)	61.04	62.81	63.94	62.89	51.79	9.23
C ₂ H ₆ (%mol)	4.50	5.17	6.35	7.88	11.57	7.10
C ₃ H ₈ (%mol)	3.06	3.72	4.58	6.02	10.62	15.07
iso C ₄ H ₁₀ (%mol)	1.05	1.30	1.67	2.30	4.06	9.97
nC ₄ H ₁₀ (%mol)	1.17	1.45	1.96	2.54	4.80	14.98
iso C ₅ H ₁₂ (%mol)	0.66	0.64	0.77	0.98	1.89	9.61
n C ₅ H ₁₂ (%mol)	0.55	0.53	0.60	0.78	1.50	8.93
pseudo C ₆ (%mol)	0.42	0.42	0.44	0.54	1.06	9.82
C ₇₊ (%mol)	0.49	0.36	0.32	0.34	0.63	11.94
Molar mass (g/mol)	24.03	24.07	24.56	25.73	30.50	61.19

Table 6.29: Liquid compositions at different pressure steps.

Pressure Composition	819 psia	652 psia	479 psia	332 psia	163 psia	15 psia
N ₂ (%mol)	1.16	0.57	0.10	-0.20	-0.40	-0.50
CO ₂ (%mol)	1.61	1.44	1.21	0.93	0.37	-0.06
H ₂ S (%mol)	0.00	0.00	0.00	0.00	0.00	0.00
CH ₄ (%mol)	9.78	7.83	5.60	3.28	0.05	-1.37
C ₂ H ₆ (%mol)	2.42	2.32	2.16	1.93	1.29	0.39
C ₃ H ₈ (%mol)	3.75	3.75	3.72	3.62	3.16	1.32
iso C ₄ H ₁₀ (%mol)	2.39	2.43	2.46	2.46	2.36	1.18
nC ₄ H ₁₀ (%mol)	3.74	3.83	3.90	3.95	3.90	2.19
iso C ₅ H ₁₂ (%mol)	2.96	3.05	3.14	3.23	3.32	2.34
n C ₅ H ₁₂ (%mol)	3.01	3.10	3.20	3.30	3.42	2.56
pseudo C ₆ (%mol)	5.47	5.66	5.86	6.08	6.41	5.89
C ₇₊ (%mol)	63.71	66.04	68.65	71.42	76.13	86.05
Molar mass (g/mol)	148.24	152.81	157.90	163.26	172.09	189.23

Negative compositions imply that an error occurred during DV, possibly due to gas chromatography. The GC cannot track the traces in detail, so the composition can either over- or under- estimated. Negative sign in the computed liquid compositions implies that the gas composition was overestimated for some components. The values of molar masses for the liquid phases increase as pressure decreases.

The plot of k values at each pressure step and per component is made and the results are presented in the following Figure.

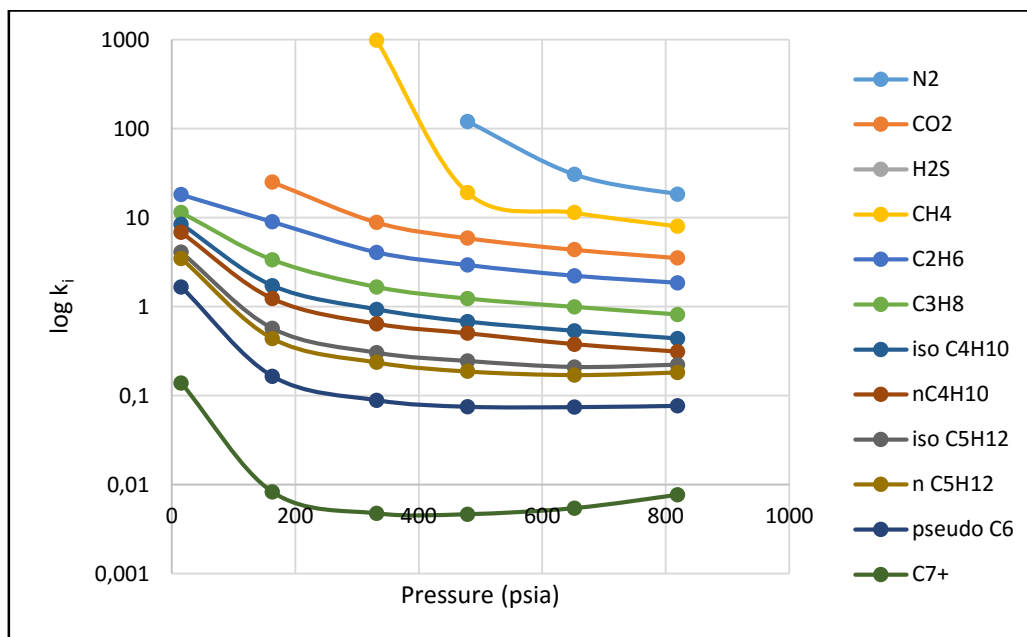


Figure 6.17: Semi logarithmic plot of k versus pressure for each component at DV test.

In Figures 6.18 and 6.19, the compositions of the gaseous and the liquid phase for all the components and pressure steps are presented.

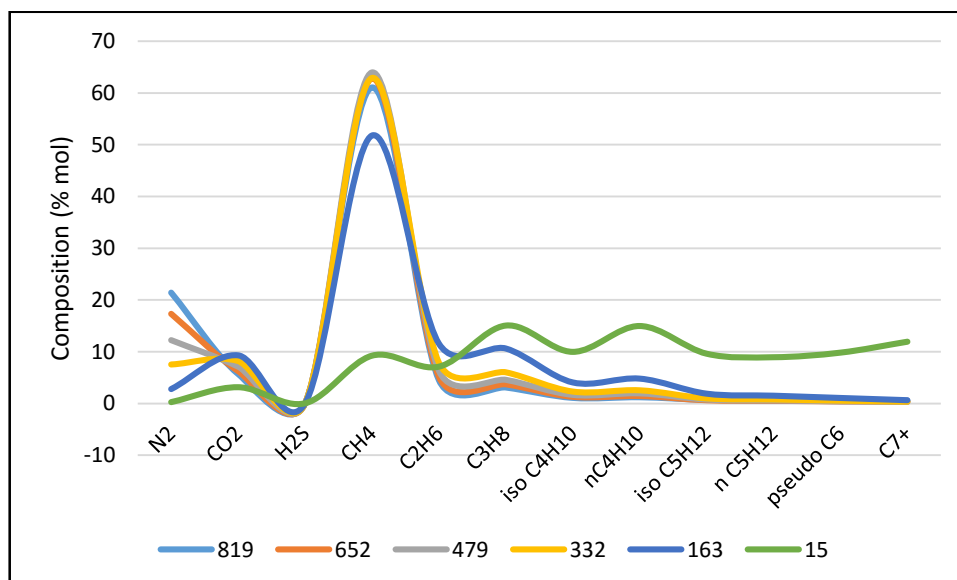


Figure 6.18: DV gas compositions for all the components and pressure steps.

The DV gas compositions have similar distributions for all the pressure steps except than at 15 psia. As pressure decreases the gas becomes richer in components heavier than C_2H_6 while the % mol compositions of the other components slightly decrease. For $p = 163$ psia, the gas phase contains less methane and more heavy components (lighter than iso C_5H_{12}). For $p = 15$ psia the gas contains significant quantity of heavy components.

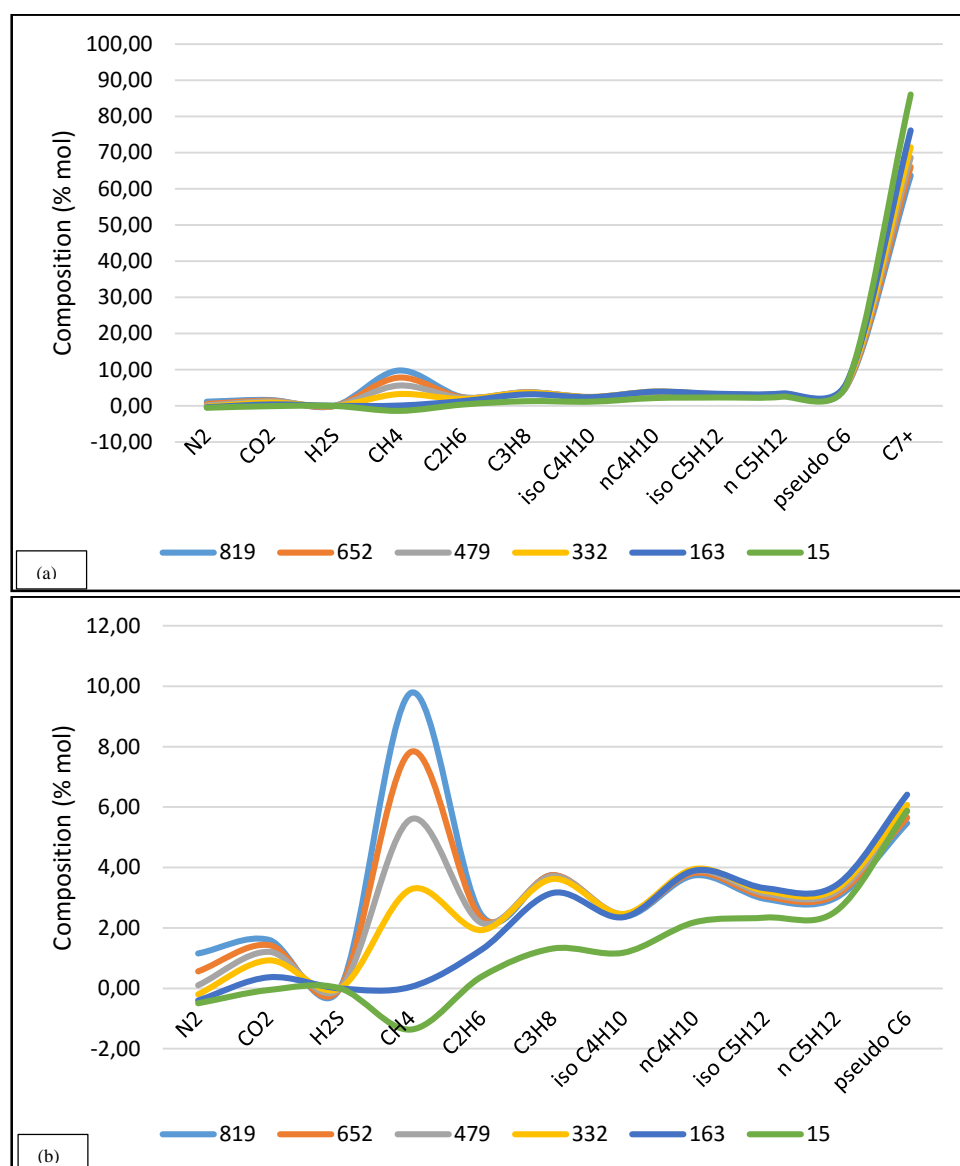


Figure 6.19: DV liquid compositions for all the components and pressure steps:
(a) original plot, (b) zoom in.

The DV liquid compositions in Figure 6.19 have the same shape of distribution except from methane for $p = 163$ psia and $p = 15$ psia. At $p = 163$ psia, it seems that all CH_4 has been evaporated. In Figure 6.19 (b) it is observed that the heavy components are not affected drastically.

The Figures of material balances for all the pressure steps follow:

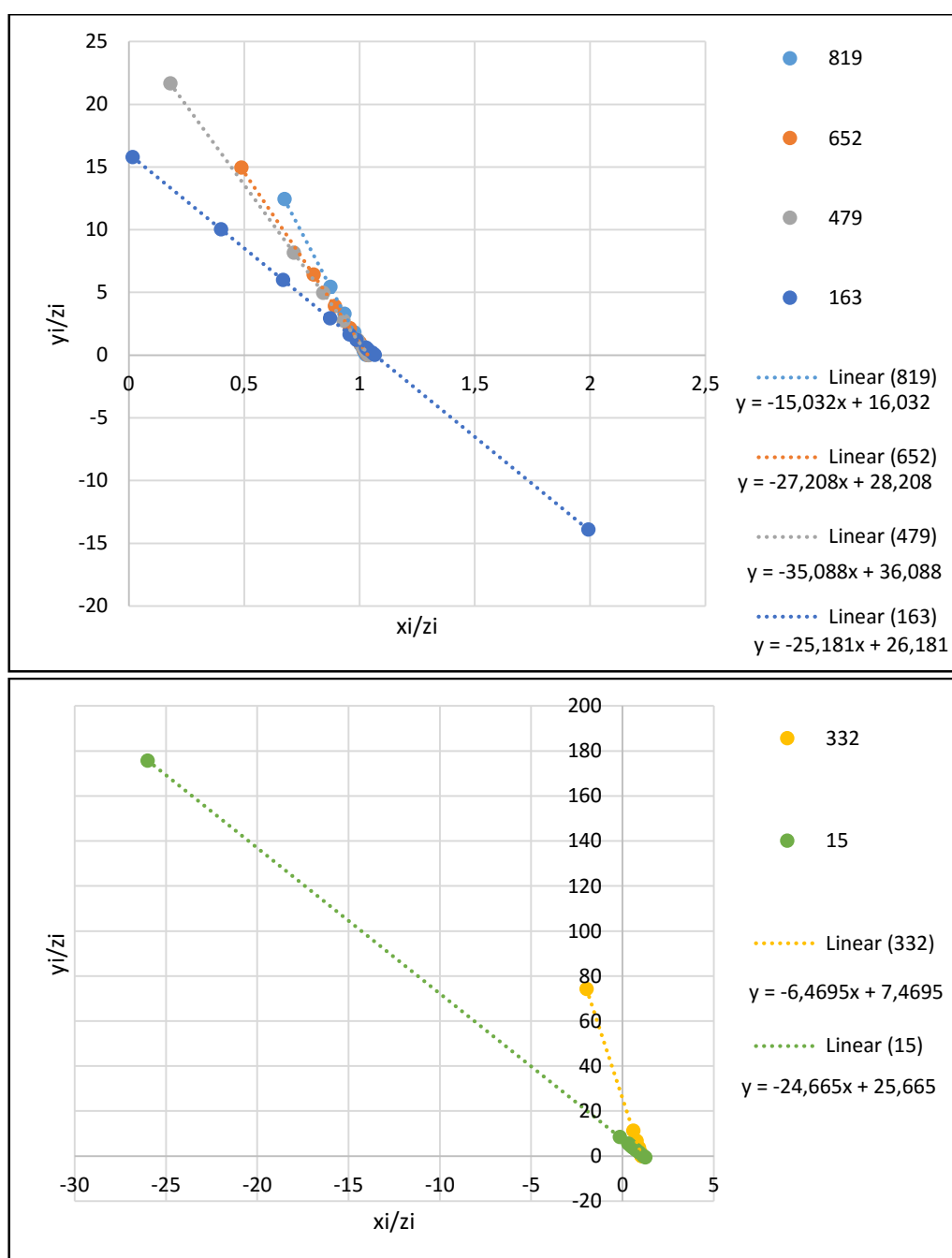


Figure 6.20: Material balance for each pressure step at DV test.

There is linearity for the material balance at each pressure step. In *Figure 6.21* the material balance per component is presented and is not satisfied for all of them. According to the line that characterizes each component at the y_i/z_i versus x_i/z_i plot, the CO_2 and the C_3H_8 have not very good R^2 while the C_{7+} exhibits wrong sign of slope (positive).

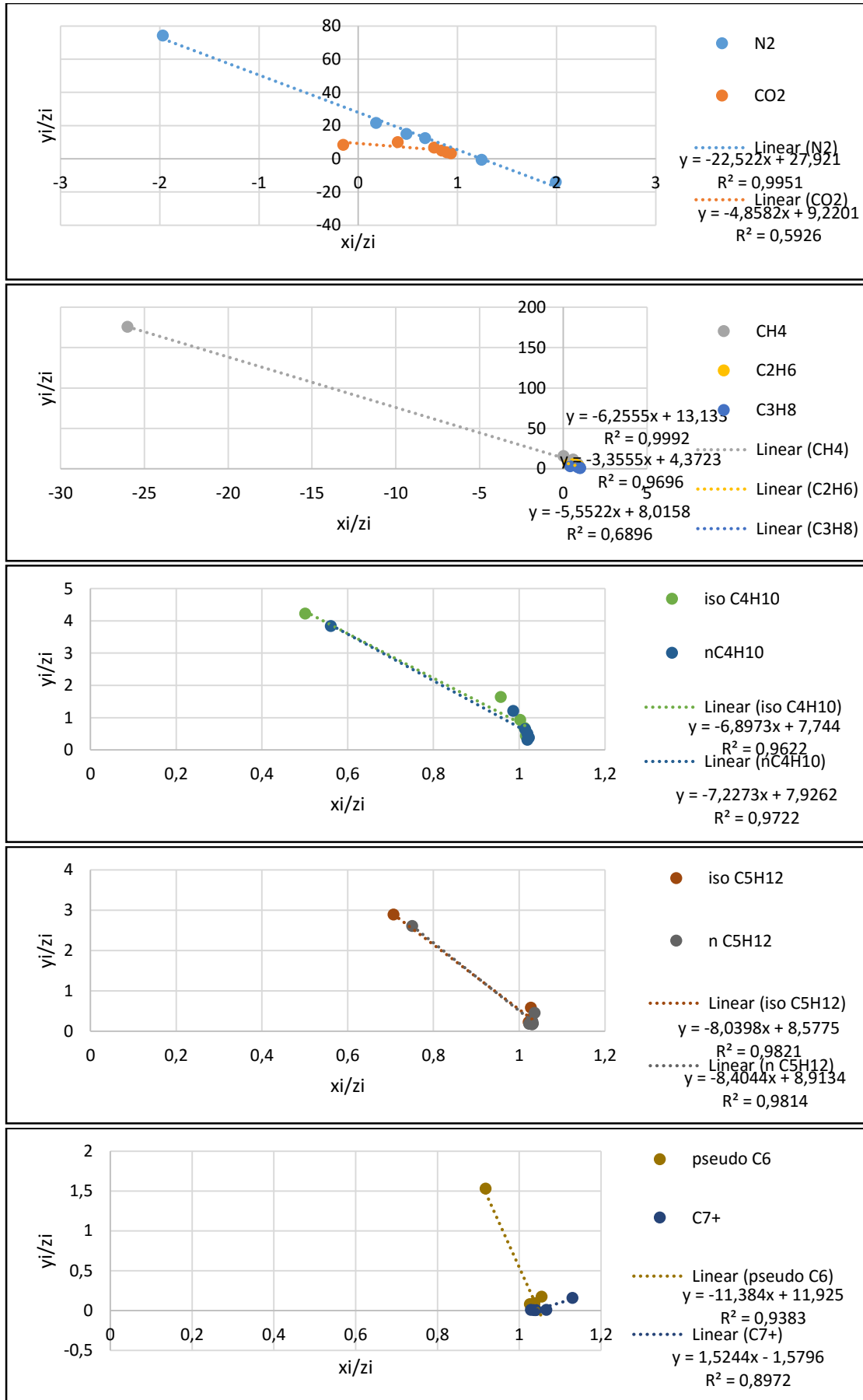


Figure 6.21: Material balance for each component at DV test.

Finally, the calculated composition of the residual oil is compared to the stock tank oil one (Table 6.30).

Table 6.30: Comparison of the back calculated residual oil and the measured stock tank oil compositions.

Composition	Residual oil from DV	Stock tank oil
N ₂ (%mol)	-0.50	0.08
CO ₂ (%mol)	-0.06	0.56
H ₂ S (%mol)	0.00	0.00
CH ₄ (%mol)	-1.37	2.23
C ₂ H ₆ (%mol)	0.39	1.42
C ₃ H ₈ (%mol)	1.32	3.19
iso C ₄ H ₁₀ (%mol)	1.18	2.37
nC ₄ H ₁₀ (%mol)	2.19	3.89
iso C ₅ H ₁₂ (%mol)	2.34	3.28
n C ₅ H ₁₂ (%mol)	2.56	3.36
pseudo C ₆ (%mol)	5.89	6.23
C ₇₊ (%mol)	86.05	73.40
Molar mass (g/mol)	189.23	166.80

The DV data lead to heavier residual oil than the stock tank oil, as expected. The composition of the residual oil, despite the negative signs, has similar distribution to the stock tank oil. The CH₄ and the heavy end seem to have the biggest errors.

6.2.4 Laboratory separator tests

Material balance is also held for the separator test. The mass of removed gas at each pressure step is presented in Table 6.31.

Table 6.31: Mass of removed gas at each pressure step for the laboratory separator tests.

p=200 psia				
	Gas liquid ratio (sm ³ /sm ³)	Moles of removed gas	Molar mass of removed gas (g/mol)	Mass of removed gas (kg)
Separator	19.7	831.6	23.46	19.509
Tank	17.4	734.5	41.06	30.158
p=145 psia				
	Gas liquid ratio (sm ³ /sm ³)	Moles of removed gas	Molar mass of removed gas (g/mol)	Mass of removed gas (kg)
Separator	22.5	949.8	24.62	23.383
Tank	14.2	599.4	41.8	25.055
p=50 psia				
	Gas liquid ratio (sm ³ /sm ³)	Moles of removed gas	Molar mass of removed gas (g/mol)	Mass of removed gas (kg)
Separator	32.3	1363.4	29.55	40.290
Tank	4.1	173.1	42.92	7.428
p=15 psia				
	Gas liquid ratio (sm ³ /sm ³)	Moles of removed gas	Molar mass of removed gas (g/mol)	Mass of removed gas (kg)
Separator	41	1730.7	32.62	56.455

The mass of the stock tank oil is found through the tank density for 1sm³ stock tank oil:

Table 6.32: Mass of stock tank oil at each pressure step.

p (psia)	Tank density (g/cm³)	Mass of stock tank oil (kg)
200	0.824	824
145	0.822	822
50	0.822	822
15	0.826	826

The mass and the mole of the reservoir oil are calculated according to the following Table.

Table 6.33: Moles of reservoir fluid for the laboratory separator tests.

p (psia)	Mass of removed gas from separator (kg)	Mass of removed gas from tank (kg)	Mass of stock tank oil (kg)	Mass of reservoir fluid (kg)	Molar mass of reservoir fluid (g/mol)	Mole of reservoir fluid (mol)
200	19.509	30.158	824	873.667	144.8	6,033.6
145	23.383	25.055	822	870.439		6,011.3
50	40.290	7.428	822	869.718		6,006.3
15	56.455	0.000	826	882.455		6,094.3

From the number of moles of gas removed at each step, the liquid phase compositions are calculated at each pressure step by material balance. The liquid compositions for p = 145 psia are given in the following Table:

Table 6.34: Compositions of laboratory separator test at p = 145 psia.

	Separator gas	Separator liquid	Tank gas	Tank liquid
N₂	11.47	-0.11	1.26	-0.29
CO₂	7.66	0.61	6.26	-0.15
H₂S	0.00	0.00	0.00	0.00
CH₄	62.94	1.49	24.14	-1.55
C₂H₆	7.26	1.58	12.86	0.07
C₃H₈	5.51	3.40	22.87	0.78
iso C₄H₁₀	1.73	2.47	10.30	1.41
nC₄H₁₀	1.86	4.01	12.17	2.91
iso C₅H₁₂	0.61	3.33	4.35	3.19
n C₅H₁₂	0.47	3.40	3.20	3.43
pseudo C₆	0.30	6.27	1.83	6.87
C₇₊	0.19	73.55	0.76	83.33
Molar mass (g/mol)	24.6	167.3	41.8	184.2
Moles	949.8	5,061.5	599.409	4,462.1

The tank liquid has negative % mol composition for some components. Possibly the gas composition was mistakenly given from the chromatograph.

The material balance of the separator for $p = 145$ psia is presented in the following figure:

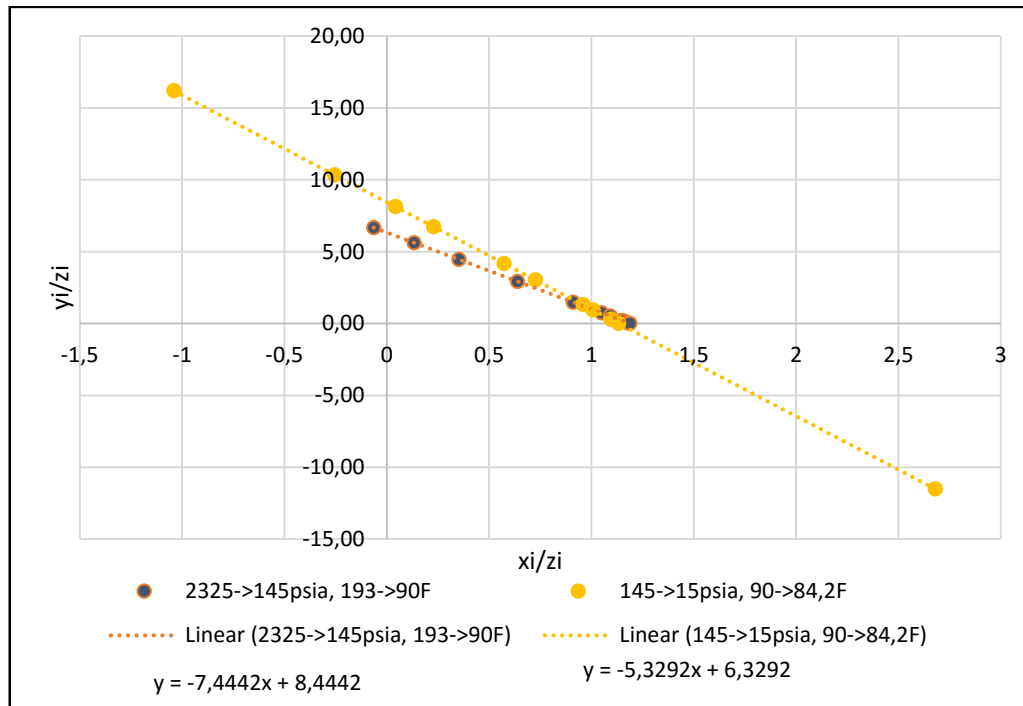


Figure 6.22: Material balance for the separator tests for $p=145$ psia.

The optimum pressure of the separator test is selected from *Figure 6.23* and is equal to $p = 50$ psia.

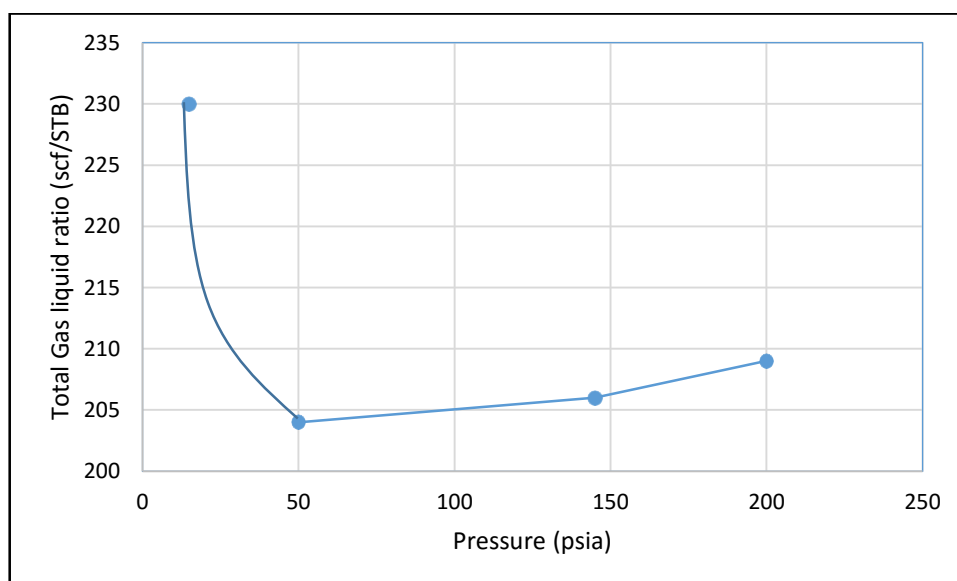


Figure 6.23: Optimization of the separator pressure.

6.2.5 Comparison of differential liberation and laboratory separator test data

The solution GOR and the formation volume factor from the differential liberation test and the optimum separator test are compared in the next Table:

Table 6.35: Comparison of volumetric output from differential liberation and laboratory separator tests.

	R_{sb} (scf/STB)	B_{ob} (barrel/STB)
Laboratory separation	205	1.181
Differential liberation	246	1.248

The differential liberation test occurs at higher temperature than the laboratory separator tests, so it will result to higher solution GOR and heavier residual oil (*Table 6.36*).

Table 6.36: Comparison of API gravity, density and molar mass between differential liberation and laboratory separator test.

	Residual oil from DV	Stock tank oil from laboratory test
API gravity	38.5	40.6
Density (g/cm³)	0.832	0.822
Molar mass (g/mol)	189.2	184.2

Nevertheless, the difference in molar mass, density and API gravity is negligible.

The application of the conversion of DV data to stock tank oil basis is presented in the following Table:

Table 6.37: Conversion of differential volumetrics to stock tank oil basis.

Pressure (psia)	R_{sd} (scf/barrel residual)	R_s (scf/STB)	B_{od} (barrel/barrel residual)	B_o (barrel/STB)
996	246	205	1.248	1.181
819	223	183	1.234	1.168
652	194	156	1.224	1.158
479	164	127	1.211	1.146
332	135	100	1.197	1.133
163	90	57	1.173	1.110
15	0	-28	1.066	1.008

The negative value in *Table 6.37* for the R_s indicates once more, the weakness of the method to convert differential volumetric values to stock tank oil basis at low pressures.

6.2.6 Viscosity test

Finally, the viscosity of the reservoir fluid versus the pressure is studied and has the expected behavior.

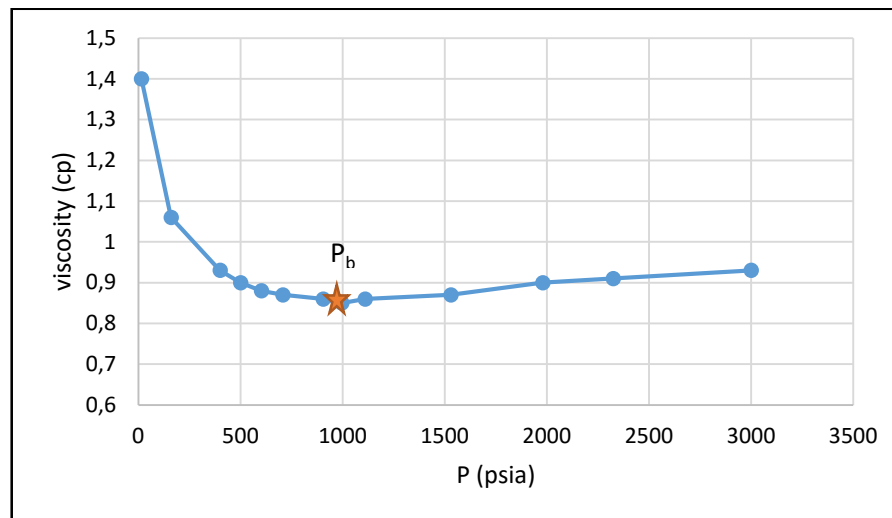


Figure 6.24: Viscosity experiment.

6.2.7 Results for Tunisian oil 2

It is concluded that the Tunisian oil 2 PVT report has shown some problems. In more details:

Table 6.38: Summary of the PVT quality control test for Tunisian oil 2.

	Comments	Acceptability
Quality control of the recorded samples	Confirmation of the selected samples, thermodynamic consistency of liquid and gas phase, acceptable compositions	Yes
CCE test	Linearity for isothermal oil compressibility, linearity for the Y function	Yes
DV	Material balance at each pressure step is satisfied, material of each component is not satisfied, negative values for % mol concentration	Yes / No
Laboratory separator tests	Material balance is satisfied, negative values for % mol concentration at some pressure steps	Yes / No
Viscosity	Logical values	Yes

The errors at % mol composition for the DV study and laboratory separator tests are not very important and could probably avoided if the gas chromatograph was more sensitive. The B_o , B_g and R_s are the most important values in reservoir engineering applications and for both tests are logical sound values.

6.3 Congo oil

The results of the Congo oil are presented in the following subchapters.

6.3.1 Quality control of the analyzed samples

Separator samples for an oil coming from Congo were used for the study. The separator and well head conditions are described in the following Table:

Table 6.39: Condition of separator and well head.

Separator pressure (psia)	Separator temperature (°F)	Well head pressure (psia)	Well head temperature (°F)
168	78	400	94.6

The following Table depicts the results of checking each sample taken.

Table 6.40: Separator samples for Congo oil.

Gas				
#	Time	Opening pressure (psia)	Carry over	Air (mole %)
SG01	8:30	205 at 82.4 F	0	0
SG02	8:30	195 at 80.6 F	0	0
Liquid				
#	Time	Bubble point pressure (psia) at 78 F	BS&W	
SLS01	8:30	162	0	

The SLS01 does not contain water, mud and sediments while it has bubble point pressure very close to separator pressure. The SLS01 is a valid liquid sample, so it is logical that it was not taken other liquid samples. None of the gas samples, contain air or carry over, so the opening pressure and the composition (*Table 6.41*) will be used for their evaluation.

Table 6.41: Compositions of the gas field separator samples for Congo oil.

	SG01	SG02
N ₂ (%mol)	0.20	0.31
CO ₂ (%mol)	0.91	0.88
H ₂ S (%mol)	0.00	0.00
CH ₄ (%mol)	81.13	81.29
C ₂ H ₆ (%mol)	8.78	8.89
C ₃ H ₈ (%mol)	5.35	5.12
iso C ₄ H ₁₀ (%mol)	0.63	0.61
nC ₄ H ₁₀ (%mol)	1.62	1.56
iso C ₅ H ₁₂ (%mol)	0.30	0.29
n C ₅ H ₁₂ (%mol)	0.58	0.57
pseudo C ₆ (%mol)	0.30	0.29
C ₇₊ (%mol)	0.20	0.19
Molar mass (g/mol)	20.88	20.77

The compositions of the gas samples are almost identical, while their opening pressures have acceptable values. As a result both of them can be considered to be representative of the reservoir fluid. It was requested by the company to recombine SLS01 and SG01. Their thermodynamic consistency is studied by Hoffman plot (Figure 6.25) and Buckley plot (Figure 6.26), as follows:

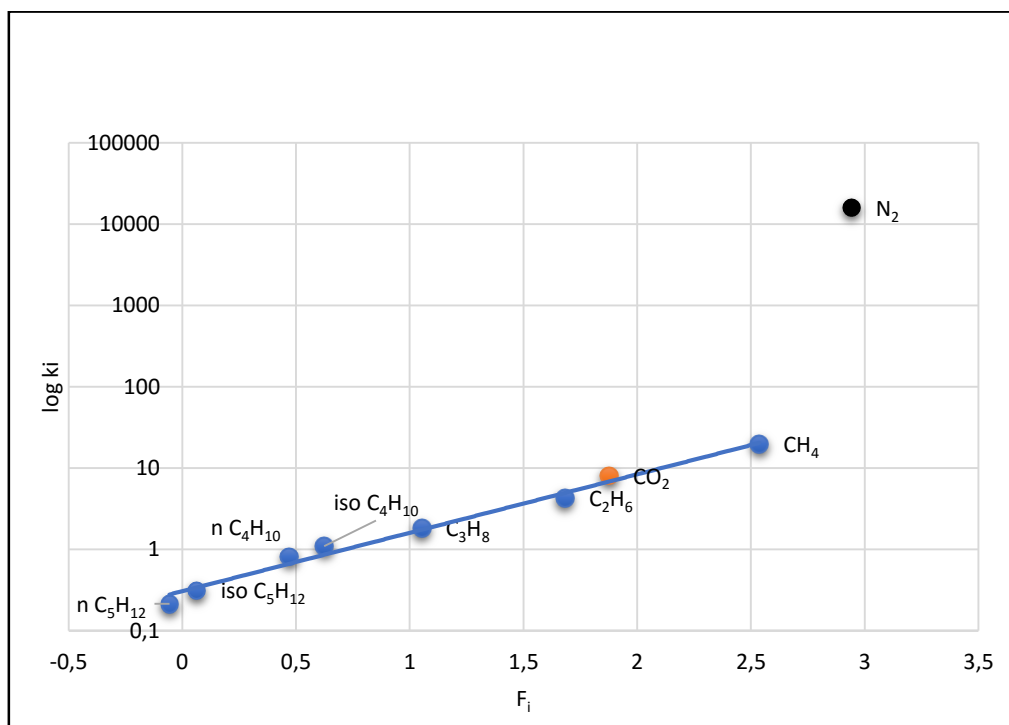


Figure 6.25: Hoffman plot for Congo oil – SLS01 and SG01.

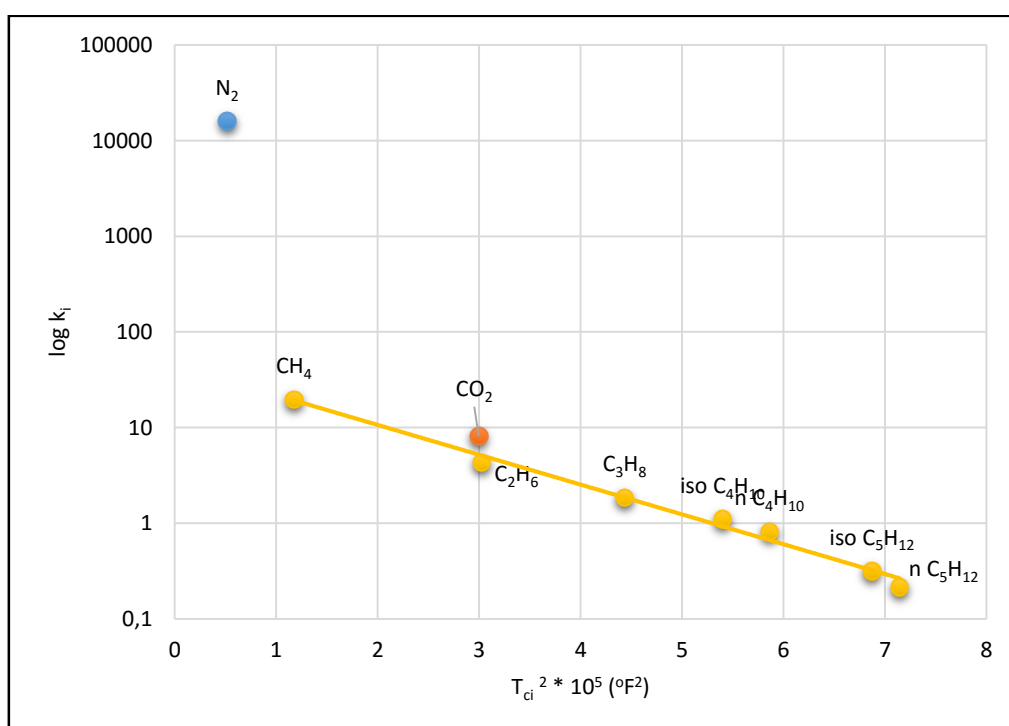


Figure 6.26: Buckley plot for Congo oil – SLS01 and SG01.

From the previous figures it is concluded that the samples were in thermodynamic equilibrium.

The recombination process for the reservoir fluid took place with molar ratio according to the following Table:

Table 6.42: Correction of gas to oil ratio.

	Z	Specific gravity	R_{sp} (scf/bbl)
Field	0.971	0.72	1,200
Laboratory	0.971	0.72	1,200

During the recombination process, the resulted fluid had bubble point greater than the initial reservoir pressure at reservoir temperature! As a result, it was requested by the company to liberate some equilibrium gas of the fluid (flash GOR = 1,387 scf/sbbl) in order to obtain reservoir fluid with bubble point pressure equal to the initial reservoir pressure. The chromatographically obtained compositions of the separator gas, separator liquid and recombined fluid are presented in *Table 6.43*.

Table 6.43: Compositions and molar masses of the separator liquid, separator gas and recombined reservoir fluid.

	Separator liquid	Separator gas	Recombined fluid
N₂ (%mol)	0.00	0.16	0.11
CO₂ (%mol)	0.10	0.93	0.65
H₂S (%mol)	0.00	0.00	0.00
CH₄ (%mol)	3.55	78.86	53.33
C₂H₆ (%mol)	1.90	9.21	6.73
C₃H₈ (%mol)	2.84	5.85	4.83
iso C₄H₁₀ (%mol)	0.64	0.77	0.73
nC₄H₁₀ (%mol)	2.36	2.06	2.16
iso C₅H₁₂ (%mol)	1.37	0.44	0.76
n C₅H₁₂ (%mol)	3.92	0.85	1.89
pseudo C₆ (%mol)	8.80	0.50	3.31
pseudo C₇ (%mol)	12.73	0.28	4.50
pseudo C₈ (%mol)	13.53	0.08	4.64
pseudo C₉ (%mol)	9.99	0.01	3.39
pseudo C₁₀ (%mol)	6.52	0.00	2.21
pseudo C₁₁ (%mol)	4.90	0.00	1.66
C₁₂₊ (%mol)	26.85	0.00	9.10
Molar mass (g/mol)	160.7	21.85	67.7

The separator gas in *Table 6.43* is slightly heavier than the gas sample in *Table 6.41*, as expected, due to the additional liberation of gas.

6.3.2 CCE test

The CCE test provides the relative volume according to *Table 6.44*:

Table 6.44: CCE data for Congo oil.

Pressure (psia)	Relative volume
5,015	0.9756
4,757	0.9803
4,513	0.9850
4,317	0.9893
4,113	0.994
3,933	0.9984
3,882 = P_b	1.0000
3,832	1.0029
3,763	1.008
3,642	1.0185
3,482	1.0342
3,299	1.0553
3,071	1.0873
2,727	1.1519
2,268	1.2829
1,722	1.5587
1,359	1.8916
1,019	2.4482

It is worth mentioning that the oil has initial reservoir conditions equal to the bubble point pressure due to the additional liberation of gas during the recombination process.

The Y-function in *Figure 6.27* exhibits erratic behavior around bubble point pressure due to possible measurement errors:

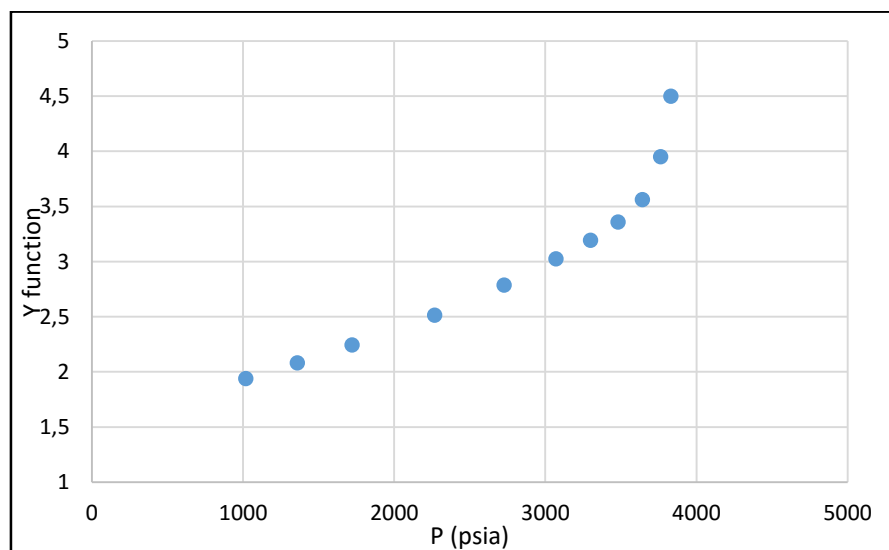


Figure 6.27: Y function.

The isothermal oil compressibility for pressures above bubble point decreases linearly as pressure increases (*Figure 6.28*).

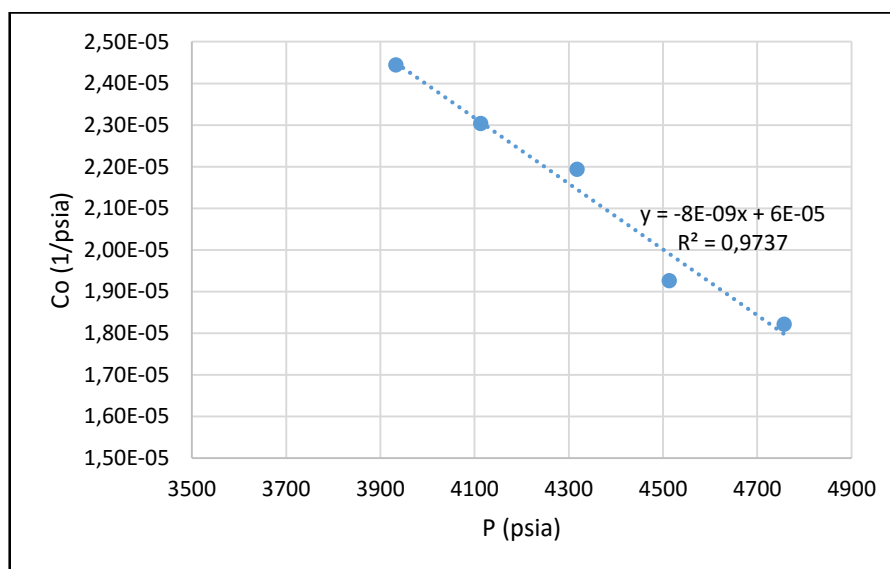


Figure 6.28: Isothermal oil compressibility for pressures above bubble point.

6.3.3 Differential vaporization test

The procedure that will be used for the differential vaporization test is the same with the other relevant subchapters. The mass of removed gas is calculated according to *Table 6.45*.

Table 6.45: Mass of removed gas at each pressure step at DV for Congo oil.

Pressure (psia)	R_s (sm ³ /sm ³)	Moles of gas (moles)	Moles of removed gas	Molar mass of gas (g/mol)	Mass of removed gas (kg)
3,882	268.8	11,346.6			
3,482	230.2	9,717.2	1,629.4	23.95	39.024
2,875	183.9	7,762.8	1,954.4	21.9	42.802
2,100	138.6	5,850.6	1,912.2	21.42	40.959
1,703	114.4	4,829.0	1,021.5	21.39	21.850
1,153	85.4	3,604.9	1,224.1	21.8	26.686
525	53.3	2,249.9	1,355.0	23.8	32.249
155	31.0	1,308.6	941.3	32.22	30.330
15	0.0	0.0	1,308.6	62.84	82.230

The mass of the residual oil and the mass and moles of the bubble point fluid are reported in *Table 6.46*.

Table 6.46: Mass of residual oil and moles of bubble point fluid.

Residual oil relative density	Mass of residual oil(kg)	Mass of bubble point fluid (kg)	Molar mass of reservoir fluid (g/mol)	Moles of bubble point fluid
0.837	837	1,153.130	67.7	5,686.4

The compositions of the liquid and the gas phase for each pressure step are given in the following Tables:

Table 6.47: Gas compositions at different pressure steps.

Pressure (psia) Composition	3,482	2,875	2,100	1,703	1,153	525	155	15
N ₂ (%mol)	0.62	0.48	0.37	0.29	0.19	0.09	0.03	0.01
CO ₂ (%mol)	0.75	0.79	0.82	0.85	0.93	1.07	1.08	0.33
H ₂ S (%mol)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CH ₄ (%mol)	79.57	82.26	82.72	82.20	80.13	72.64	48.15	8.91
C ₂ H ₆ (%mol)	6.90	6.86	7.08	7.49	8.63	11.93	17.66	10.00
C ₃ H ₈ (%mol)	4.14	3.80	3.88	4.16	4.91	7.27	15.81	17.97
iso C ₄ H ₁₀ (%mol)	0.63	0.64	0.54	0.56	0.64	0.95	2.33	4.08
nC ₄ H ₁₀ (%mol)	1.91	1.61	1.57	1.62	1.82	2.64	6.95	14.92
iso C ₅ H ₁₂ (%mol)	0.59	0.47	0.43	0.43	0.45	0.62	1.66	4.99
n C ₅ H ₁₂ (%mol)	1.32	1.06	0.96	0.93	0.95	1.29	3.38	11.71
pseudo C ₆ (%mol)	1.33	1.02	0.87	0.80	0.75	0.89	2.01	11.27
C ₇₊ (%mol)	2.24	1.01	0.76	0.67	0.60	0.61	0.94	15.81
Molar mass (g/mol)	23.95	21.90	21.42	21.39	21.80	23.80	32.22	62.84

The methane at 155 psia seems to have been liberated almost totally, since at 15 psia it occupies only ~9% mol.

Table 6.48: Liquid compositions at different pressure steps.

Pressure (psia) Composition	3,482	2,875	2,100	1,703	1,153	525	155	15
N ₂ (%mol)	0.06	-0.01	-0.07	-0.10	-0.14	-0.18	-0.21	-0.26
CO ₂ (%mol)	0.64	0.62	0.58	0.56	0.51	0.41	0.32	0.32
H ₂ S (%mol)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CH ₄ (%mol)	50.55	45.95	39.85	35.74	29.89	22.59	19.15	21.51
C ₂ H ₆ (%mol)	6.71	6.69	6.63	6.54	6.27	5.30	3.64	2.17
C ₃ H ₈ (%mol)	4.90	5.06	5.26	5.37	5.43	5.11	3.67	0.38
iso C ₄ H ₁₀ (%mol)	0.74	0.76	0.79	0.81	0.84	0.82	0.61	-0.18
nC ₄ H ₁₀ (%mol)	2.19	2.27	2.39	2.46	2.55	2.53	1.93	-1.05
iso C ₅ H ₁₂ (%mol)	0.78	0.82	0.89	0.93	1.00	1.06	0.98	0.06
n C ₅ H ₁₂ (%mol)	1.95	2.08	2.27	2.39	2.59	2.81	2.73	0.66
pseudo C ₆ (%mol)	3.52	3.88	4.38	4.73	5.25	6.00	6.54	5.45
C ₇₊ (%mol)	27.96	31.88	37.03	40.57	45.83	53.55	60.63	70.95
Molar mass (g/mol)	72.33	79.66	89.31	95.91	105.67	119.65	131.41	147.19

Negative compositions resulted due to the weakness of the chromatograph to track the traces during gas analysis. The molar mass of the liquid is increased as pressure decreases, with maximum value for the residual oil at 15 psia.

The semi logarithmic plot of k values at each pressure step and per component is presented in the following figure.

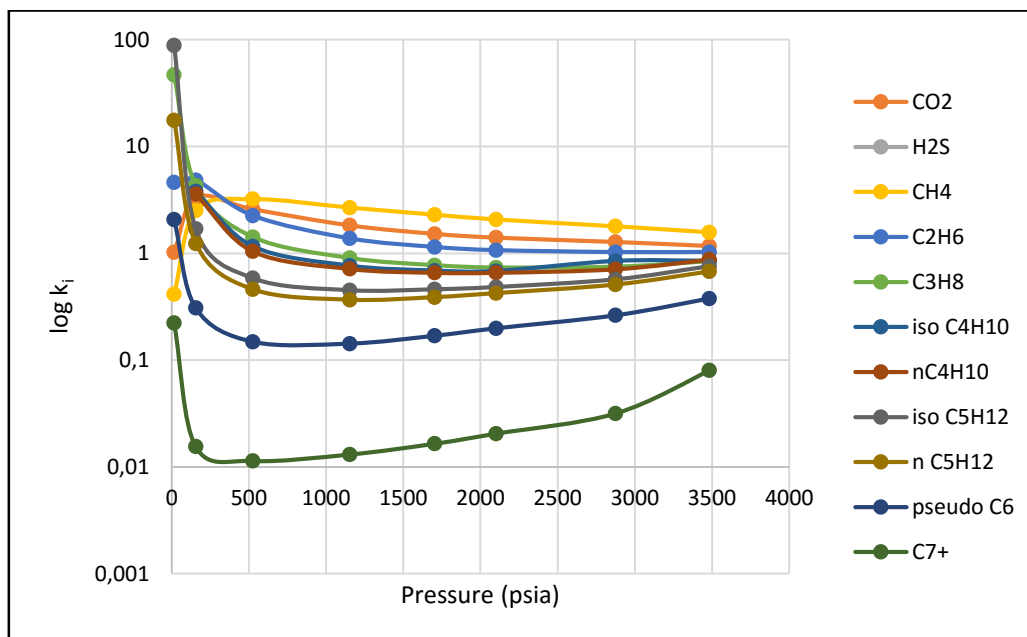


Figure 6.29: Semi logarithmic plot of k versus pressure for each component at DV test.

The k value lines of some components cross each other, behavior that is not physically sound. The gas and liquid phase are not thermodynamically consistent during the experimentation.

In Figures 6.30 and 6.31, the compositions of the gas and the liquid phases for all the pressure steps are presented.

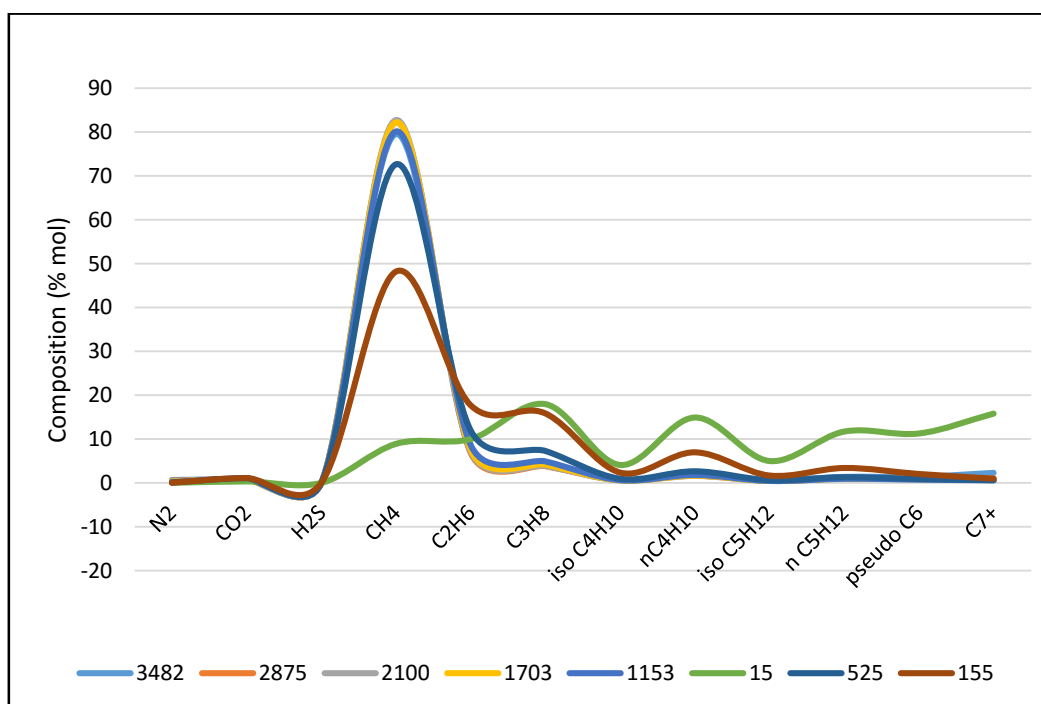


Figure 6.30: DV gas compositions for all the components and pressure steps.

The DV gas compositions have similar distributions until pressure 1,153 psia. Then, the shape of the distribution changes. For pressure 525 psia it changes for the methane and ethane by occupying less and more % mol concentration respectively; for pressure 155 psia the methane decreases while the ethane, propane and n butane increases; for pressure 15 psia the methane and ethane concentration decreases while the concentrations of components heavier than the iso butane are increased.

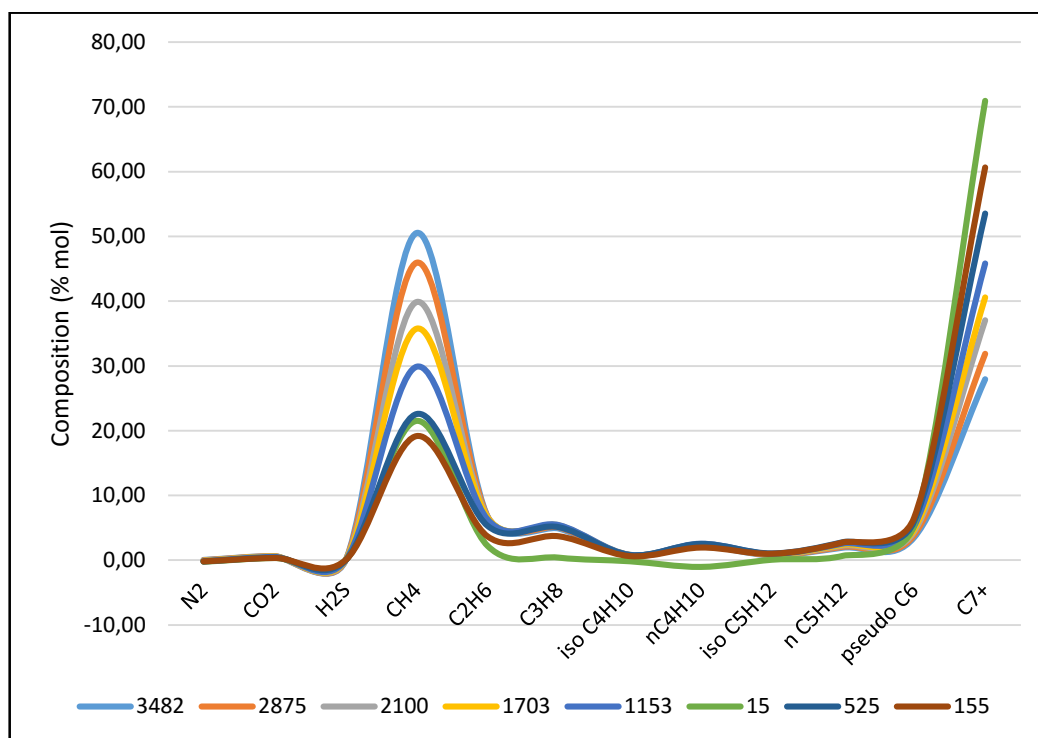


Figure 6.31: DV liquid compositions for all the components and pressure steps.

For the DV liquid compositions the shape of the distribution is almost perfect with exception at 15 psia (negative values of % mol composition and increase in methane composition).

The material balances for the DV data of Congo oil are presented in *Figures 6.32 and 6.33*. In *Figure 6.32*, there is linearity for each pressure step, so, the material balance plot at each pressure step visualizes that the calculation of the liquid composition was held right. In the case that the material balance is held per component, then abnormalities appear (*Figure 6.33*).

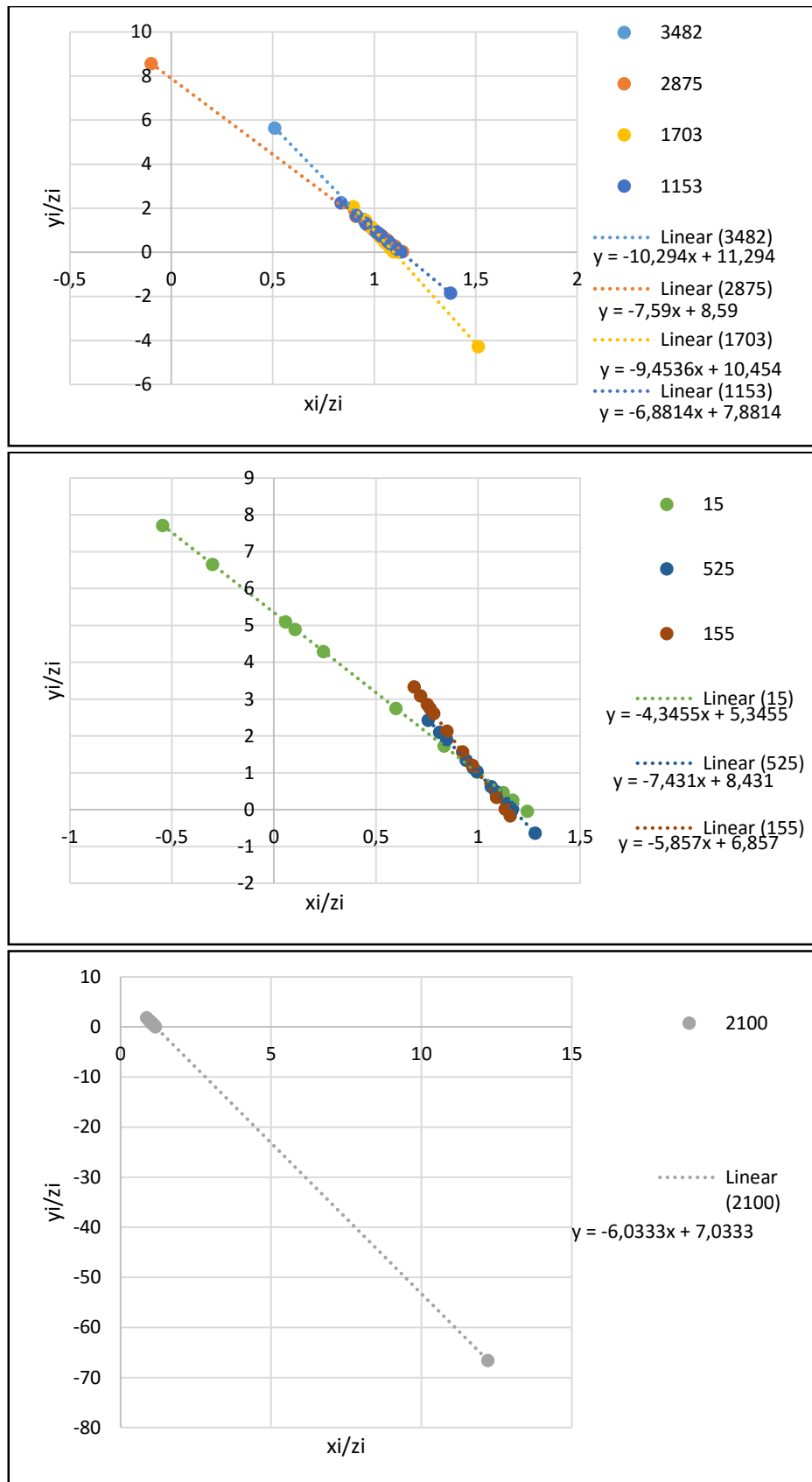


Figure 6.32: Material balance foreach pressure step at DV test.

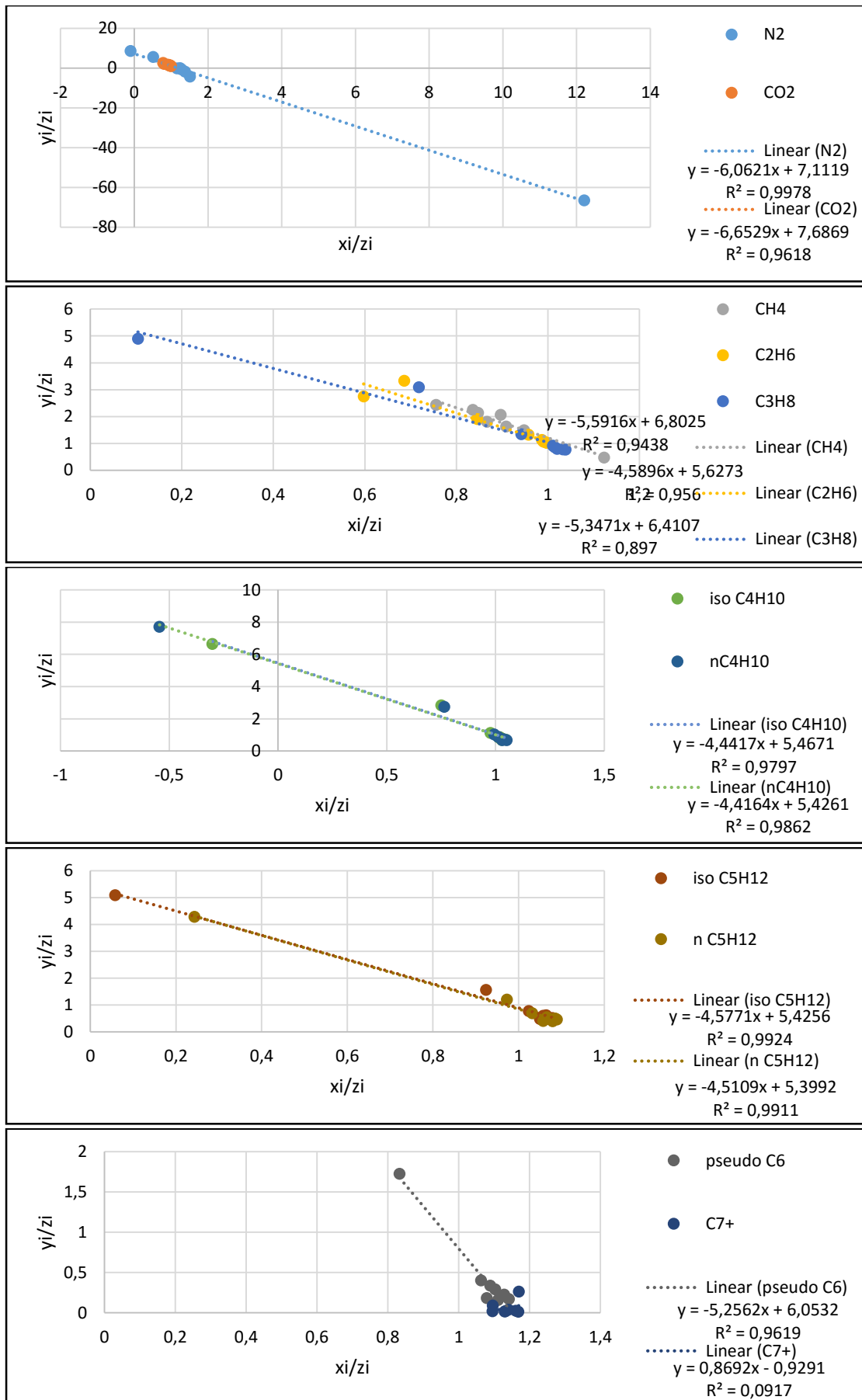


Figure 6.33: Material balance for each component at DV test.

Finally, the calculated composition and the molar mass of the residual oil are compared to the stock tank oil ones (*Table 6.49*).

Table 6.49: Comparison of the back calculated residual oil and the measured stock tank oil compositions.

Composition	Residual oil from DV	Stock tank oil
N ₂ (%mol)	-0.26	0.00
CO ₂ (%mol)	0.32	0.10
H ₂ S (%mol)	0.00	0.00
CH ₄ (%mol)	21.51	3.55
C ₂ H ₆ (%mol)	2.17	1.90
C ₃ H ₈ (%mol)	0.38	2.84
iso C ₄ H ₁₀ (%mol)	-0.18	0.64
nC ₄ H ₁₀ (%mol)	-1.05	2.36
iso C ₅ H ₁₂ (%mol)	0.06	1.37
n C ₅ H ₁₂ (%mol)	0.66	3.92
pseudo C ₆ (%mol)	5.45	8.80
C ₇₊ (%mol)	70.95	74.72
Molar mass (g/mol)	147.19	160.7

The DV test data lead to lighter residual oil from the stock tank oil! It is an indication that errors occurred during the manipulation of the fluid. It is worth mentioning that the methane concentration is totally different between the residual oil from the DV and the stock tank oil, which was also pointed at previous Tables and Figures.

6.3.4 Laboratory separator tests

Material balance is also held for the separator tests (*Table 6.50*).

Table 6.50: Mass of removed gas at laboratory separator tests for $p = 150$ psia.

	Gas liquid ratio (sm ³ /sm ³)	Moles of removed gas (moles)	Molar mass of removed gas (g/mol)	Mass of removed gas (kg)
Separator	209.4	8,839.2	21.85	193.136
Tank	13.6	574.1	39.07	22.429

The mol of the reservoir fluid are:

Table 6.51: Moles of reservoir fluid for the laboratory separator tests.

p (psia)	Tank density (g/cm ³)	Mass of stock tank oil (kg)	Mass of reservoir fluid (kg)	Molar mass of reservoir fluid (g/mol)	Mol of reservoir fluid
150	0.816	816	1,031.565	67.6	15,237.3

The liquid compositions for $p = 150$ psia are given in the following Table:

Table 6.52: Compositions of laboratory separator tests at $p = 150$ psia.

	Separator gas	Separator liquid	Tank gas	Tank liquid
N₂	0.16	0.04	0.00	0.04
CO₂	0.93	0.26	0.90	0.20
H₂S	0.00	0.00	0.00	0.00
CH₄	78.86	18.06	31.40	16.74
C₂H₆	9.21	3.30	16.62	1.99
C₃H₈	5.85	3.42	23.39	1.45
iso C₄H₁₀	0.77	0.67	4.12	0.34
nC₄H₁₀	2.06	2.30	12.24	1.32
iso C₅H₁₂	0.44	1.20	2.72	1.05
n C₅H₁₂	0.85	3.33	5.15	3.15
pseudo C₆	0.50	7.19	2.50	7.65
C₇₊	0.37	60.22	0.96	66.06
Molar mass (g/mol)	21.9	131.0	39.1	140.1
Moles	8,839.2	6,398.1	574.1	5,824.0

The material balance for $p = 150$ psia of the separator is presented in the following figure:

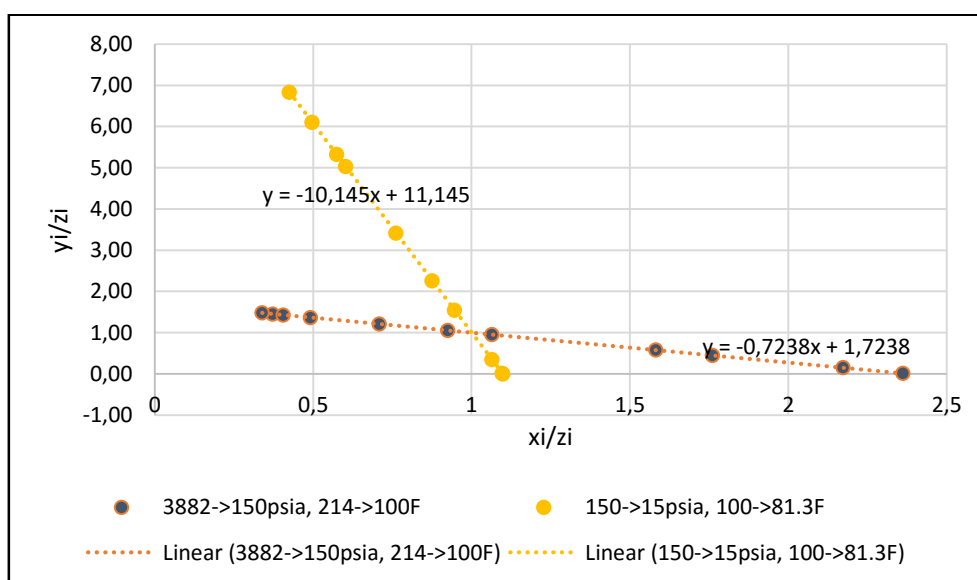


Figure 6.34: Material balance for the separator tests for $p=150$ psia.

6.3.5 Comparison of differential liberation and laboratory separator test data

The solution GOR and the formation volume factor from the differential liberation test and the laboratory separator tests are compared in the next Table:

Table 6.53: Comparison of volumetric output from differential liberation and laboratory separator tests.

	R_{sb} (scf/STB)	B_{ob} (barrel/STB)
Laboratory separation	1,252	1.718
Differential liberation	1,509	1.967

The residual oil resulted from DV is heavier than the stock tank oil from the laboratory separator tests, as expected (Table 6.54).

Table 6.54: Comparison of API gravity, density and molar mass between differential liberation and laboratory separator test.

	Residual oil from DV	Stock tank oil from laboratory test
API gravity	37.5	41.9
Density (g/cm³)	0.837	0.816
Molar mass (g/mol)	147.2	140.1

The conversion of the differential vaporization data to stock tank oil basis is studied in the following Table while once more the weakness of the method to convert the volumetric values at low pressures is observed:

Table 6.55: Conversion of differential volumetrics to stock tank oil basis.

Pressure (psia)	R_{sd} (scf/barrel residual)	R_s (scf/STB)	B_{od} (barrel/barrel residual)	B_o (barrel/STB)
3,882	1,509	1,252	1.967	1.718
3,482	1,293	1,063.3	1.853	1.618
2,875	1,033	836.2	1.698	1.483
2,100	778	613.5	1.546	1.350
1,703	643	495.6	1.487	1.299
1,153	480	353.3	1.416	1.237
525	299	195.1	1.338	1.1686
155	174	85.9	1.246	1.088
15	0	-65.9	1.076	0.939

6.3.6 Viscosity test

Finally, the viscosity of the reservoir fluid versus the pressure is studied.

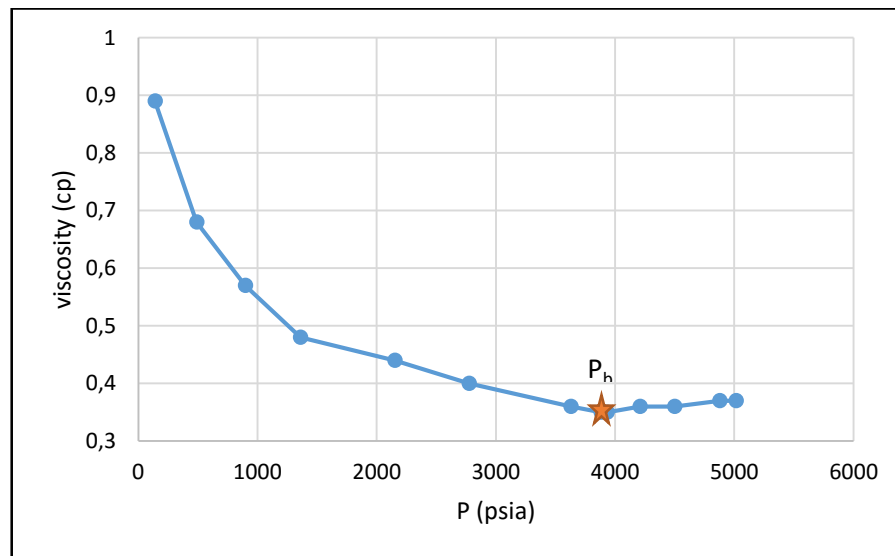


Figure 6.35: Viscosity experiment.

6.3.7 Results for Congo oil

It is concluded that the Congo oil PVT report has shown some problems. The following Table summarizes the results of the quality control check:

Table 6.56: Summary of the PVT quality control test for Congo oil.

	Comments	Acceptability
Quality control of the recorded samples	Thermodynamic consistency of liquid and gas phase, uncertainty of the selected samples and the recombination process	Yes / No
CCE test	Linearity for the isothermal oil compressibility, erratic behavior for Y function around bubble point pressure	Yes / No
DV	Material balance at each pressure step is satisfied, material balance for each component is not satisfied, negative values of % mol concentration, smaller molar mass of the residual oil than the stock tank oil, not expected so high CH ₄ concentration, cross of lines at plot log k_i versus pressure	No
Laboratory separator tests	Material balance is satisfied, logical values of concentration and molar mass	Yes
Viscosity	Logical values	Yes

6.4 Unknown oil 9

For the PVT report of Fluid 9 the results of the quality control are presented below:

6.4.1 Quality control of the analyzed samples

Separator samples were used for the study. In the following Table the recorded conditions of separator and well head are presented:

Table 6.57: Condition of separator and well head.

Separator pressure (kg/cm ²)	Separator temperature (°C)	Well head pressure (kg/cm ²)	Well head temperature (°C)
6	37	16	30

The analyzed samples are described in the following Table:

Table 6.58: Separator samples for Unknown oil 9.

Gas				
#	Time	Opening pressure (kg/cm ²)	Carry over	Air (mole %)
SG01	15:45	6.2	0	0
SG02	16:15	6.3	0	0
SG03	16:15	5.6	0	0
Liquid				
#	Time	Bubble point pressure (kg/cm ²)	BS&W	
SLS01	15:35	6.4 at 37 °C	0	
SLS02	16:00	6.3 at 37°C	0	
SLS03	16:30	6.4 at 37 °C	0	

None of the liquid samples contain BS&W while the bubble point pressure is very close to the separator pressure.

None of the gas samples, contain air, liquid hydrocarbons, water, mud and sediments so their opening pressures and compositions will be used for the evaluation of the samples. The SG01 has better value of opening pressure.

The compositions of the gas samples are presented in the following Table:

Table 6.59: Compositions of the gas field separator samples for Unknown oil 9.

	SG01	SG02	SG03
N₂ (%mol)	0.00	0.16	0.06
CO₂ (%mol)	8.01	6.84	8.15
H₂S (%mol)	0.47	0.78	0.16
CH₄ (%mol)	81.97	74.41	82.27
C₂H₆ (%mol)	4.02	6.55	3.95
C₃H₈ (%mol)	2.87	6.17	2.83
iso C₄H₁₀ (%mol)	1.13	1.64	1.12
nC₄H₁₀ (%mol)	0.86	1.93	0.84
iso C₅H₁₂ (%mol)	0.43	0.60	0.40
n C₅H₁₂ (%mol)	0.05	0.38	0.05
pseudo C₆ (%mol)	0.08	0.25	0.07
C₇₊ (%mol)	0.11	0.29	0.10
Molar mass (g/mol)	21.00	23.26	20.92

All of the samples have similar composition distribution and molar masses so all of them are well specified.

Finally, the samples SG01 and SLS01 seem to be the best samples to be recombined, so their thermodynamic consistency is tested in the following Figures:

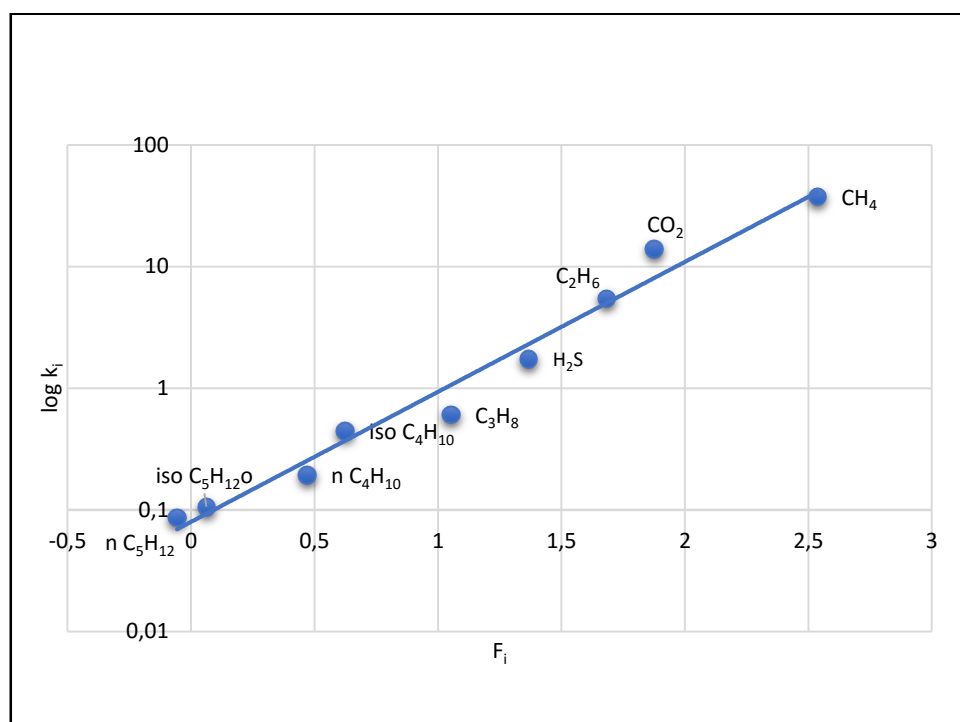


Figure 6.36: Hoffman plot for Unknown oil 9 - SG01 and SLS01.

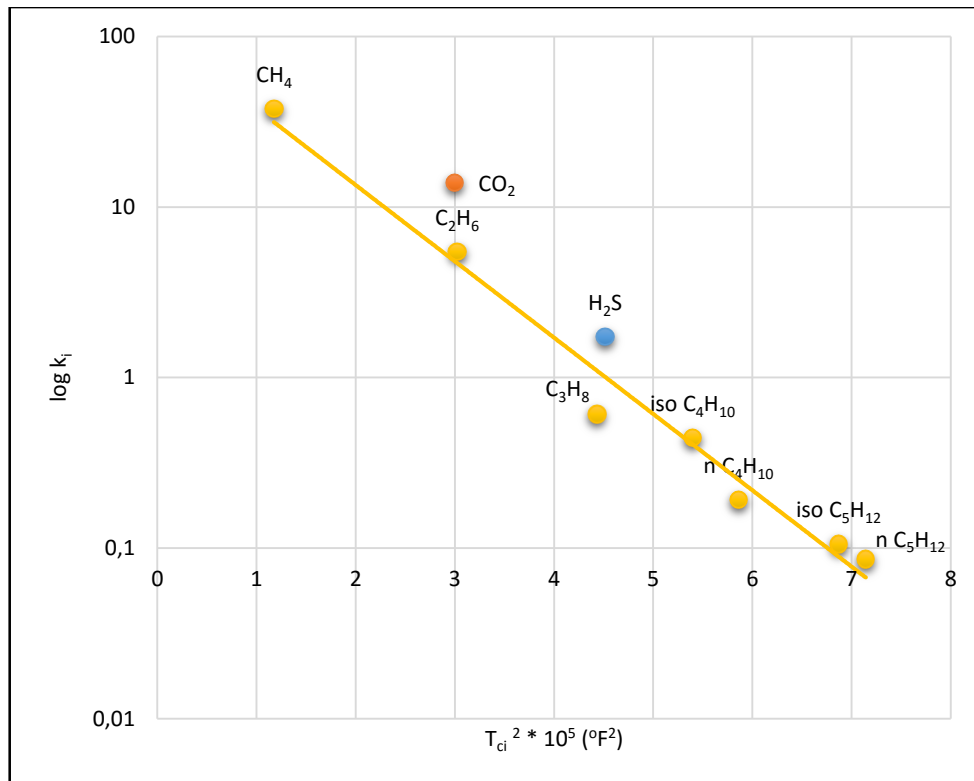


Figure 6.37: Buckley plot for Unknown oil 9 - SG01 and SLS01.

As can be derived from the previous plots, the behavior of the components is the anticipated one, so the thermodynamic consistency is guaranteed. The non hydrocarbon components are also very close to the lines.

The recombination process for the reservoir fluid took place with molar ratio according to the corrected gas to oil ratio.

Table 6.60: Correction of gas to oil ratio.

	<i>Z</i>	<i>Specific gravity</i>	<i>R_{sp}</i> (scf/bbl)
<i>Field</i>	0.980	0.735	88
<i>Laboratory</i>	0.990	0.725	88

The chromatographically obtained compositions of the separator gas, separator liquid and recombined fluid are presented in *Table 6.61*.

Table 6.61: Compositions and molar masses of the separator liquid, separator gas and recombined reservoir fluid.

	Separator liquid	Separator gas	Recombined fluid
N₂ (%mol)	0.00	0.00	0.00
CO₂ (%mol)	0.59	8.01	1.98
H₂S (%mol)	0.27	0.47	0.31
CH₄ (%mol)	2.23	81.97	17.20
C₂H₆ (%mol)	0.75	4.02	1.36
C₃H₈ (%mol)	4.73	2.87	4.38
iso C₄H₁₀ (%mol)	2.54	1.13	2.27
nC₄H₁₀ (%mol)	4.45	0.86	3.78
iso C₅H₁₂ (%mol)	4.05	0.43	3.37
n C₅H₁₂ (%mol)	0.57	0.05	0.47
pseudo C₆ (%mol)	2.25	0.08	1.84
pseudo C₇ (%mol)	3.40	0.08	2.78
pseudo C₈ (%mol)	4.41	0.02	3.59
pseudo C₉ (%mol)	4.38	0.01	3.56
pseudo C₁₀ (%mol)	3.91	0.00	3.17
pseudo C₁₁ (%mol)	2.57	0.00	2.09
C₁₂₊ (%mol)	58.90	0.00	47.85
Molar mass (g/mol)	306.9	21.0	253.2

The composition of the reservoir oil has typical values of a black oil.

6.4.2 CCE test

The CCE test provides the relative volume according to *Table 6.62*:

Table 6.62: CCE data for Unknown oil 9.

Pressure (kg/cm ²)	Relative volume
140.6	0.9926
121.3	0.9940
103.1	0.9953
80.7	0.9970
63.4	0.9985
55.0	0.9992
45.7 = P _b	1.0000
44.7	1.0040
43.1	1.0114
39.5	1.0315
34.9	1.0700
31	1.1165
26.4	1.2075
21.7	1.3752
16.0	1.7828
13.9	2.0840

The Y function for the Unknown oil 9 is linearly related to the pressure and is printed in the following figure:

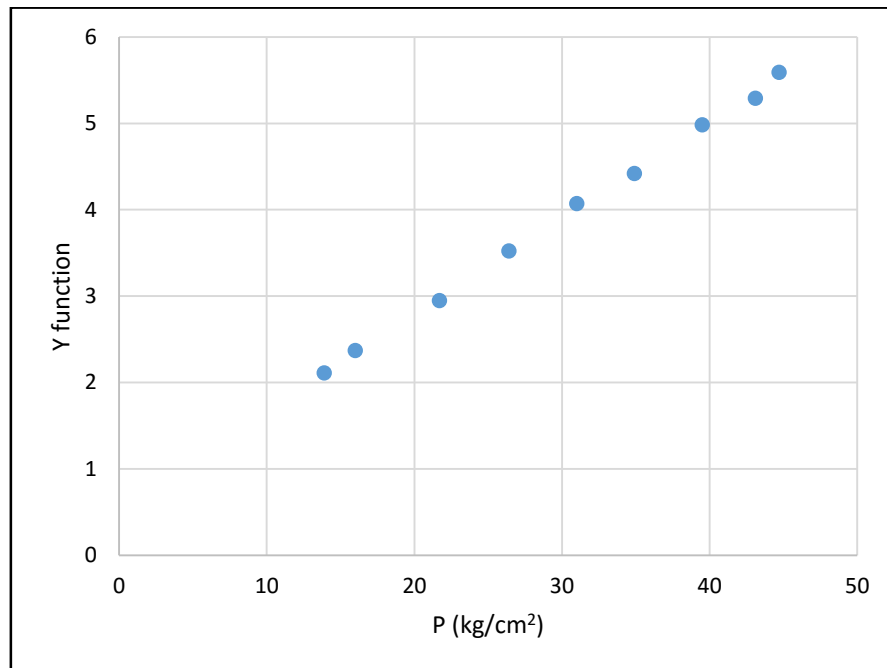


Figure 6.38: Y function.

The isothermal oil compressibility is not well related to pressure, as the points don't lie on the line $y = -2 \cdot 10^{-7} \cdot x + 10^{-4}$ in a very good manner (Figure 6.39):

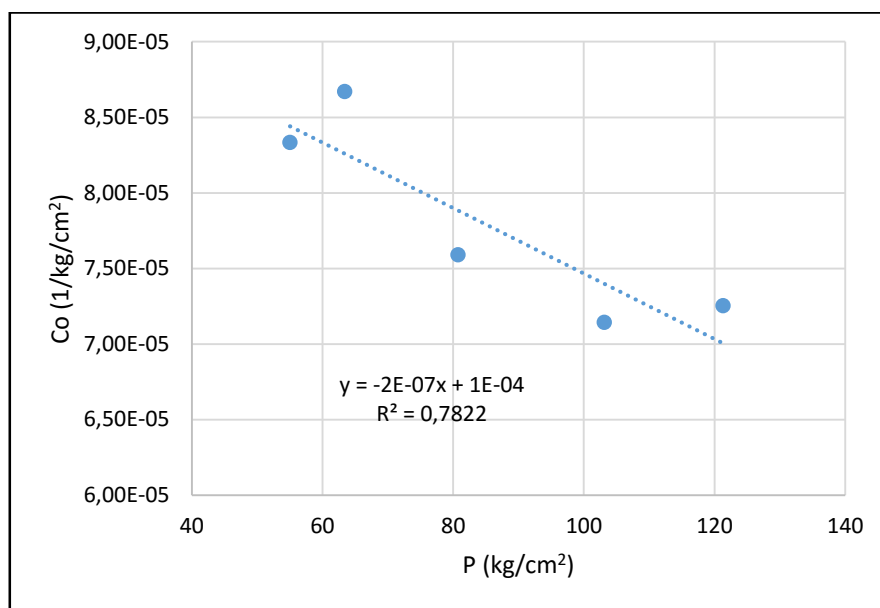


Figure 6.39: Isothermal oil compressibility for pressures above bubble point.

The values of the isothermal oil compressibility are very low and the R^2 is far away from the unity, indicating that errors at the recorded relative volume occurred.

6.4.3 Differential vaporization test

For the differential vaporization test a material balance is held. The mass of removed gas is presented in Table 6.63.

Table 6.63: Mass of removed gas at each pressure step at DV for Unknown oil 9.

Pressure (kg/cm²)	R_s (sm³/sm³)	Moles of gas (moles)	Moles of removed gas	Molar mass of gas (g/mol)	Mass of removed gas (kg)
45.7	21.8	920.2			
39.1	19.3	814.7	105.5	19.03	2.008
31.1	16.8	709.2	105.5	19.18	2.024
23.8	13.5	569.9	139.3	19.57	2.726
15.8	9.7	409.5	160.4	20.20	3.240
8.4	6.3	265.9	143.5	22.34	3.206
1.0	0.0	0.0	265.9	31.05	8.257

The following Table summarizes the calculation of the moles of bubble point fluid that correspond to 1 m³ residual oil.

Table 6.64: Mass of residual oil and moles of bubble point fluid.

Residual oil relative density	Mass of residual oil(kg)	Mass of bubble point fluid (kg)	Molar mass of reservoir fluid (g/mol)	Moles of bubble point fluid
0.898	898	919.462	253.2	3,631.4

The compositions of the liquid and the gas phase for each pressure are:

Table 6.65: Gas compositions at different pressure steps.

Pressure (kg/cm ²) Composition	39.1	31.1	23.8	15.8	8.4	1
N ₂ (%mol)	0.00	0.00	0.00	0.00	0.00	0.00
CO ₂ (%mol)	4.86	5.14	5.90	6.70	9.18	9.65
H ₂ S (%mol)	0.25	0.29	0.38	0.44	0.86	3.15
CH ₄ (%mol)	89.81	89.17	87.41	84.88	77.27	49.68
C ₂ H ₆ (%mol)	2.10	2.28	2.80	3.59	5.38	10.44
C ₃ H ₈ (%mol)	1.38	1.46	1.77	2.28	3.74	12.98
iso C ₄ H ₁₀ (%mol)	0.43	0.45	0.53	0.68	1.12	5.06
nC ₄ H ₁₀ (%mol)	0.45	0.51	0.56	0.73	1.16	5.53
iso C ₅ H ₁₂ (%mol)	0.22	0.23	0.25	0.31	0.53	2.03
n C ₅ H ₁₂ (%mol)	0.07	0.08	0.10	0.14	0.37	0.41
pseudo C ₆ (%mol)	0.13	0.12	0.09	0.09	0.22	0.79
C ₇₊ (%mol)	0.30	0.27	0.21	0.16	0.17	0.28
Molar mass (g/mol)	19.03	19.18	19.57	20.20	22.34	31.05

Table 6.66: Liquid compositions at different pressure steps.

Pressure (kg/cm ²) Composition	39.1	31.1	23.8	15.8	8.4	1
N ₂ (%mol)	0.00	0.00	0.00	0.00	0.00	0.00
CO ₂ (%mol)	1.89	1.79	1.62	1.36	0.98	0.13
H ₂ S (%mol)	0.31	0.31	0.31	0.30	0.28	-0.01
CH ₄ (%mol)	15.03	12.74	9.57	5.70	2.25	-2.41
C ₂ H ₆ (%mol)	1.34	1.31	1.25	1.12	0.92	-0.01
C ₃ H ₈ (%mol)	4.47	4.56	4.68	4.80	4.86	4.06
iso C ₄ H ₁₀ (%mol)	2.33	2.38	2.46	2.55	2.62	2.38
nC ₄ H ₁₀ (%mol)	3.88	3.98	4.13	4.30	4.46	4.35
iso C ₅ H ₁₂ (%mol)	3.46	3.56	3.70	3.88	4.04	4.24
n C ₅ H ₁₂ (%mol)	0.48	0.49	0.51	0.53	0.54	0.55
pseudo C ₆ (%mol)	1.89	1.95	2.02	2.12	2.22	2.36
C ₇₊ (%mol)	64.92	66.91	69.74	73.32	76.85	84.36
Molar mass (g/mol)	260.21	267.65	278.18	291.44	304.41	331.23

Negative compositions indicate that error occurred during DV gas chromatography.

The semi logarithmic plot of k values at each pressure step and per component is made and it is observed that the $n\text{C}_5\text{H}_{12}$ cross lines from other components.

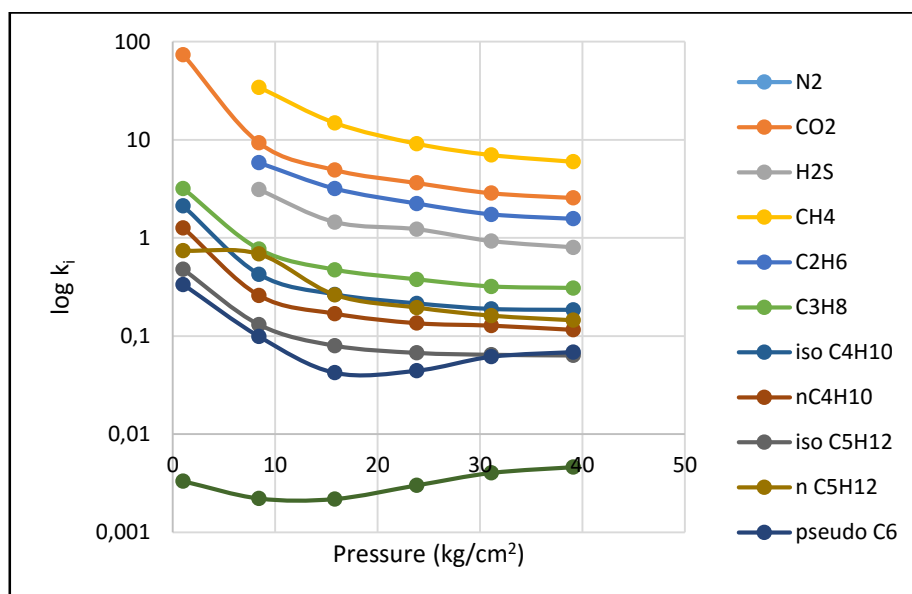


Figure 6.40: Semi logarithmic plot of k versus pressure for each component at DV test.

In Figures 6.41 and 6.42, the compositions of the gaseous and the liquid phase for all the components and pressure steps are presented.

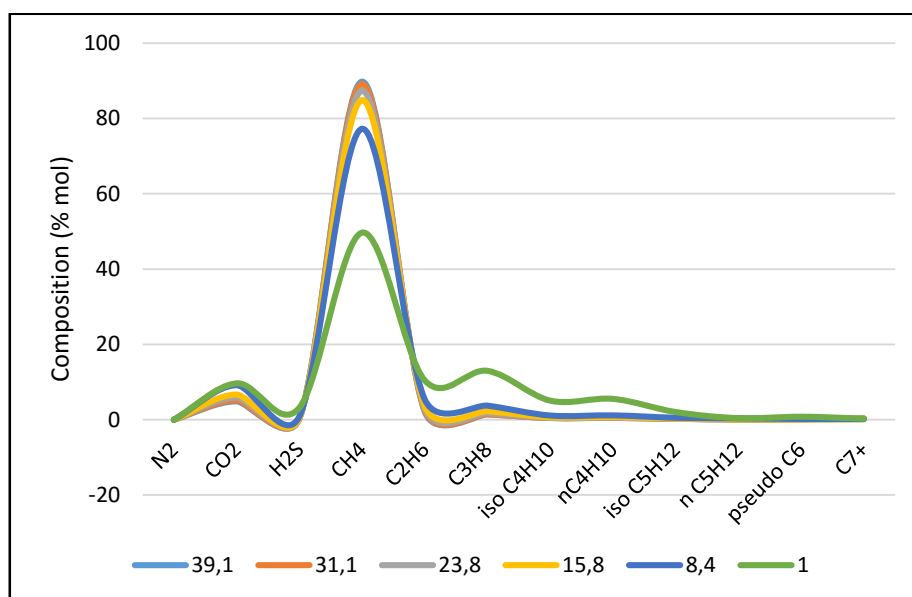


Figure 6.41: DV gas compositions for all the components and pressure steps.

The DV gas compositions have similar distributions for all pressures except from 1 kg/cm^2 . As pressure decreases, the enclosed hydrocarbons at the gaseous phase become heavier by the same manner. For pressure 1 kg/cm^2 , the C_2H_6 , C_3H_8 and C_4H_{10} differentiate from the general behavior.

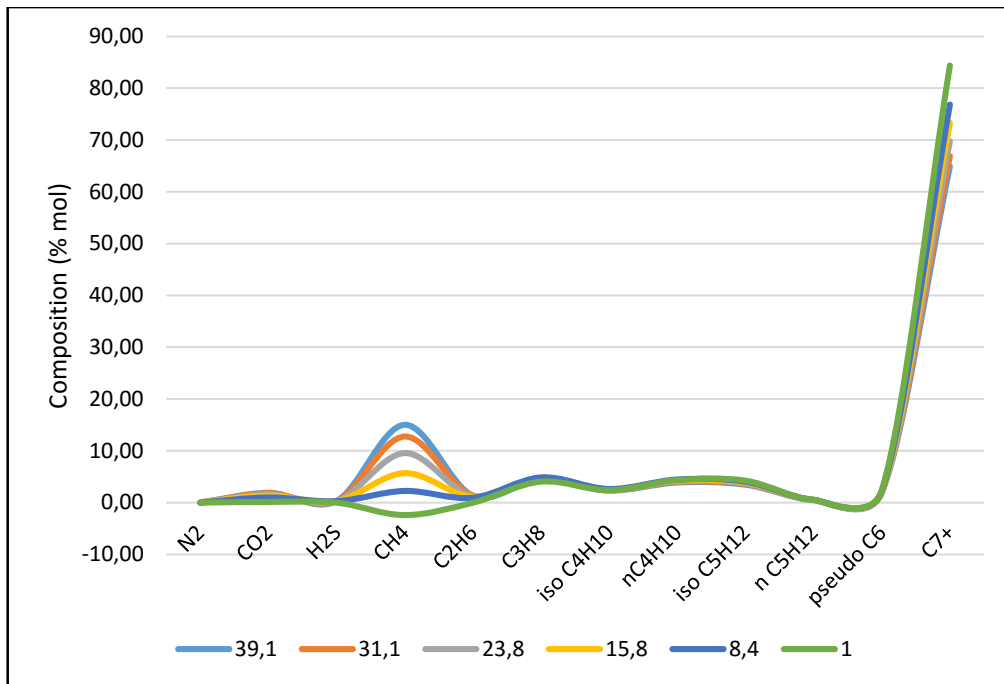


Figure 6.42: DV liquid compositions for all the components and pressure steps.

For the DV liquid compositions all the components obey the same distribution. The methane for pressure equal to 1kg/cm² has negative value.

The plots of the material balance at each pressure step are:

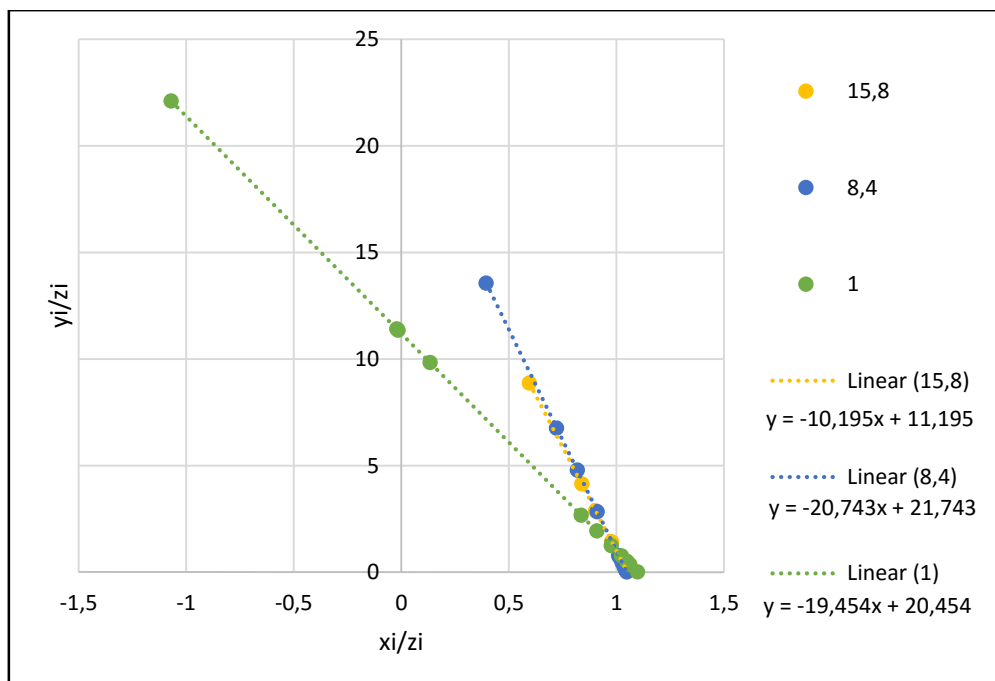


Figure 6.43: Material balance at each pressure step for the DV test.

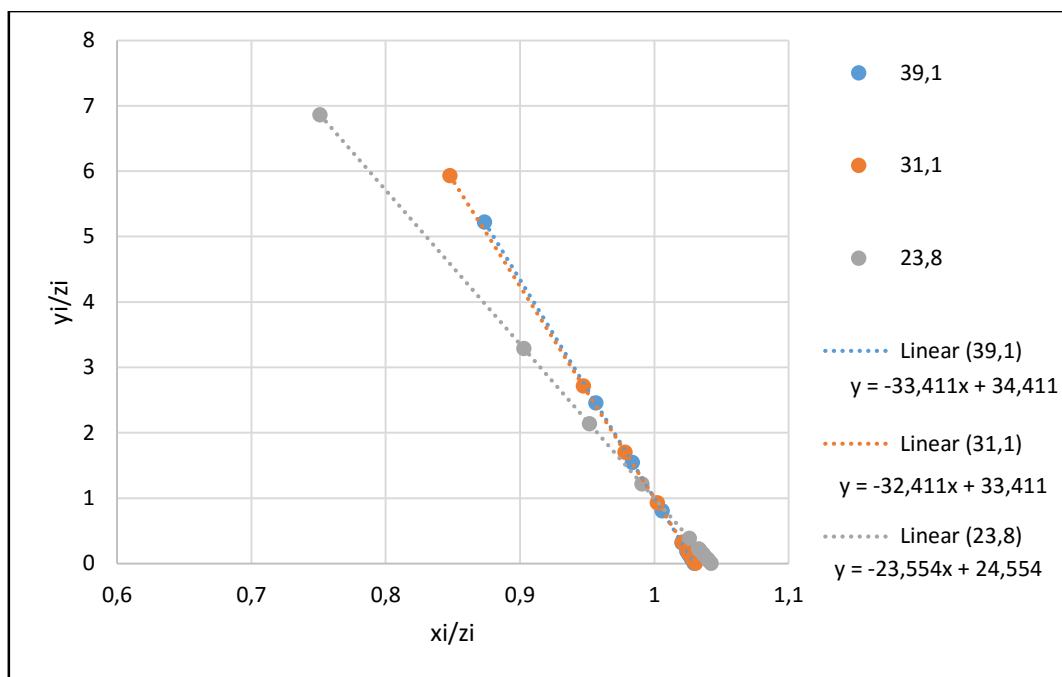


Figure 6.43: Material balance for each pressure step at DV test.

The material balance at each pressure step is satisfied. The material balance for each component (Figure 6.44) is not satisfied since errors in their behavior were identified for CO_2 , $n\text{C}_5\text{H}_{12}$ and C_{7+} (squared correlation coefficient) and for iso C_5H_{12} and pseudo C_6 (positive slope).

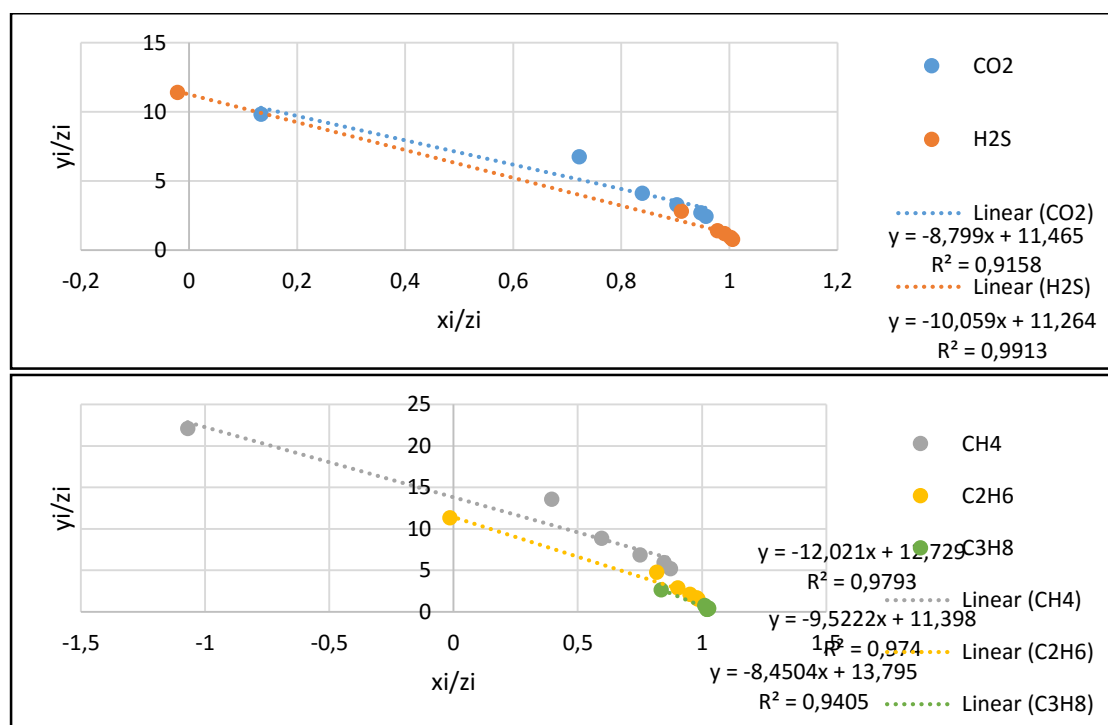


Figure 6.44: Material balance for each component at DV test.

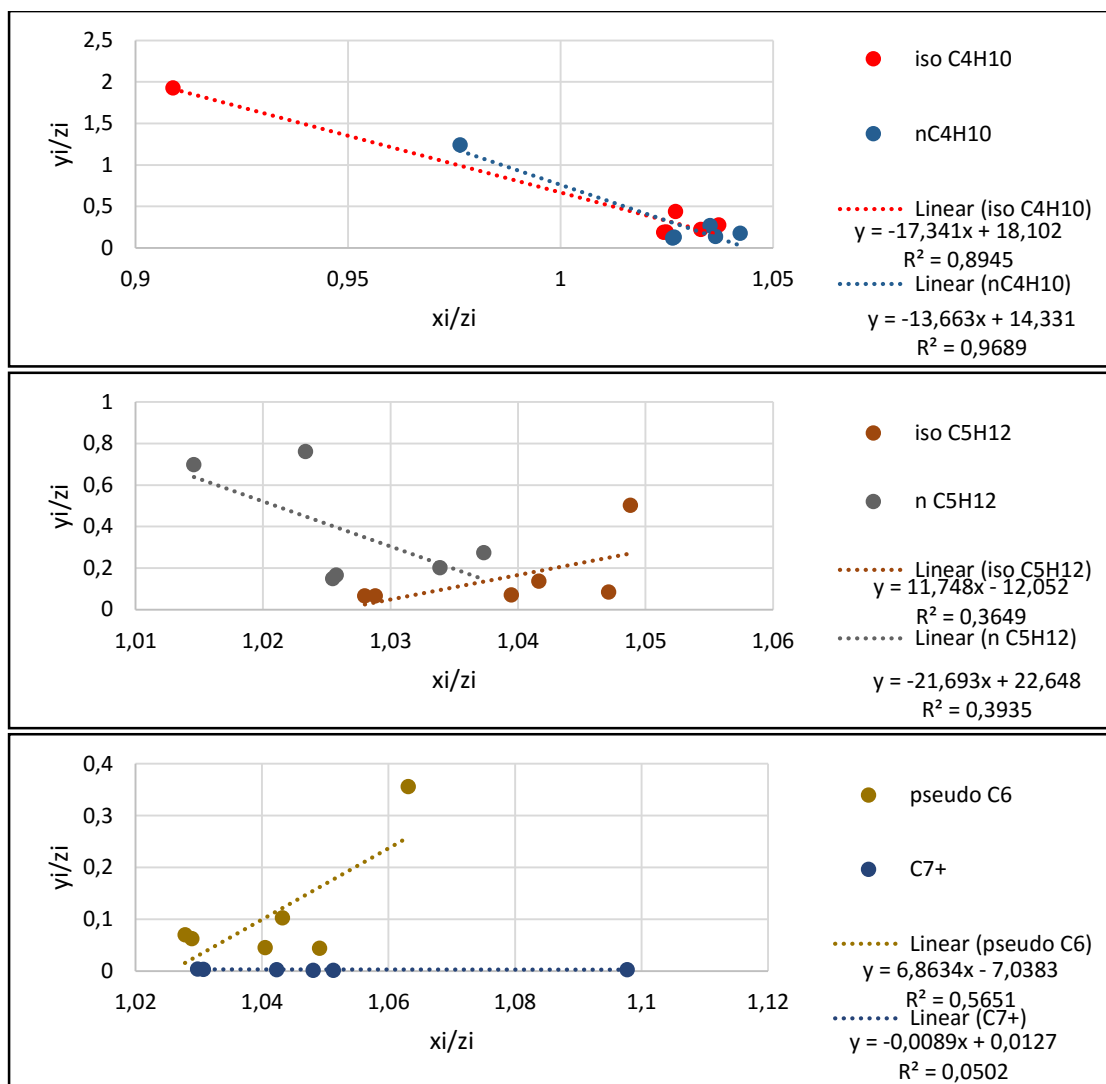


Figure 6.44: Material balance for each component at DV test.

The calculated composition of the residual oil is compared to the stock tank oil one.

Table 6.67: Comparison of the back calculated residual oil and the measured stock tank oil compositions.

Composition	Residual oil from DV	Stock tank oil
N ₂ (%mol)	0.00	0.00
CO ₂ (%mol)	0.13	0.59
H ₂ S (%mol)	-0.01	0.27
CH ₄ (%mol)	-2.41	2.23
C ₂ H ₆ (%mol)	-0.01	0.75
C ₃ H ₈ (%mol)	4.06	4.73
iso C ₄ H ₁₀ (%mol)	2.38	2.54
nC ₄ H ₁₀ (%mol)	4.35	4.45
iso C ₅ H ₁₂ (%mol)	4.24	4.05
n C ₅ H ₁₂ (%mol)	0.55	0.57
pseudo C ₆ (%mol)	2.36	2.25
C ₇ + (%mol)	84.36	77.57
Molar mass (g/mol)	331.23	306.9

The DV data led to heavier residual oil than the measured stock tank oil due to larger evaporation of the gas phase. It is observed that the composition of the residual oil and the stock tank oil, despite the negative sign for the residual oil's composition, does not have very differentiations except for the CH₄.

6.4.4 Laboratory separator tests

Material balance is also held for the separator test. The mass removed at each pressure step is presented in the following Table:

Table 6.68: Mass of removed gas at each pressure step for the laboratory separator tests.

p=14 kg/cm²				
	Gas liquid ratio (sm ³ /sm ³)	Moles of removed gas (moles)	Molar mass of removed gas (g/mol)	Mass of removed gas (kg)
Separator	12.8	540.3	20.85	11.266
Tank	8.5	358.8	27.7	9.939
p= 10 kg/cm²				
	Gas liquid ratio (sm ³ /sm ³)	Moles of removed gas (moles)	Molar mass of removed gas (g/mol)	Mass of removed gas (kg)
Separator	14.5	612.1	21.47	13.141
Tank	6.3	265.9	27.91	7.422
p= 5 kg/cm²				
	Gas liquid ratio (sm ³ /sm ³)	Moles of removed gas (moles)	Molar mass of removed gas (g/mol)	Mass of removed gas (kg)
Separator	17.5	738.7	22.06	16.296
Tank	3.1	130.9	25.92	3.392
p= 1 kg/cm²				
	Gas liquid ratio (sm ³ /sm ³)	Moles of removed gas (moles)	Molar mass of removed gas (g/mol)	Mass of removed gas (kg)
Separator	22.5	949.8	26.05	24.741

The mass of the stock tank oil is found through the tank density for 1sm³ stock tank oil:

Table 6.69: Mass of stock tank oil at each pressure step.

p (kg/cm²)	Tank density (g/cm³)	Mass of stock tank oil (kg)
14	0.898	898
10	0.898	898
5	0.897	897
1	0.899	899

The moles of the reservoir fluid are equal to:

Table 6.70: Moles of reservoir fluid for the laboratory separator tests.

p (kg/cm²)	Mass of removed gas from separator (kg)	Mass of removed gas from tank (kg)	Mass of stock tank oil (kg)	Mass of reservoir fluid (kg)	Molar mass of reservoir fluid (g/mol)	Mol of reservoir fluid (mol)
14	11.266	9.939	898	919.204	253.2	3,630.3
10	13.141	7.422	898	918.563		3,627.8
5	16.296	3.392	897	916.688		3,620.4
1	24.741		899	923.741		3,648.3

From the number of moles of gas removed at each pressure step, the liquid phase compositions are calculated by material balance.

Table 6.71: Compositions of laboratory separator tests at $p = 5 \text{ kg/cm}^2$.

	Separator gas	Separator liquid	Tank gas	Tank liquid
N₂	0.00	0.00	0.00	0.00
CO₂	7.17	0.65	8.18	0.29
H₂S	1.01	0.13	2.16	0.03
CH₄	78.49	1.49	65.21	-1.54
C₂H₆	5.01	0.42	7.64	0.08
C₃H₈	4.37	4.38	8.89	4.17
iso C₄H₁₀	1.42	2.49	3.14	2.46
nC₄H₁₀	1.41	4.39	3.17	4.45
iso C₅H₁₂	0.58	4.09	1.13	4.23
n C₅H₁₂	0.14	0.55	0.17	0.57
pseudo C₆	0.23	2.25	0.15	2.35
C₇₊	0.17	79.16	0.16	82.91
Molar mass (g/mol)	22.1	312.5	25.9	326.1
Moles	738.7	2,881.7	130.9	2,750.8

The material balance for $p = 5 \text{ kg/cm}^2$ for the separator is presented in the following figure:

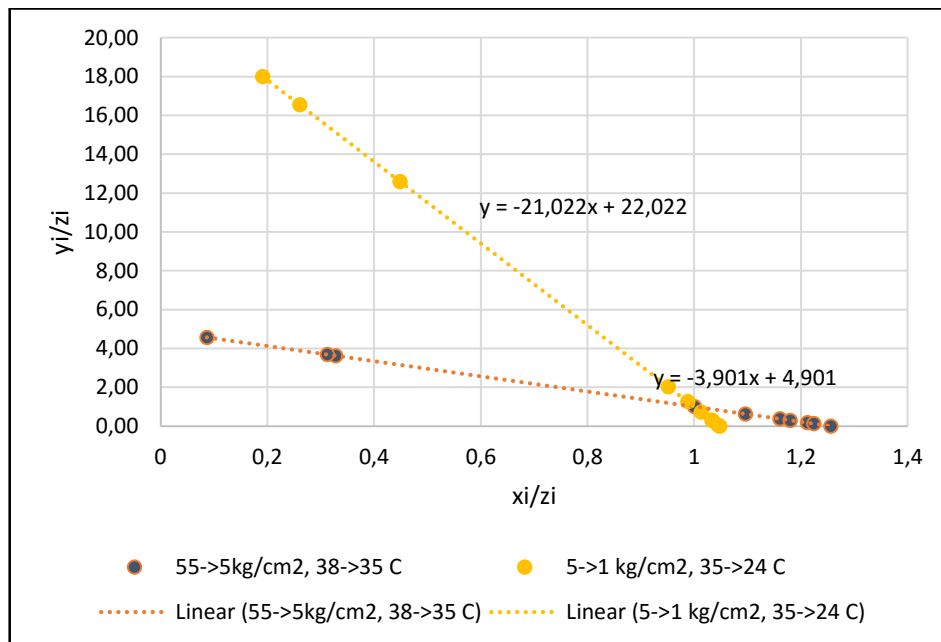


Figure 6.45: Material balance for the separator tests for $p = 5 \text{ kg/cm}^2$.

The optimum pressure for the separator test is selected from Figure 6.46 and is equal to 5 kg/cm^2 .

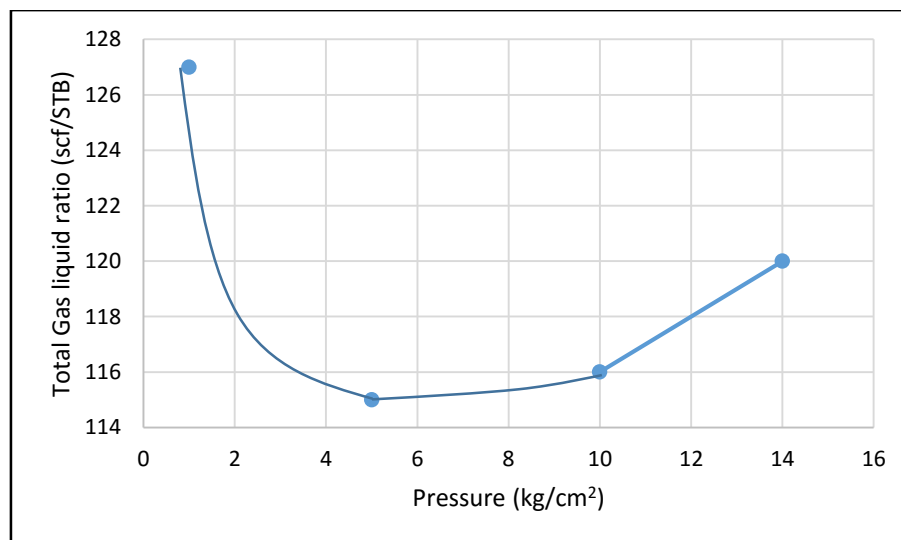


Figure 6.46: Optimization of the separator pressure.

6.4.5 Comparison of differential liberation and laboratory separator test data

The solution GOR and the formation volume factor from the differential liberation test and the optimum separator test are compared in the next Table:

Table 6.72: Comparison of volumetric output from differential liberation and laboratory separator tests.

	R_{sb} (scf/STB)	B_{ob} (barrel/STB)
Laboratory separation	116	1.072
Differential liberation	123	1.079

The differential liberation test exhibits slightly larger value of solution GOR than the laboratory separator test, which is also reflected to the slightly heavier residual oil.

Table 6.73: Comparison of API gravity, density and molar mass between differential liberation and laboratory separator test.

	Residual oil from DV	Stock tank oil from laboratory test
API gravity	26.2	26.2
Density (g/cm³)	0.898	0.897
Molar mass (g/mol)	331.23	326.1

The differential vaporization test gives results on a residual tank basis, so in order to convert it to stock tank oil basis, data from the separator test are used:

Table 6.74: Conversion of differential volumetrics to stock tank oil basis.

Pressure (kg/cm²)	R_{sd} (scf/barrel residual)	R_s (scf/STB)	B_{od} (barrel/barrel residual)	B_o (barrel/STB)
45.7	123	115	1.079	1.072
39.1	108	100	1.074	1.067
31.1	94	86	1.069	1.062
23.8	76	68	1.063	1.056
15.8	55	47	1.055	1.048
8.4	35	27	1.044	1.037
1	0	-7	1.017	1.0104

6.4.6 Viscosity test

Finally, the viscosity of the reservoir fluid versus the pressure is studied.

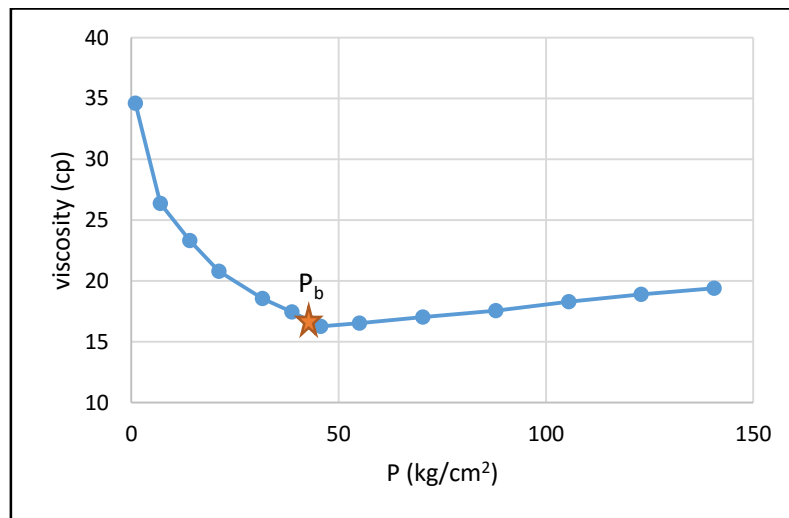


Figure 6.47: Viscosity experiment.

6.4.7 Results for Unknown oil 9

The following Table summarizes the results of the PVT quality control for the Unknown oil 9:

Table 6.75: Summary of the PVT quality control test for Unknown oil 9.

	Comments	Acceptability
Quality control of the recorded samples	Confirmation of the selected samples, thermodynamic consistency of liquid and gas phase, acceptable compositions	Yes
CCE test	Bad agreement of the isothermal compressibility to the line, linearity in the Y function	No
DV	Material balance for each pressure step is satisfied, material balance for each component is not satisfied, negative values of % mol concentration, cross of lines at plot log k_i versus pressure	No / Yes
Laboratory separator tests	Material balance is satisfied, logical values of concentration and molar mass	Yes
Viscosity	Logical values	Yes

6.5 Unknown oil X

The results of the samples for the Unknown oil X are given below.

6.5.1 Quality control of the analyzed samples

For the fluid X, bottom hole samples were taken in order to examine the quality of the oil. The initial reservoir conditions are presented in the following Table:

Table 6.76: Initial reservoir conditions.

Bottom hole temperature (°F)	Initial static pressure (psia)
220	4,030

The following Table depicts all the available information for the samples.

Table 6.77: Subsurface samples for Unknown oil X.

	BHS01	BHS02		
		Flashed liquid	Flashed gas	Monophasic fluid
N ₂ (%mol)	-	0.00	0.47	0.33
CO ₂ (%mol)	-	0.11	5.62	3.94
H ₂ S (%mol)	-	0.05	4.07	2.84
CH ₄ (%mol)	-	0.00	58.76	40.79
C ₂ H ₆ (%mol)	-	0.71	12.28	8.74
C ₃ H ₈ (%mol)	-	2.15	8.65	6.66
iso C ₄ H ₁₀ (%mol)	-	0.95	1.63	1.42
nC ₄ H ₁₀ (%mol)	-	3.08	4.00	3.72
iso C ₅ H ₁₂ (%mol)	-	2.27	1.34	1.62
n C ₅ H ₁₂ (%mol)	-	2.89	1.52	1.94
pseudo C ₆ (%mol)	-	7.62	0.98	3.01
pseudo C ₇ (%mol)	-	10.71	0.63	3.71
pseudo C ₈ (%mol)	-	11.18	0.05	3.45
pseudo C ₉ (%mol)	-	10.20	0.00	3.12
pseudo C ₁₀ (%mol)	-	8.71	0.00	2.66
pseudo C ₁₁ (%mol)	-	6.83	0.00	2.09
pseudo C ₁₂ (%mol)	-	5.31	0.00	1.62
pseudo C ₁₃ (%mol)	-	3.15	0.00	0.96
pseudo C ₁₄ (%mol)	-	2.64	0.00	0.81
pseudo C ₁₅ (%mol)	-	2.84	0.00	0.87
pseudo C ₁₆ (%mol)	-	2.12	0.00	0.65
pseudo C ₁₇ (%mol)	-	1.82	0.00	0.56
pseudo C ₁₈ (%mol)	-	1.58	0.00	0.48
pseudo C ₁₉ (%mol)	-	1.42	0.00	0.43
C ₂₀₊ (%mol)	-	11.66	0.47	3.57
Molar mass (g/mol)	-	165.30	27.79	69.86
Saturation pressure (psia) at 220 °F	3,589	3,637		

There are no available information for the composition and the molar mass of the sample BHS01.

The BHS02 was selected for the complete PVT analysis by the reservoir engineer, so all the PVT tests will be held on it.

6.5.2 CCE test

The CCE test provides the relative volume according to *Table 6.78*:

Table 6.78: CCE data for Unknown oil X.

Pressure (psia)	Relative volume
6,015	0.9539
5,515	0.9618
5,015	0.9707
4,515	0.9799
4,265	0.9852
4,015	0.9908
3,765	0.9967
3,651	0.9997
3,639 = P_b	1.0000
3,535	1.0029
3,498	1.0067
3,460	1.0103
3,385	1.0181
3,260	1.0334
3,011	1.0667
2,679	1.1285
2,237	1.254
1,730	1.5076
1,245	1.9951
829	2.9539

The Y function for the Unknown oil X has curvature at pressures close to the saturation pressure indicating errors in measuring the relative volume:

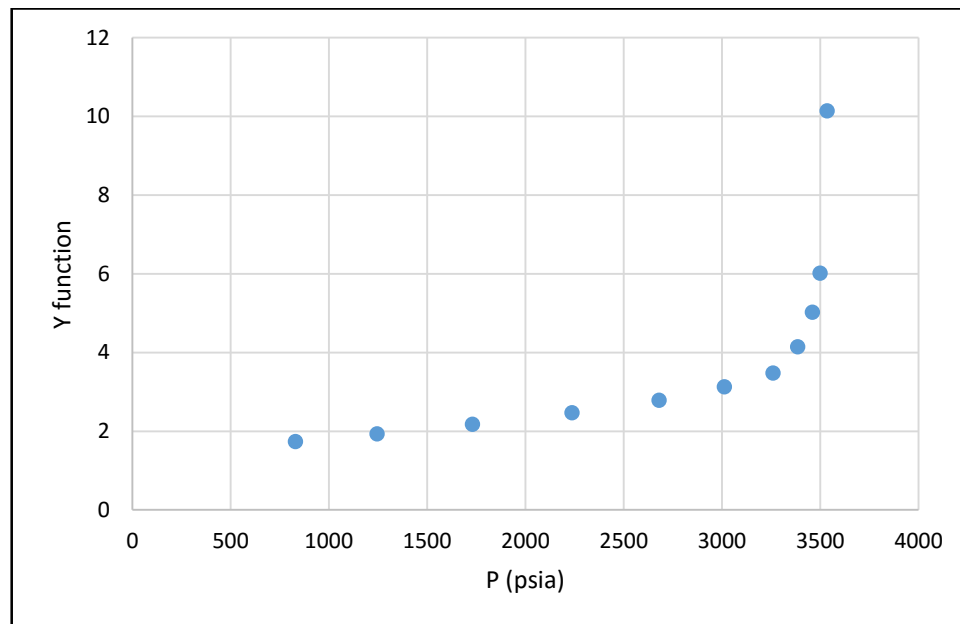


Figure 6.48: Y function.

As far as the oil compressibility is concerned it obeys fairly well a line:

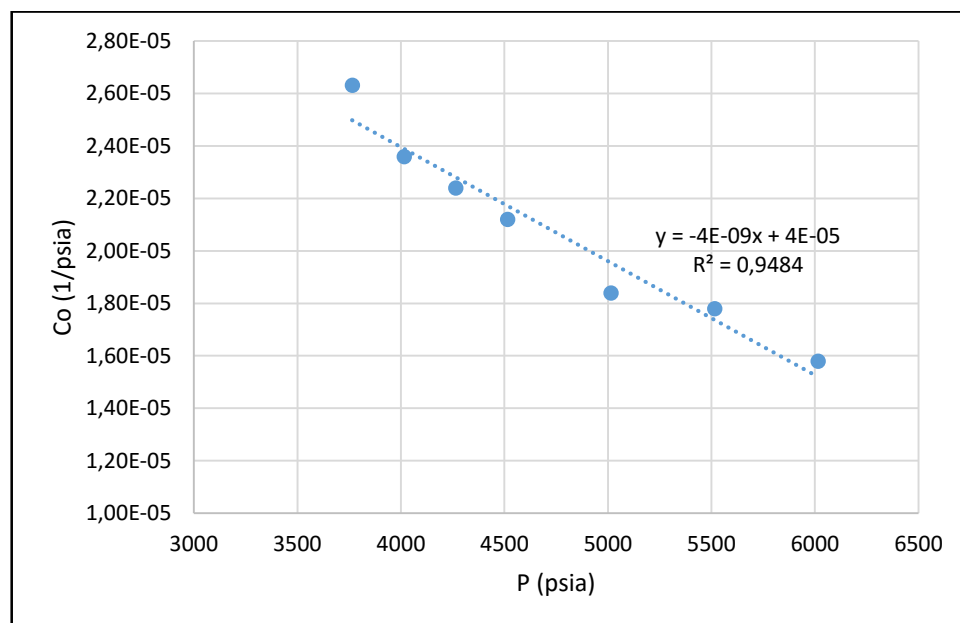


Figure 6.49: Isothermal oil compressibility for pressures above bubble point.

If Figure 6.49 (Unknown oil X) is compared to Figure 6.39 (Unknown oil 9), it is concluded that the Unknown oil X (Figure 6.49) is more compressible and has better linear performance in the plot.

6.5.3 Differential vaporization test

The differential vaporization test was studied by a material balance test. The mass of removed gas at each pressure step is calculated based on the solution GOR (Table 6.79).

Table 6.79: Mass of removed gas at each pressure step at DV for Unknown oil X.

Pressure (psia)	R _s (sm ³ /sm ³)	Moles of gas (moles)	Moles of removed gas	Molar mass of gas (g/mol)	Mass of removed gas (kg)
3,639	287.7	12,144.4			
3,115	241.9	10,211.1	1,933.3	24.17	46.728
2,515	189.1	7,982.3	2,228.8	23.62	52.644
1,815	139	5,867.5	2,114.8	23.68	50.079
1,215	100	4,221.2	1,646.3	24	39.510
615	64.2	2,710.0	1,511.2	26.41	39.910
15	0.0	0.0	2,710.0	45.46	123.197

The calculation of the moles of the bubble point fluid is described in the following Table:

Table 6.80: Mass of residual oil and moles of bubble point fluid.

Residual oil relative density	Mass of residual oil(kg)	Mass of bubble point fluid (kg)	Molar mass of reservoir fluid (g/mol)	Moles of bubble point fluid
0.842	842	1,194.068	69.86	17,092.3

The compositions of the liquid and the gas phase for each pressure are given in the following Tables:

Table 6.81: Gas compositions at different pressure steps.

Pressure (psia)	3,115	2,515	1,815	1,215	615	15
Composition						
N ₂ (%mol)	0.74	0.67	0.61	0.45	0.26	0.10
CO ₂ (%mol)	5.44	5.61	5.95	6.31	6.91	4.22
H ₂ S (%mol)	2.30	2.43	2.72	3.20	4.70	7.62
CH ₄ (%mol)	70.81	71.51	70.46	68.24	58.90	20.84
C ₂ H ₆ (%mol)	9.47	9.62	10.24	11.43	14.68	16.11
C ₃ H ₈ (%mol)	5.20	5.04	5.22	5.77	8.19	17.98
iso C ₄ H ₁₀ (%mol)	0.89	0.82	0.82	0.86	1.22	3.99
nC ₄ H ₁₀ (%mol)	2.04	1.87	1.83	1.88	2.68	10.38
iso C ₅ H ₁₂ (%mol)	0.71	0.61	0.57	0.54	0.75	3.98
n C ₅ H ₁₂ (%mol)	0.83	0.72	0.66	0.60	0.82	4.71
pseudo C ₆ (%mol)	0.71	0.57	0.52	0.41	0.55	4.22
C ₇₊ (%mol)	0.86	0.53	0.40	0.31	0.34	5.85
Molar mass (g/mol)	24.17	23.62	23.68	24.00	26.41	45.46

Table 6.82: Liquid compositions at different pressure steps.

Pressure (psia)						
Composition	3,115	2,515	1,815	1,215	615	15
N₂ (%mol)	0.28	0.21	0.13	0.07	0.04	0.00
CO₂ (%mol)	3.75	3.43	2.93	2.33	1.42	-0.11
H₂S (%mol)	2.91	2.99	3.04	3.02	2.68	-0.02
CH₄ (%mol)	36.96	31.01	23.29	15.22	6.60	-1.20
C₂H₆ (%mol)	8.65	8.48	8.13	7.54	6.13	0.67
C₃H₈ (%mol)	6.85	7.16	7.54	7.85	7.79	2.20
iso C₄H₁₀ (%mol)	1.49	1.60	1.76	1.92	2.05	0.99
nC₄H₁₀ (%mol)	3.93	4.29	4.77	5.29	5.81	3.30
iso C₅H₁₂ (%mol)	1.74	1.93	2.20	2.49	2.84	2.21
n C₅H₁₂ (%mol)	2.08	2.32	2.64	3.01	3.44	2.74
pseudo C₆ (%mol)	3.30	3.77	4.41	5.13	6.03	7.03
C₇₊ (%mol)	28.06	32.80	39.14	46.11	55.14	82.13
Molar mass (g/mol)	75.69	84.66	96.59	109.62	126.04	170.17

Negative compositions are a sign that the gas chromatograph was not very sensitive and the mol composition of the gas phase encloses errors.

The plot of k values at each pressure step and per component is constructed and the results are presented in the following figure. It must be pointed out that due to negative compositions of some components, the k values of them are not depicted in the Figure:

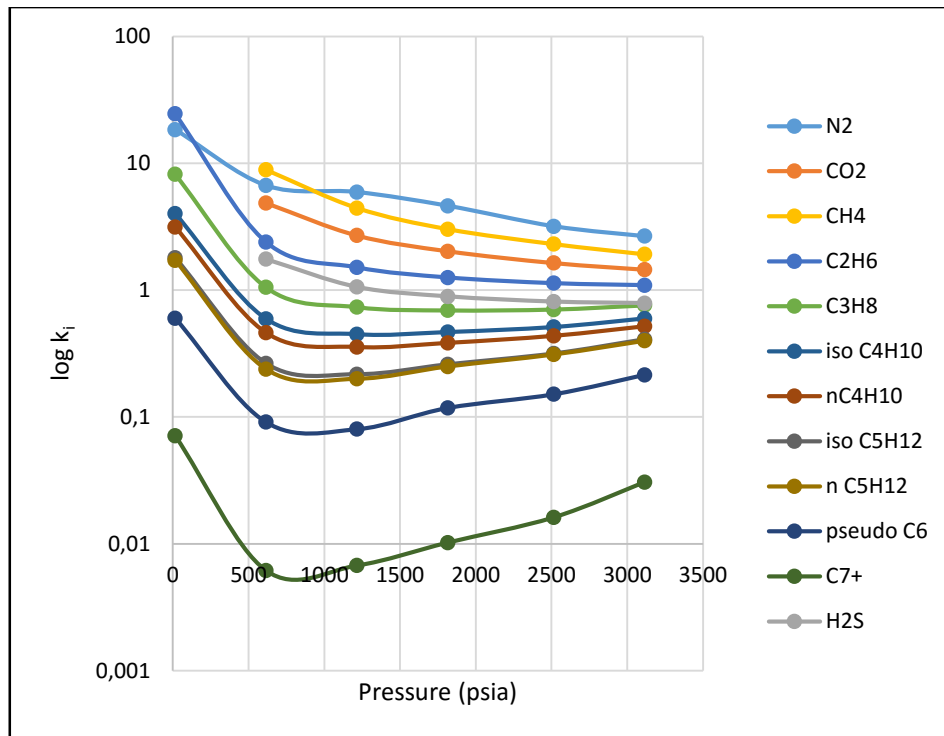


Figure 6.50: Semi logarithmic plot of k versus pressure for each component at DV test.

The nitrogen cross the lines of methane and ethane, indicating non thermodynamic consistency of the phases during the experimentation.

In the following figures the compositions of the gas and liquid phase for all the pressure steps are presented.

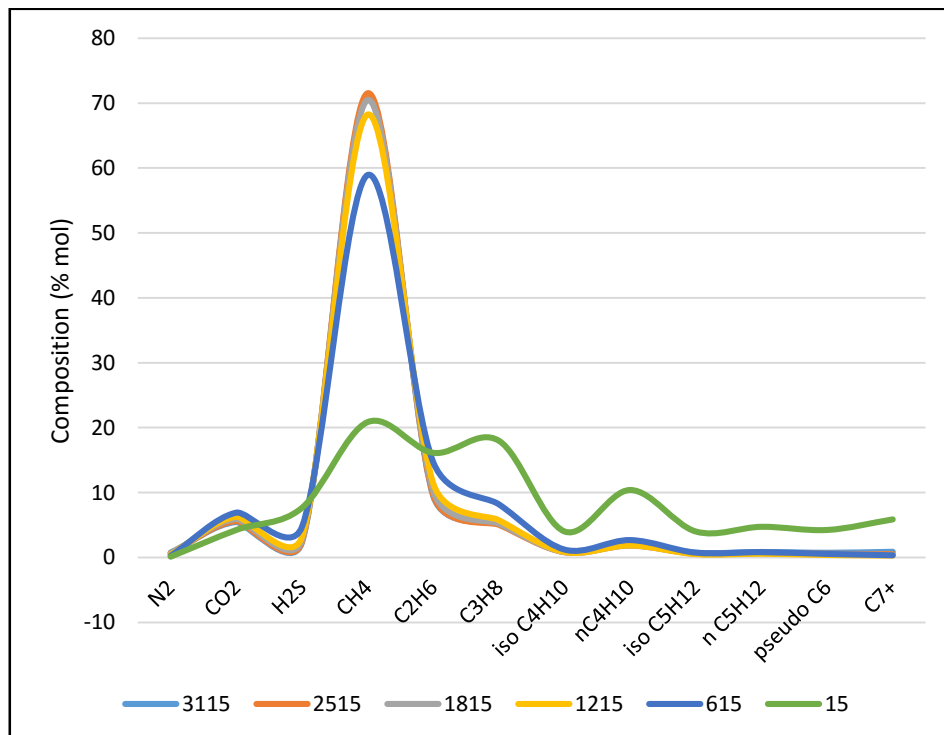


Figure 6.51: DV gas compositions for all the components and pressure steps.

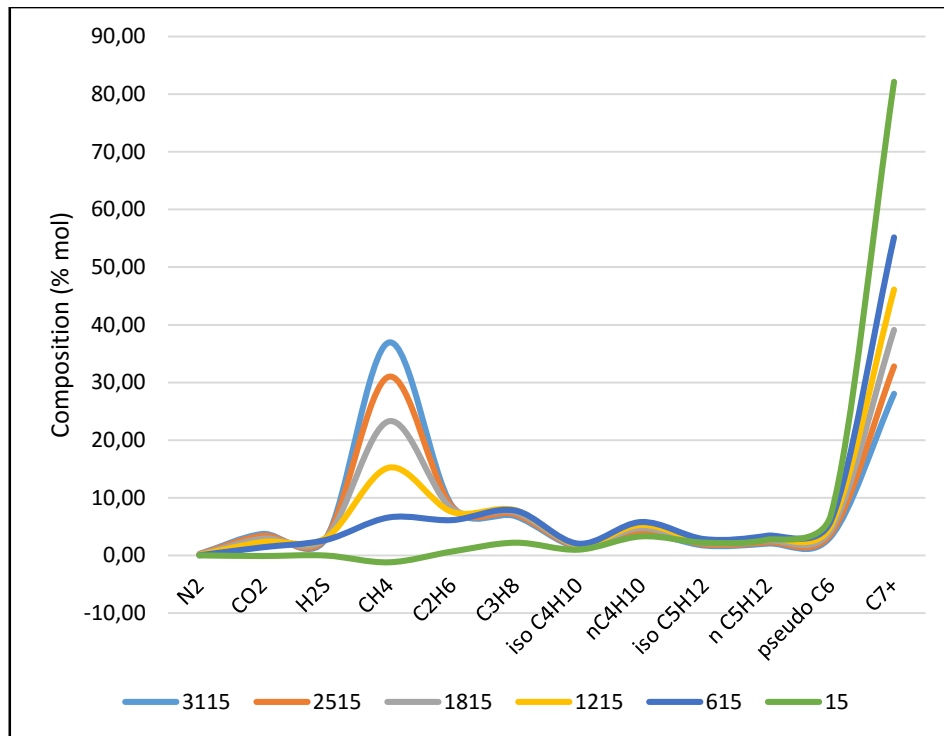


Figure 6.52: DV liquid compositions for all the components and pressure steps.

The DV gas and liquid compositions have similar distributions for all the pressures except from $p = 15$ psia.

The plots of the material balance at each pressure step for the Unknown oil X DV data are:

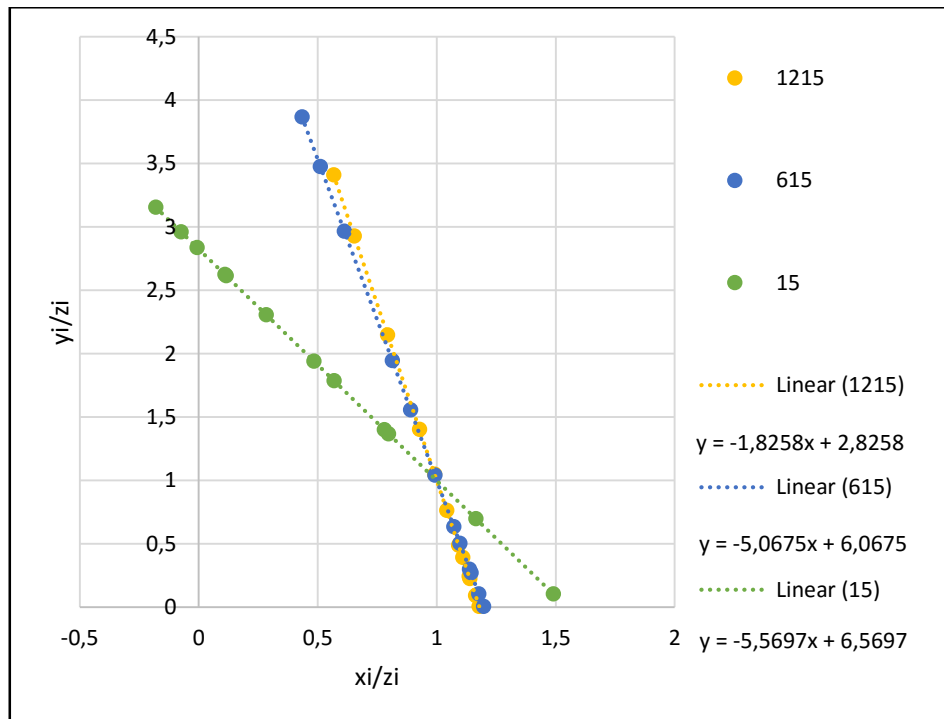


Figure 6.53: Material balance at each pressure step for the DV test.

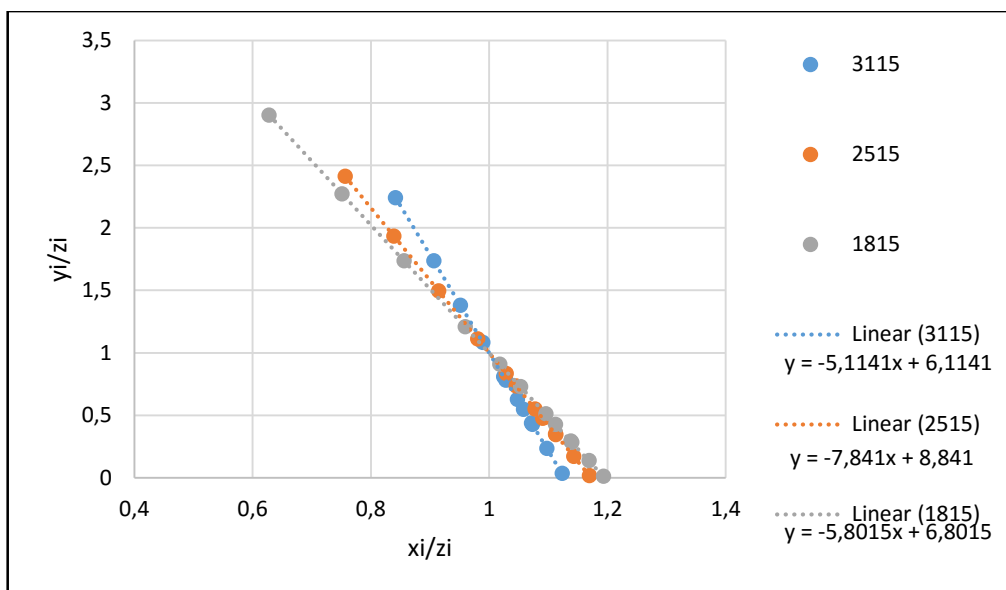


Figure 6.53: Material balance for each pressure step at DV test.

The material balance for each component:

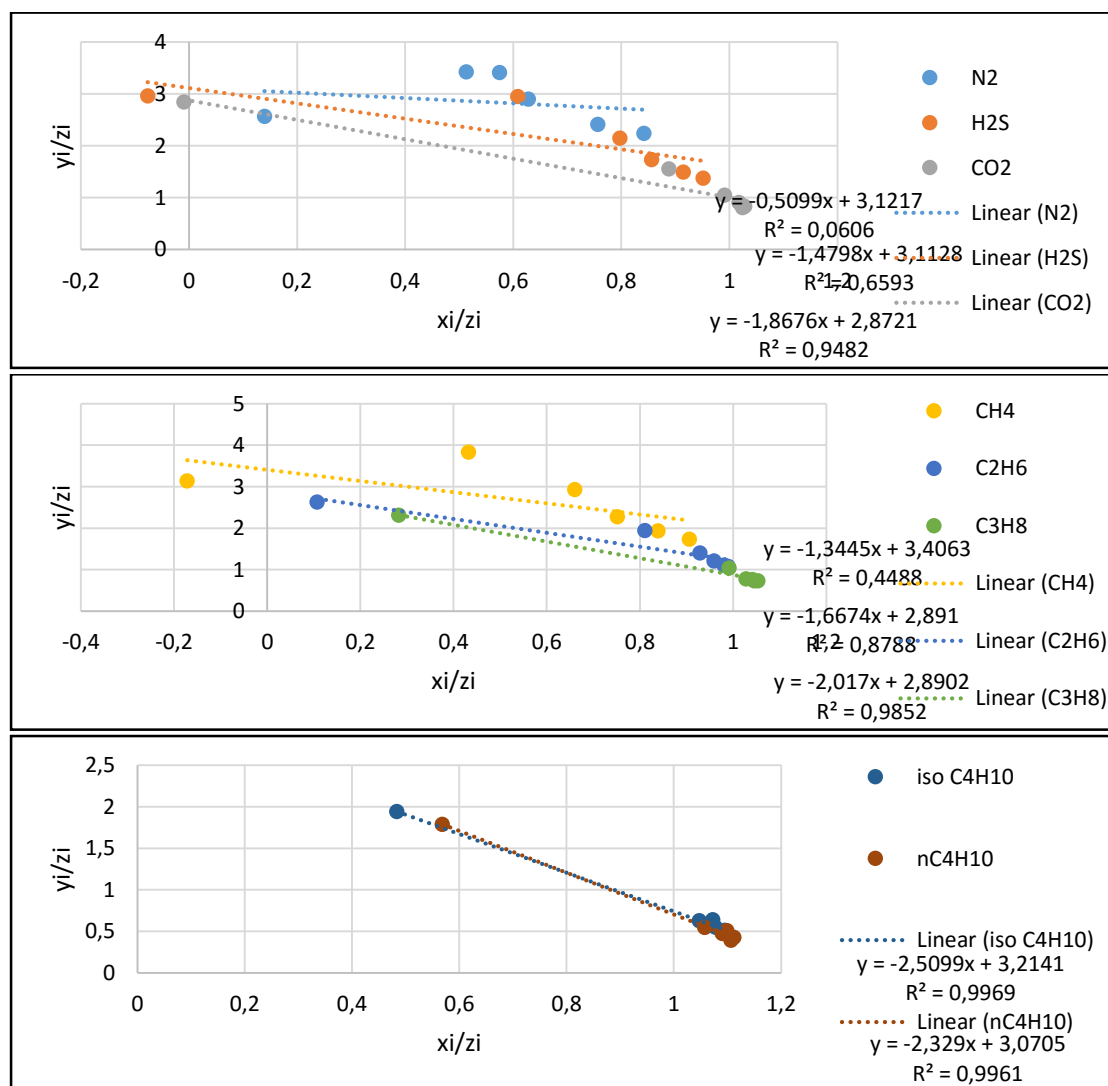


Figure 6.54: Material balance for each component at DV test.

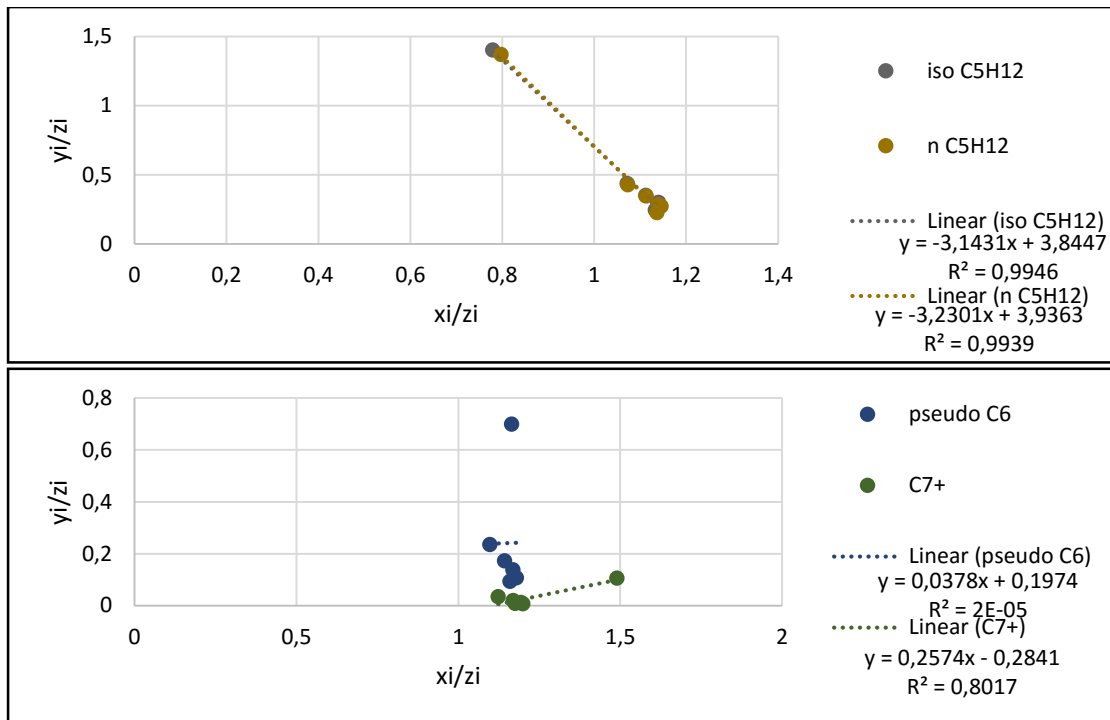


Figure 6.54: Material balance for each component at DV test.

Problems with the squared correlation coefficient have the nitrogen, hydrogen sulfide, methane and ethane while slope problem occurred for pseudo C₆ and the heavy end.

Finally, the calculated composition and the molar mass of the residual oil are compared to the stock tank oil ones.

Table 6.83: Comparison of the back calculated residual oil and the measured stock tank oil compositions.

Composition	Residual oil from DV	Stock tank oil
N ₂ (%mol)	0.00	0.00
CO ₂ (%mol)	-0.11	0.11
H ₂ S (%mol)	-0.02	0.05
CH ₄ (%mol)	-1.20	0.00
C ₂ H ₆ (%mol)	0.67	0.71
C ₃ H ₈ (%mol)	2.20	2.15
iso C ₄ H ₁₀ (%mol)	0.99	0.95
nC ₄ H ₁₀ (%mol)	3.30	3.08
iso C ₅ H ₁₂ (%mol)	2.21	2.27
n C ₅ H ₁₂ (%mol)	2.74	2.89
pseudo C ₆ (%mol)	7.03	7.62
C ₇₊ (%mol)	82.13	80.17
Molar mass (g/mol)	170.17	165.30

The DV data lead to slightly heavier residual oil than the stock tank oil. It is worth mentioning that all the components of the residual oil from DV test and the stock tank oil have similar % mol composition, except from CH₄.

6.5.4 Laboratory multistage separator test

Material balance is also held for the multistage separator test. In more details, the mass of removed gas at each pressure step is calculated according to the Gas liquid ratio.

Table 6.84: Mass of removed gas at each pressure step for the laboratory multistage separator test.

p=915 psia				
	Gas liquid ratio (sm ³ /sm ³)	Moles of removed gas (moles)	Molar mass of removed gas (g/mol)	Mass of removed gas (kg)
Separator	147	6,205.1	21.48	133.287
p=265 psia				
	Gas liquid ratio (sm ³ /sm ³)	Moles of removed gas (moles)	Molar mass of removed gas (g/mol)	Mass of removed gas (kg)
Separator	42.5	1,794.0	24.19	43.397
p=55 psia				
	Gas liquid ratio (sm ³ /sm ³)	Moles of removed gas (moles)	Molar mass of removed gas (g/mol)	Mass of removed gas (kg)
Separator	23.3	983.5	32.33	31.798
p=15 psia				
	Gas liquid ratio (sm ³ /sm ³)	Moles of removed gas (moles)	Molar mass of removed gas (g/mol)	Mass of removed gas (kg)
Tank	14.4	607.9	39.73	24.150

The calculation of the moles of the reservoir fluid is described in the following Table:

Table 6.85: Mol of reservoir fluid.

Tank density (g/cm³)	Mass of stock tank oil (kg)	Mass of removed gas (kg)	Mass of reservoir fluid (kg)	Molar mass of reservoir fluid (g/mol)	Mol of reservoir fluid (mol)
0.809	809	232.631	1,041.631	69.86	14,910.3

From the number of moles of gas removed at each step, the liquid phase compositions and the molar ratios of each phase are calculated at each pressure step by material balance. The liquid and gas compositions for each pressure step are given in the following Tables.

Table 6.86: Compositions of laboratory separator tests for the gaseous phase.

	915 psia	265psia	55psia	15psia
N ₂	0.64	0.37	0.25	0.13
CO ₂	5.88	7.53	7.36	4.16
CH ₄	2.71	4.58	10.06	13.04
C ₂ H ₆	75.94	63.26	30.19	8.03
C ₃ H ₈	9.26	15.16	26.35	27.13
iso C ₄ H ₁₀	3.67	6.37	17.59	30.23
nC ₄ H ₁₀	0.45	0.72	2.22	4.59
iso C ₅ H ₁₂	0.90	1.36	4.18	8.97
n C ₅ H ₁₂	0.21	0.27	0.78	1.73
pseudo C ₆	0.22	0.27	0.71	1.49
C ₇₊	0.11	0.10	0.29	0.47
Molar mass (g/mol)	0.01	0.01	0.02	0.03
Moles	21.48	24.19	32.33	39.73

Table 6.87: Compositions of laboratory separator tests for the liquid phase.

	915 psia	265psia	55psia	15psia
N ₂	0.11	0.04	0.01	0.00
CO ₂	2.70	1.51	0.59	0.20
CH ₄	3.14	2.78	1.63	0.40
C ₂ H ₆	16.81	5.23	1.35	0.60
C ₃ H ₈	8.59	6.96	3.91	1.40
iso C ₄ H ₁₀	8.59	9.15	7.82	5.40
nC ₄ H ₁₀	2.01	2.33	2.34	2.10
iso C ₅ H ₁₂	5.45	6.47	6.83	6.60
n C ₅ H ₁₂	2.50	3.06	3.42	3.60
pseudo C ₆	3.07	3.77	4.25	4.55
C ₇₊	4.58	5.69	6.54	7.20
Molar mass (g/mol)	42.45	53.01	61.31	67.95
Moles	102.82	122.36	136.51	146.96

The evolution of the liquid and gas compositions at the multistage separation test is presented in the following figures (as 1: first stage, 2: 2nd stage, 3: 3rd stage):

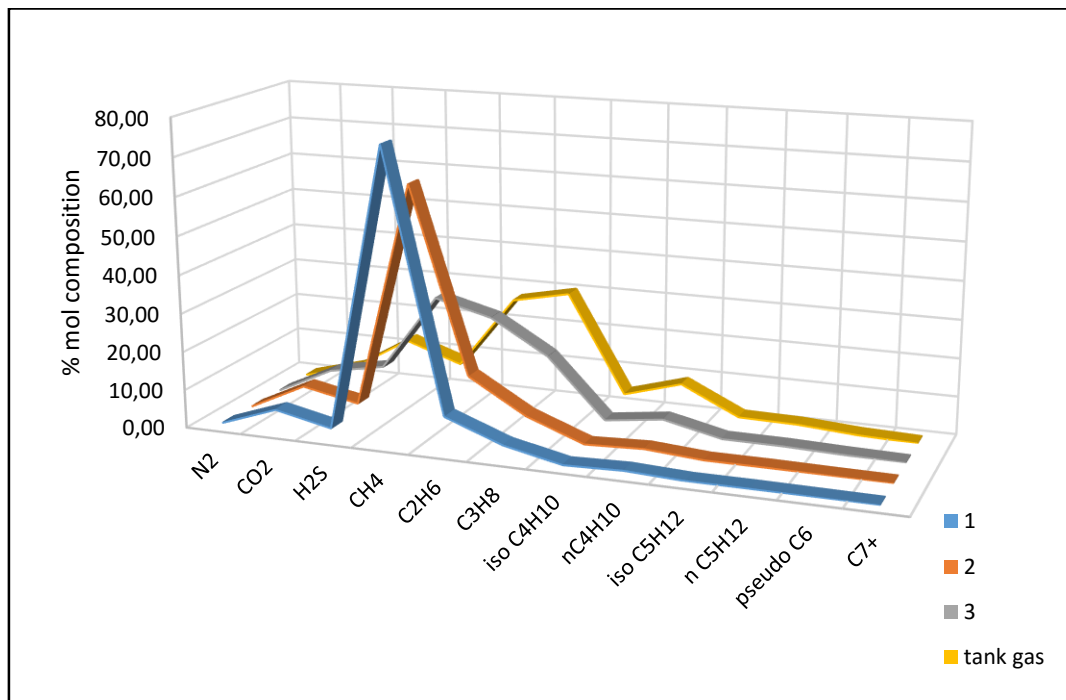


Figure 6.55: Gas compositions for the multistage separator experiment.

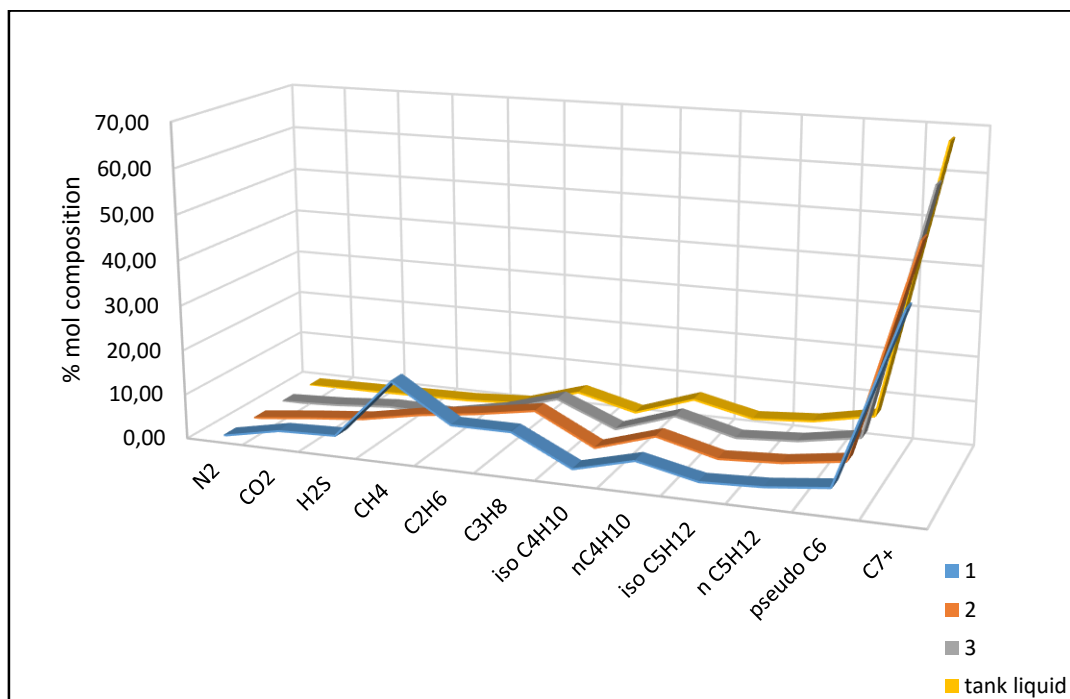


Figure 6.56: Liquid compositions for the multistage separator experiment.

The shape of the distributions was expected.

The material balance for each component for the laboratory multistage separator test:

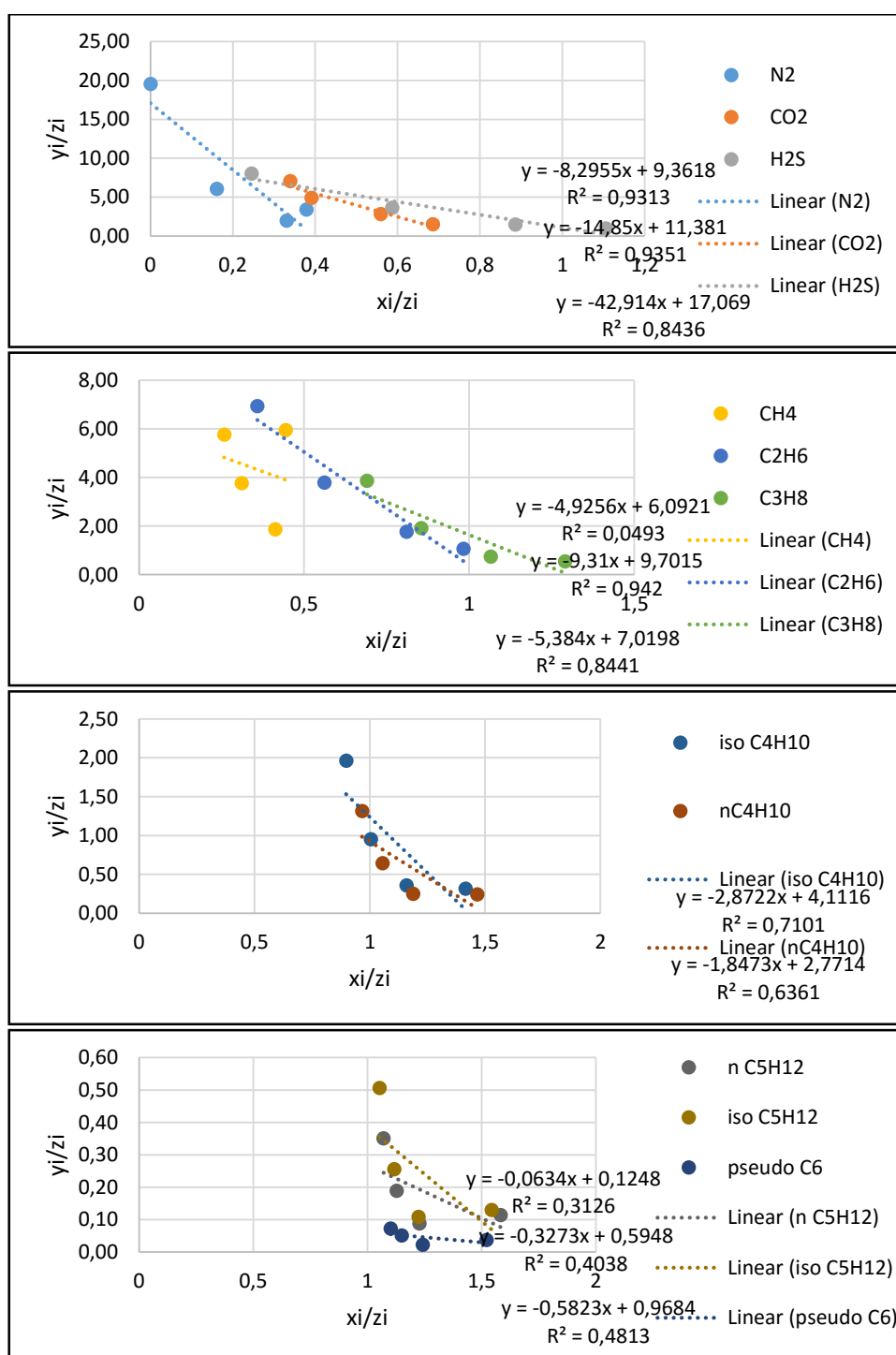


Figure 6.57: Material balance for each component for the laboratory multistage separator test.

Some of the components do not satisfy the mass balance as either the slope or the R^2 does not have the expected behavior.

6.5.5 Comparison of differential liberation and laboratory multistage separator test data

In Table 6.88 the differential liberation test results to heavier residual oil than the multistage laboratory separator test.

Table 6.88: Comparison of density and molar mass between differential liberation and laboratory multistage separator test.

	Residual oil from DV	Stock tank oil from laboratory test
API gravity	36.7	41.2
Density (g/cm ³)	0.842	0.819
Molar mass (g/mol)	170.17	146.96

6.5.6 Viscosity test

Finally, the viscosity of the reservoir fluid versus the pressure is studied.

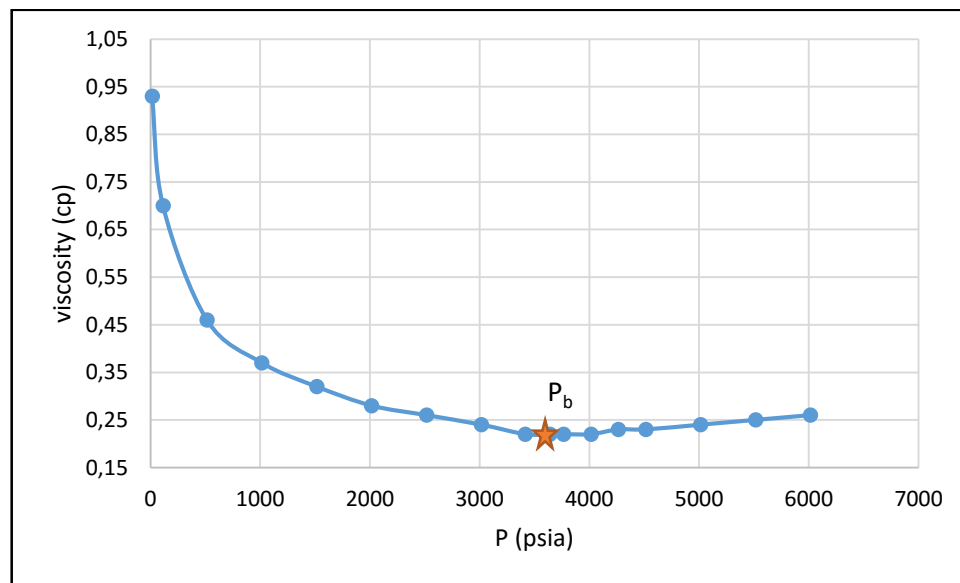


Figure 6.58: Viscosity experiment.

The behavior of the viscosity is right.

6.5.7 Results for Unknown oil X

The Unknown oil X PVT report has shown some problems.

Table 6.89: Summary of the PVT quality control test for Unknown oil X.

	Comments	Acceptability
Quality control of the recorded samples	Lack of data for the evaluation of samples, acceptable composition	Yes / No
CCE test	Linearity for isothermal oil compressibility, curved Y function	Yes / No
DV	Material balance for each pressure step is satisfied, material balance for each component is not satisfied, negative values of % mol composition, cross of lines at plot $\log k_i$ versus pressure	No / Yes
Laboratory multistage separator test	Material balance for each component is not satisfied, logical values of concentration and molar mass	Yes / No
Viscosity	Logical values	Yes

7. Conclusions

In order to obtain trustworthy PVT fluid properties, the quality of the samples must be examined carefully. The most fundamental error occurs when the fluid sample that is being studied is not representative of the fluid in the reservoir. Although thorough sample checking procedures can identify some of the most obvious problems, there is never absolute certainty that the fluid under study is truly representative of the reservoir fluid. On occasions, laboratory measurements can show that a fluid is definitely not representative. As a result the fluid must be tested both in the field and in the laboratory and check all the PVT properties.

When the representativity of the analyzed separator samples is studied at the laboratory, the following procedure is used. The liquid separator samples are evaluated from the comparison of the bubble point pressure to the separator pressure and the content of water, mud and sediments. The preferred liquid sample should contain only hydrocarbons and have the minimum difference of bubble point pressure to the separator pressure among the other liquid samples. On the other hand, the preferred gas separator sample must have opening pressure close to the separator pressure and do not contain air and carry over. If compositional analysis of the gas separator samples is performed, each gas sample is compared to the others in order to find abnormalities on the composition and the molar mass. For example, the PVT laboratory analysis of Tunisian oil 1 analyzes separator samples. The gas sample that is selected has similar composition distribution with the other gas samples, but closer opening pressure to the separator pressure. Furthermore it does not contain air, liquid hydrocarbons, water, mud and sediments, indications that the separator was working successfully and the used sampling procedure was held correctly. On the other hand the preferred liquid sample has bubble point pressure close to the separator pressure and does not contain water, mud and sediments. The analysis of the Congo oil exhibits uncertainties for the selected samples and the sampling procedure followed, since the resulted recombined fluid had higher bubble point than the initial reservoir pressure at reservoir temperature. It was a discrepancy that was solved by flashing the recombined fluid to the initial static pressure and liberating the equilibrium gas.

Then, the preferred gas and liquid separator samples are examined for their thermodynamic consistency through the Hoffman and Buckley plot. All the analyzed PVT analysis showed the anticipated behavior; linearity in the Hoffman plot and a negative slope in the Buckley plot. It is worth mentioning that for all oils with the exception of the Congo one, not only the hydrocarbons were lying on the line in the Hoffman plot, but the non hydrocarbon ones were also very close to that line.

The reservoir fluid composition is given by the mathematical recombination of the flashed phases compositions using the molar ratios obtained from the corrected value of solution GOR. There were some cases (Tunisian oil 2, Congo oil, Unknown oil 9) that the corrected GORs had exactly the same value as the field values, indication thus that the field measurements were very accurate.

In the case that bottom hole samples are analyzed at the PVT lab for their representativity, then the bubble point pressure of the sample is compared to the bubble point pressure resulted from CCE test. Bottom hole samples were recorded only for the case of Unknown oil X. Nevertheless limited information for the composition and the molar mass of the samples were given, so the selection procedure cannot be evaluated.

The validation process of the PVT properties presented in a PVT report is based on mass balance equations and behavior of some properties (viscosity, molar mass, density), in order to enhance the credibility of the measurements. High quality, accurate PVT data can reduce uncertainty in reservoir fluid properties values and provide a sound foundation for reservoir engineering studies. On the other hand, poor quality of PVT data might affect fluid characterization and the accuracy of equation of state modelling. In the following paragraphs, a summary for each PVT test is given.

The CCE test was found for most of the PVT reports checked to be rather satisfying. The general behavior at the recorded relative volume is as oil becomes less compressible then it has smaller changes than a more compressible oil for the same pressure step. The Y function exhibited linear relationship with pressure for the Tunisian oils and for the Unknown oil 9 while erratic behavior was observed around the bubble point pressure for the Congo oil due to possible measurement errors. The Y function for the Unknown oil X was very curved near the bubble point pressure due to errors at the recorded relative volume. The plot of isothermal oil compressibility versus pressure most of the times was found to satisfy the anticipated behavior since the points lied on the line rather nicely. Nevertheless, a small error in relative volume leads to big deviation of the derivative of the volume, so the isothermal oil compressibility could deviate from linearity with pressure. The Unknown oil 9 exhibits bad relationship of isothermal oil compressibility to pressure since the point didn't lie on the line very well. The recorded relative volumes of Unknown oil 9 are close to unity and lead to very low values of isothermal oil compressibility ($7.3 \cdot 10^{-5} - 8.6 \cdot 10^{-5} \text{ 1/ kg/cm}^2$).

All the given PVT analysis reports were found to be sensitive to errors at the compositional analysis of the liberated gas during the DV test. Nevertheless, the errors at the % mol composition of the residual oil are not very significant since the B_o , B_g and R_s are the most important values for reservoir engineering applications. Negative compositions and compositions adding up to over 100% are indications of errors that had occurred during the DV study experimentation. The calculated composition of the residual oil for each PVT analysis report when compared to the recorded composition of the stock tank oil, showed that the biggest errors occurred for the lightest components (non hydrocarbons and light hydrocarbons). Such results are attributed to the overestimation of the light components in the gaseous phase during gas chromatography. Also, the gas chromatograph might have failed to trace the heavy compounds in the liberated gas during DV, so perhaps, a cold trap would help to avoid this situation. Nevertheless, this method is expensive and demands large volume of reservoir fluid sample.

The behavior of the residual oil's molar mass from the DV test for all the analyzed PVT lab reports except from the one for the Congo oil is the expected one; larger than the stock tank oil one. The smaller molar mass of the residual oil coming from Congo is unreasonable.

The DV study was also evaluated for its quality through plots:

- The plot of the logarithmic k value per component versus pressure exhibited non physically sound behavior for the Congo oil and the Unknown ones due to crossing of the equilibrium constants curves for some components. The crossing is indication of thermodynamic inconsistency of the phases during DV experimentation.
- The plot of the (liquid and gas) compositions versus pressure for all the analyzed oils showed discrepancies for some components. In more details, the composition for some components had anomalies during the pressure steps, indicating errors.
- The material balance at each pressure step for the DV test for all the analyzed PVT analysis reports were found to be satisfactory as far as the points were perfectly lying on a line at the x_i/z_i versus y_i/z_i plot. So, the material balance at each pressure step was held correctly.
- The material balance per component was never satisfied for the analyzed PVT reports. Some components at the plot x_i/z_i versus y_i/z_i exhibited either wrong slope (positive) or the squared correlation coefficient was far away from unity.

Generally it is believed that the reported molar mass values of the liberated gas phase during the DV experimentation are lower than the real ones, so the molar mass of the calculated residual oil appears to be larger. It is recommended for future work, to use only moles in the material balance for the DV test. For that reason the molar mass of the residual oil should be given or found through simulation, in order to calculate the moles of the residual oil that correspond to 1 m³ residual oil. Then, the computed moles of the liberated gas phase would be added to the moles of the residual oil in order to obtain the moles of the bubble point fluid. In that way, the conversion of the moles of liberated gas to mass would not be needed (elimination of the enclosed errors in the reported molar mass of the gas phase), as also the conversion of the mass of the bubble point fluid to moles (no use of the molar mass of the reservoir fluid).

The laboratory separator tests exhibited also problems on the calculation of the composition of the stock tank oil through material balance since the reported gas phase compositions lead to negative values of the stock tank oil's composition. The errors are attributed to gas chromatography.

The viscosity test was always satisfactory since the plot of the viscosity of the reservoir fluid versus pressure showed the anticipated behavior. For pressures lower than the saturation pressure, the viscosity of the oil increased as pressure decreased due to the evaporation of the volatile components, while for $p > P_b$ the viscosity increased almost linearly as pressure increased.

Also, a comparison between the residual oil from DV test and the stock tank oil from laboratory separator tests was accomplished. The differential liberation test exhibits higher value of solution GOR at bubble point pressure than the laboratory separator tests due to the temperature regime and therefore the higher quantity of gas released. Moreover, the DV test leads to heavier residual oil than the stock tank oil from the laboratory separator tests since it exhibits higher molar mass, higher density and lower API gravity.

Finally, it is recommended to study the use of correlations for black oils, in order to compare the reported properties and volumetric values to the predicted from correlation ones. Last but not least, a very useful tool would be a regression model such as the Artificial Neural Network (ANN) model. ANN provides a rapid technique to predict the desired properties for the specific oil with high accuracy if the data to be trained are well defined. An ANN model cannot replace the lab PVT tests, but it can save money and time.

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