SOLID PRECIPITATION IN VOLATILE OILS UNDER GAS INJECTION

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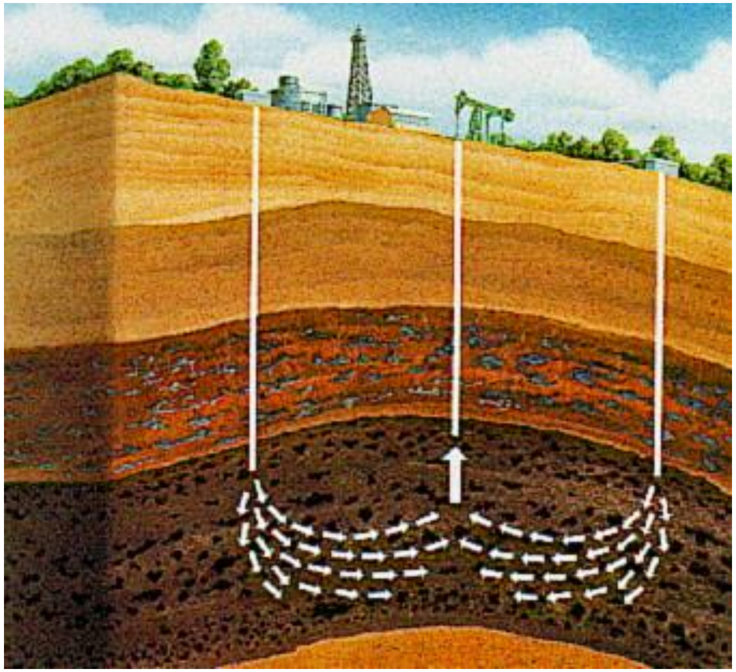
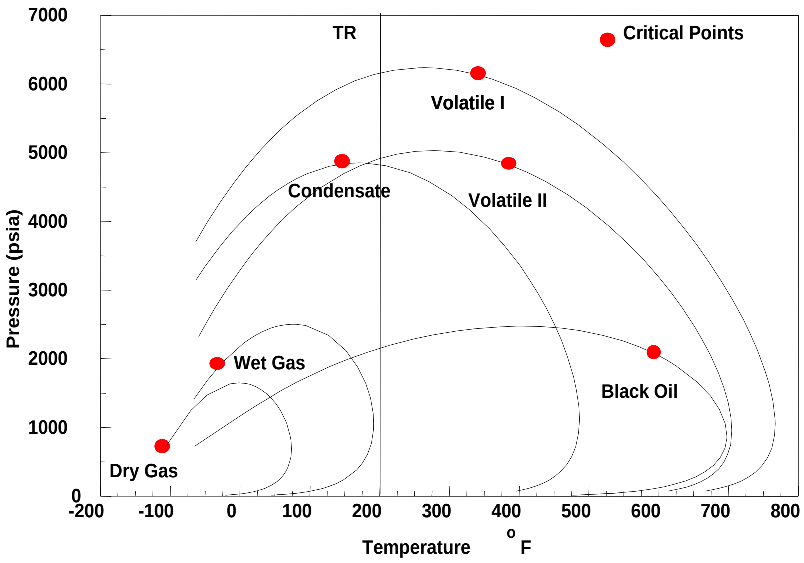
Introduction



The Volatile field of this study presents different reservoir pressures, fluid properties and contacts. The combined geologic and thermodynamic conditions (i.e. deep, high temperature and high pressure, and a continuous hydrocarbon column) imply complex reservoir fluid phase behavior and PVT properties. Gas displacement appears to be a very promising enhanced oil recovery technique for these reservoirs.

Introduction

This study discusses results of a laboratory investigation, including pressure/ volume/ temperature - PVT studies, swelling and SDS experiments and thermodynamic modeling, for assessing the suitability and efficiency of three injection gases for this volatile-oil recovery. The gases investigated were : injection with separator gas , with a synthetic gas mix with 50% of CO_2 and 50% of separator gas and pure CO_2.



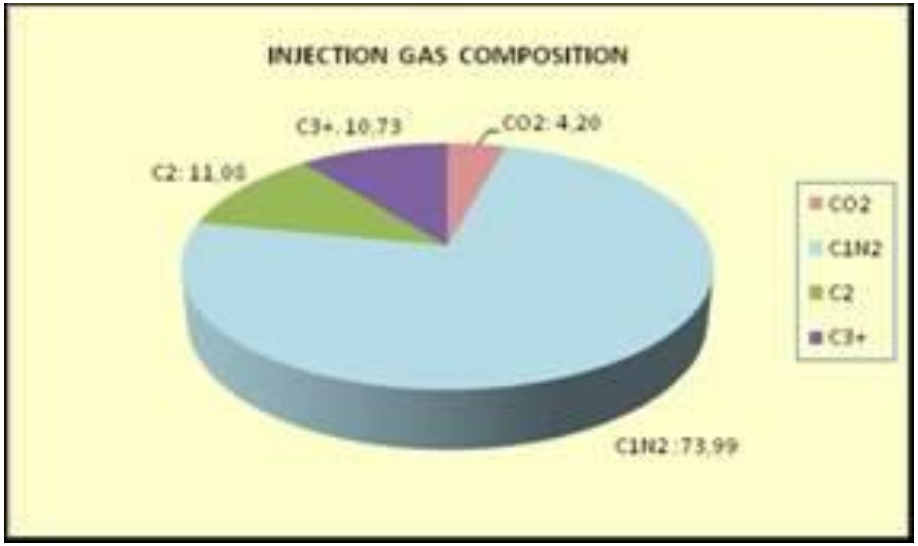
A volatile-oil of ~38° API gravity was collected for the experimental study

The Field and the Hydrocarbon System.

GENERAL DATA OF THE FLUID	
Reservoir Pressure:	6000 Psia
Reservoir Temperature:	260ªF
Perforated Interval:	14320 - 14780 ft
Field GOR:	**1920** scf/stb
Bubble Point Pressure:	4472 Psia
Density @ Pres:	0.5736 gr/cc
Fluid Type:	**Volatile**

Source: Ecopetrol S.A.

GENERAL DATA OF THE FLUID



Separator gas composition is defined by the following percentage amounts :

74% C_1N_2,

1.3% C_2,

4.8% CO_2

19.9% C_3+.

Total balance of the field indicates an availability of 2.5 bfc/d separator gas approximately, so 120 MMscf/d of CO_2 could be get initially to be injected in the field.

Source: Ecopetrol S.A.

GENERAL DATA

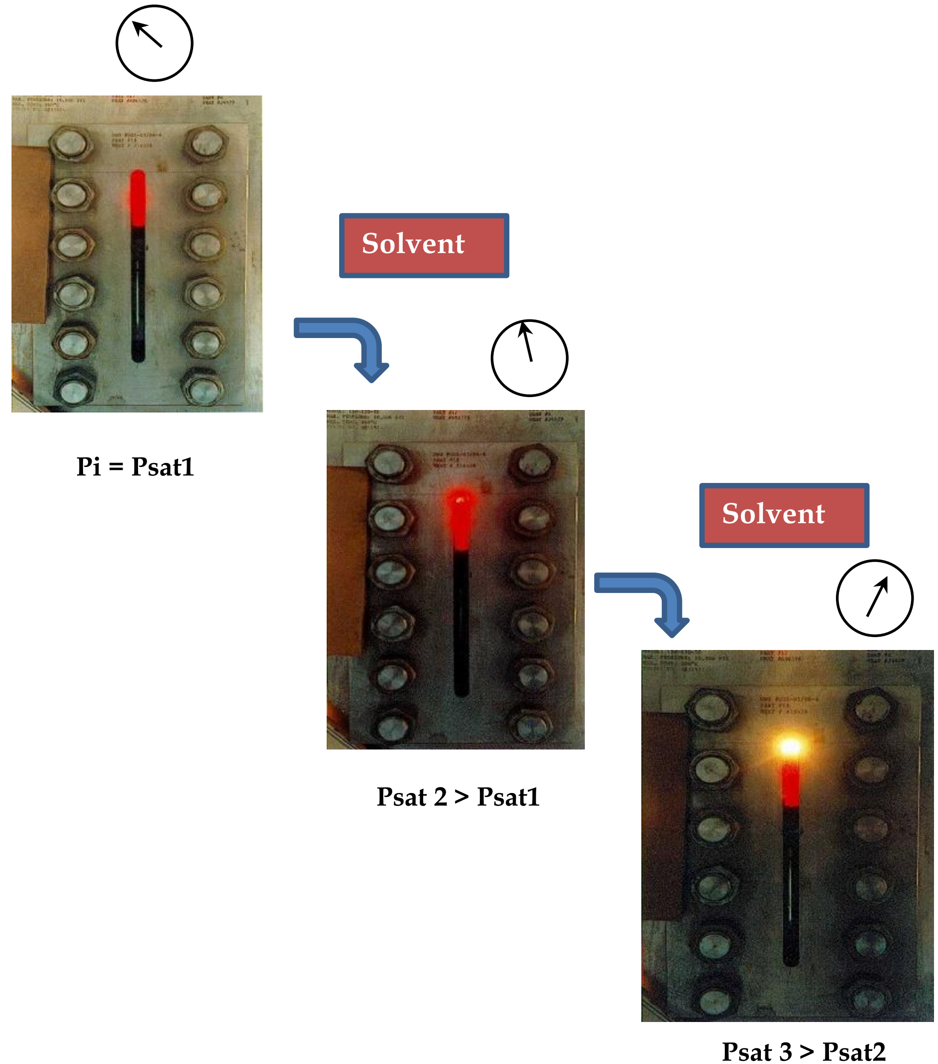
Several tests were conducted in those samples including basic and special experiments such as:

- ✓ Constant composition expansion (CCE)
- ✓ Constant volume expansion (CVD)
- ✓ Multistage separator
- ✓ Viscosity
- ✓ Swelling (SWL) Studies
- ✓ Minimum Miscibility Pressure (MMP)
- ✓ SDS Experiments
- ✓ SARA Analysis

EXPERIMENTAL PROCEDURES

Swelling Test

This test was performed in the DBR – JEFRI Phase Behavior Cell which includes a Solid Detection System with the objective to determine the behavior of the reservoir fluid to the addition of measured incremental volumes (molar%) of a solvent .



Source: Ecopetrol S.A.

Recombined Reservoir Fluid Composition

Components	Mol % Measured	wt % Measured
Nitrogen	0,2301	0,0961
Carbon Dioxide	4,1423	2,7178
Methane	50,2042	12,0053
Ethane	9,1595	4,1061
Propane	6,5544	4,3092
Butane	4,5957	3,9820
Pentane	2,5425	2,7348
Hexanes	1,7814	2,2309

PROPERTIES OF HEAVY FRACTIONS OF MEASURED SAMPLE

Plus Fraction	Mol %	wt %
C7 +	20,790	67,818
C10+	14,429	57,655
C20+	5,941	33,916
C30+	1,860	16,084

Source: Ecopetrol S.A.

EXPERIMENTAL ANALYSYS

Solvent Gas Composition

Cylinder I.D. At Temperature (°F)	A00123 68	A00124 68	A00125 68
Components	**(Mol %)**	**(Mol %)**	**(Mol %)**
Nitrogen	0,37	0,27	
Carbon Dioxide	4,20	48,32	100,00
Methane	73,56	41,43	
Ethane	11,10	5,66	
Propane	5,95	2,70	
Butanes	3,11	1,17	
Pentanes	0,99	0,31	
Hexanes	0,32	0,08	
Heptanes	0,40	0,05	

Source: Cupiagua South .
Ecopetrol S.A. – BP Colombia

EXPERIMENTAL ANALYSYS

Swelling Study Summary with Separator gas injection Case

Swelling Step % Molar	*Type of* Fluid	*Saturation* Pressure	*Swelling Fact*
Original Fluid			1,0000
First Stage (10%)	Bubble	4732	1,0740
Second stage (20%)	Bubble	4882	1,1617
Third stage (30%)	Bubble	5112	1,2693
Fourth stage (35%)	Bubble	5258	1,3505
Fifth Stage (40%)	Dew	5387	1,4068
Sixth Stage (50%)	Dew	6021	1,5956
Seventh Stage (60%)	Dew	6831	1,8868
Eighth stage (70%)	Dew	7588	2,3829

Source: Cupiagua South - Ecopetrol S.A.

SWELLING TEST

Swelling Study Summary with 50% CO_2 injection Case

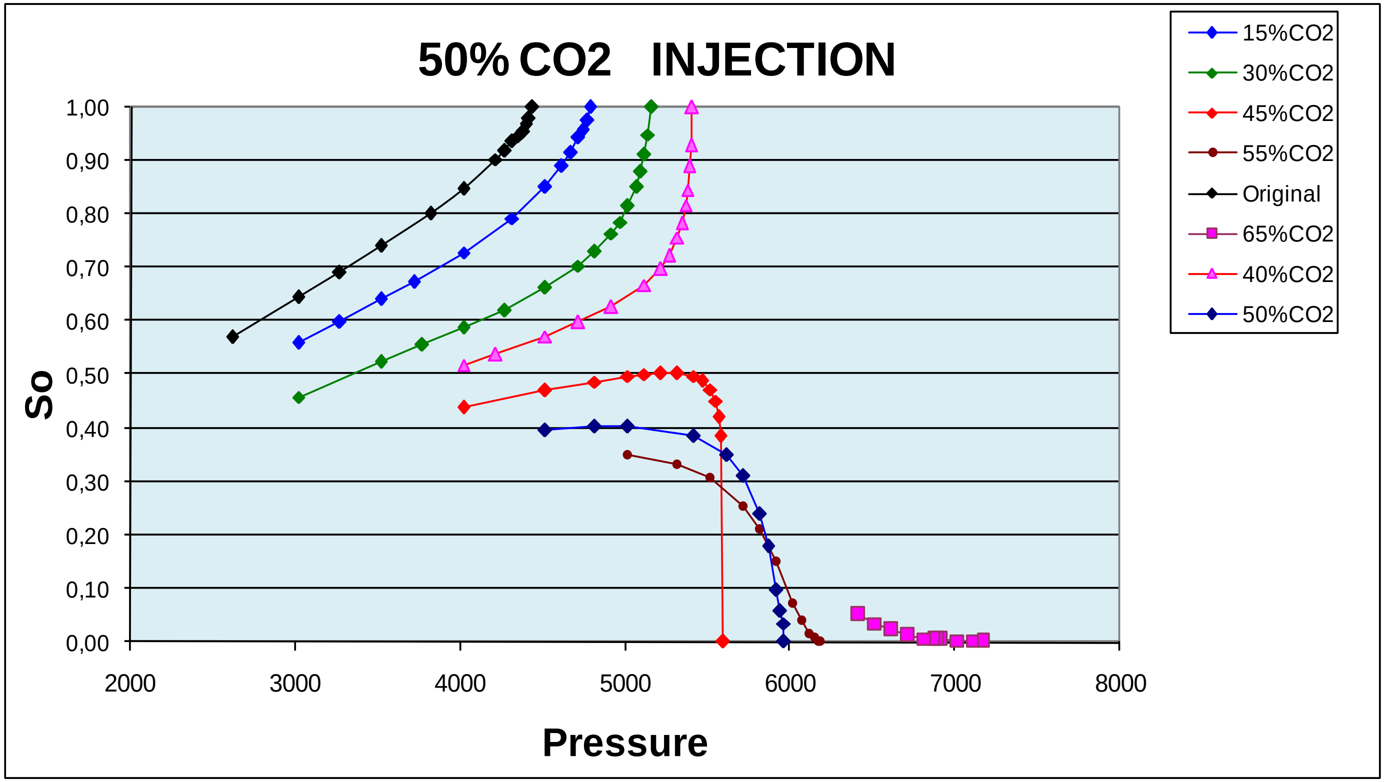
Swelling Step % Molar	*Type of* Fluid	*Saturation* Pressure	*Swelling Fact*	*Density* At Psat
Original Fluid		4415	1,0000	0,5706
First Stage (15%)	Bubble	4785	1,0990	0,5602
Second stage (30%)	Bubble	5155	1,2357	0,5532
Third stage (45%)	Dew	5595	1,4476	0,5445
Fourth stage (55%)	Dew	6181	1,6536	0,5422
Fifth Stage (65%)	Dew	7166	1,9235	0,5547
Cross Check				
Second stage (40%)	Bubble	5401	1,3536	0,5521
Fifth Stage (50%)	Dew	5963	1,5553	0,5421

Source: Cupiagua South .

Ecopetrol S.A. – BP Colombia

SWELLING TEST

Liquid Drop out with 50% CO_2 injection Case



Source: Ecopetrol S.A.

SWELLING TEST

Swelling Study Summary with 100% CO_2 injection Case

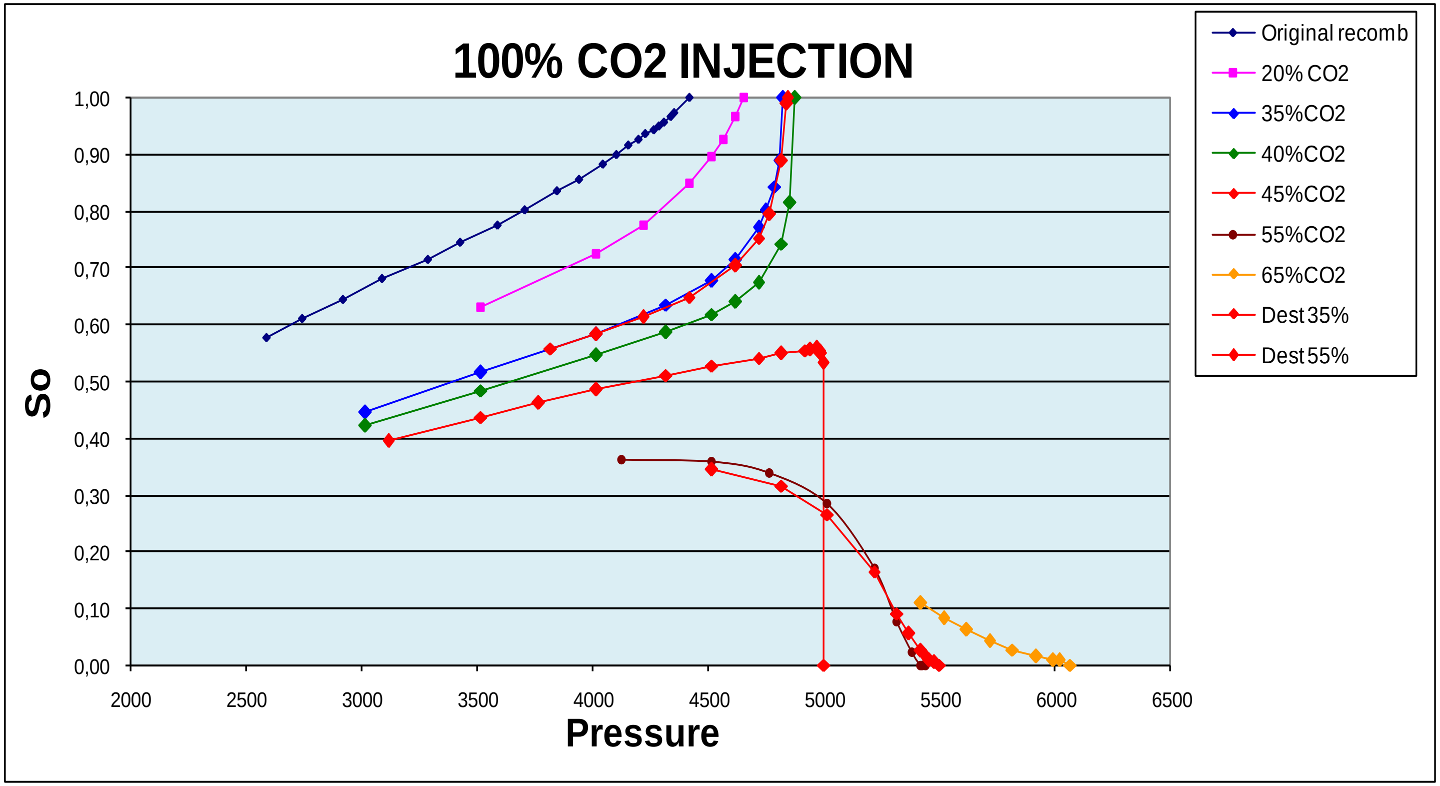
Swelling Step % Molar	*Type of* Fluid	*Saturation* Pressure	*Swelling Fact*	*Density*
Fluido original		4415	1,0000	0,5706
First Stage (20%)	Bubble	4648	1,1694	0,5785
Second stage (35%)	Bubble	4821	1,3166	0,5895
Third stage (40%)	Bubble	4875	1,3658	0,5941
Fourth stage (45%)	Dew	5000	1,4415	0,5970
Fifth Stage (55%)	Dew	5435	1,6549	0,6175
Sixth stage (65%)	Dew	6066	1,9363	0,6532
Cross Check				
Second stage (35%)	Bubble	4839	1,3106	0,5878
Fifth Stage (55%)	Dew	5500	1,664	0,6176

Source: Cupiagua South .

Ecopetrol S.A. – BP Colombia

SWELLING TEST

Liquid Drop Out with 100% CO_2 injection Case

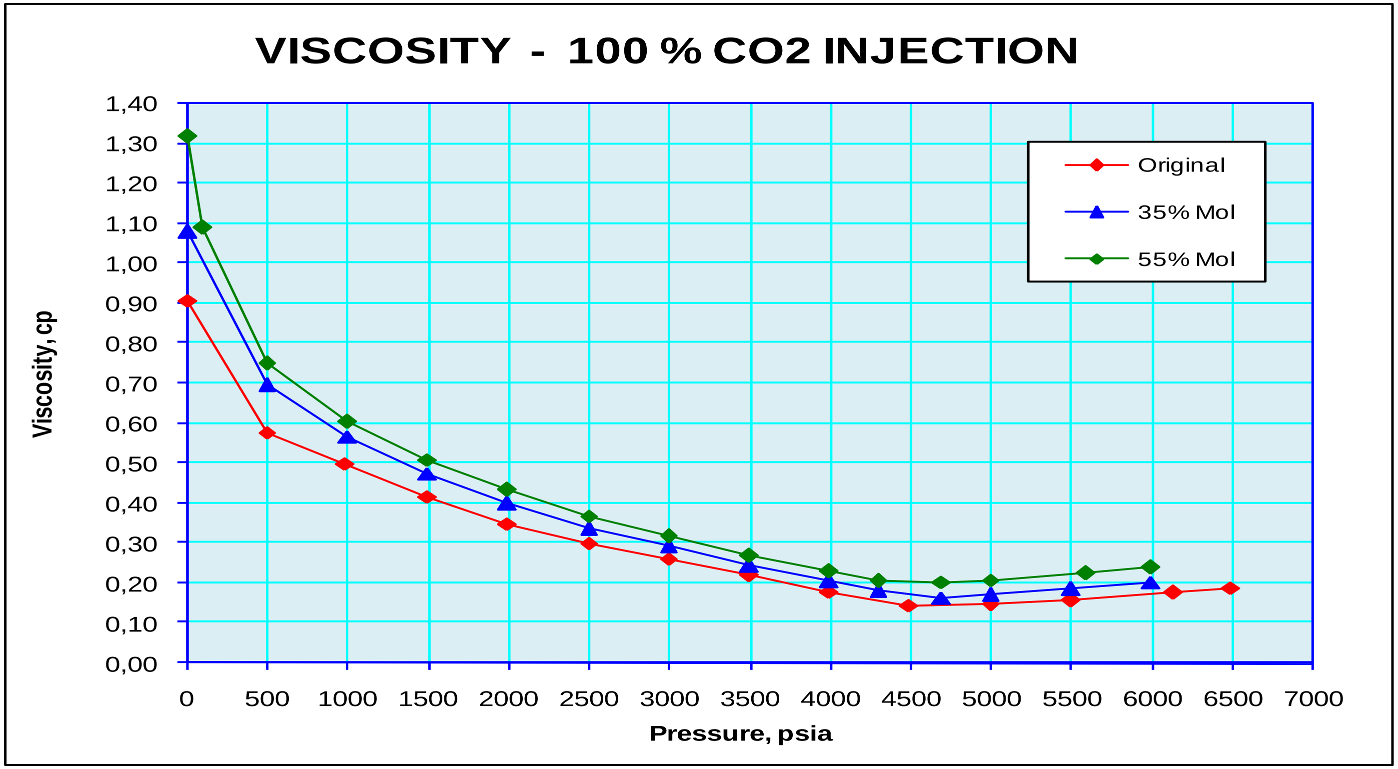


Source: Cupiagua South .

Ecopetrol S.A. – BP Colombia

SWELLING TEST

Comparative Viscosity Analysis of the Original Fluid and the two destructive tests in the 100% CO_2 injection case.



Source: Cupiagua South .

Ecopetrol S.A. – BP Colombia

SWELLING TEST

Liquid Drop Out with Separator Gas Case

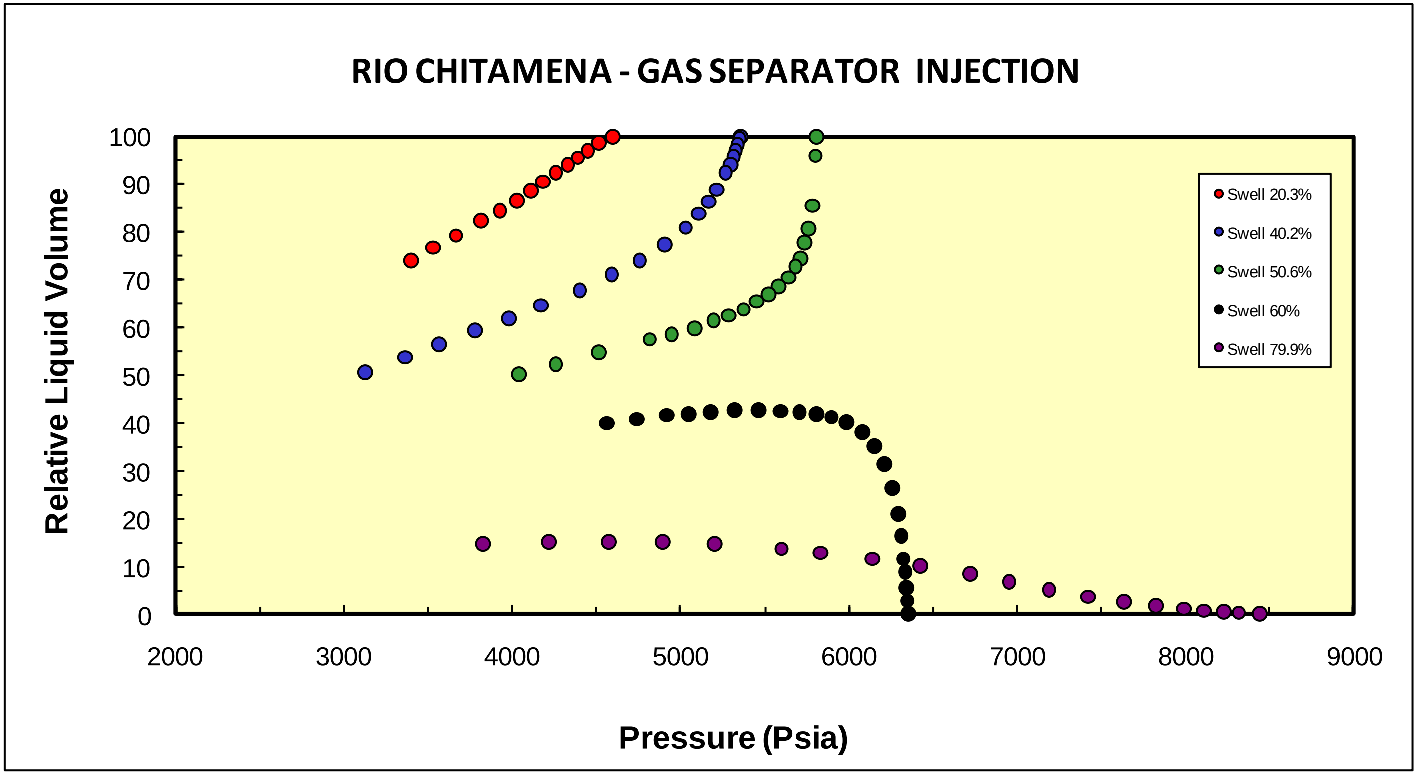
Swelling Step % Molar	Saturation Pressure Psia	Swelling Factor	Density @ Sat. P gr/cc
Original Fluid	3840	1,0000	0,6164
First Stage (20.3%)	4605	1,1731	0,5695
Second Stage (40.2%)	5359	1,3875	0,5291
Third Stage (50.6%)	5811	1,5694	0,5028
Fourth Stage (60.0%)*	6357	1,8132	0,4816
Fifth Stage (79.9%) *	8444	3,0530	0,4248

Source: Rio Chitamena

Ecopetrol S.A. – BP Colombia

SWELLING TEST

Liquid Drop Out with Separator Gas Case



Source: Rio Chitamena

Ecopetrol S.A. – BP Colombia

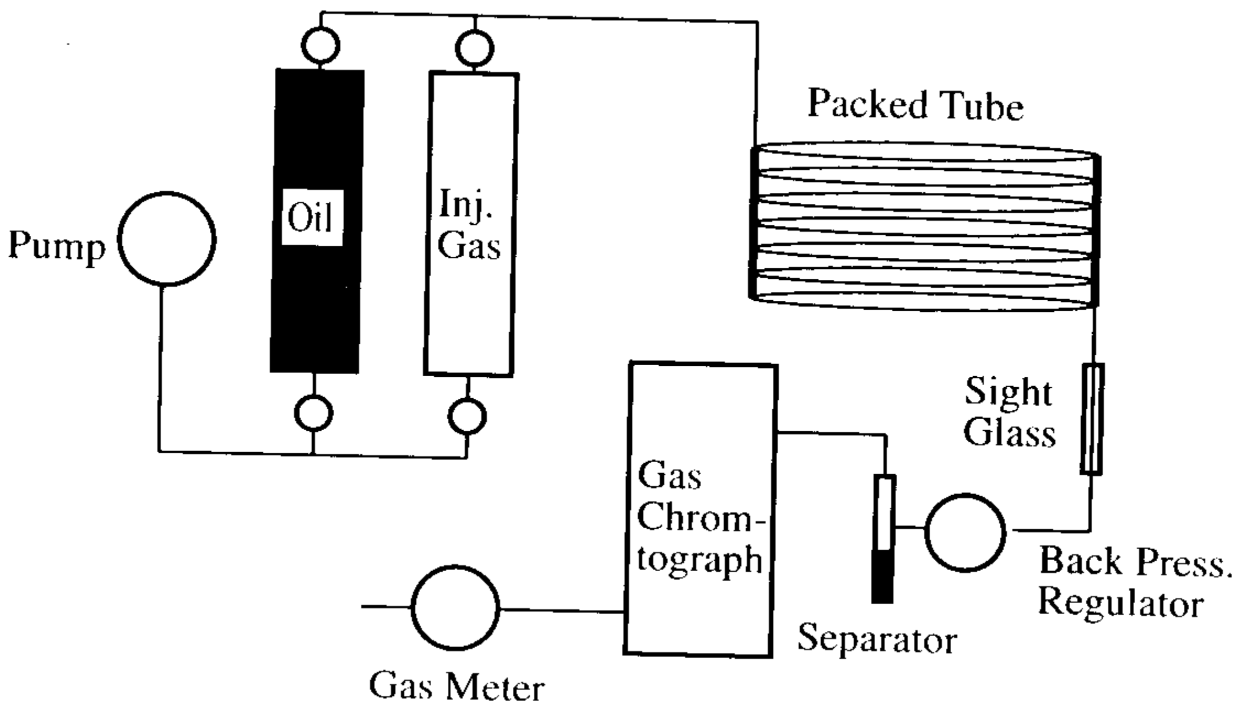
SLIM TUBE

Slim tube is a narrow tube packed with sand, or glass beads, with a length between 5 and 40 m. The tube is initially saturated with the oil at reservoir temperature above the bubble point pressure. The oil is then displaced by injecting gas into the tube at a constant inlet, or more often outlet, pressure controlled by a backpressure regulator.

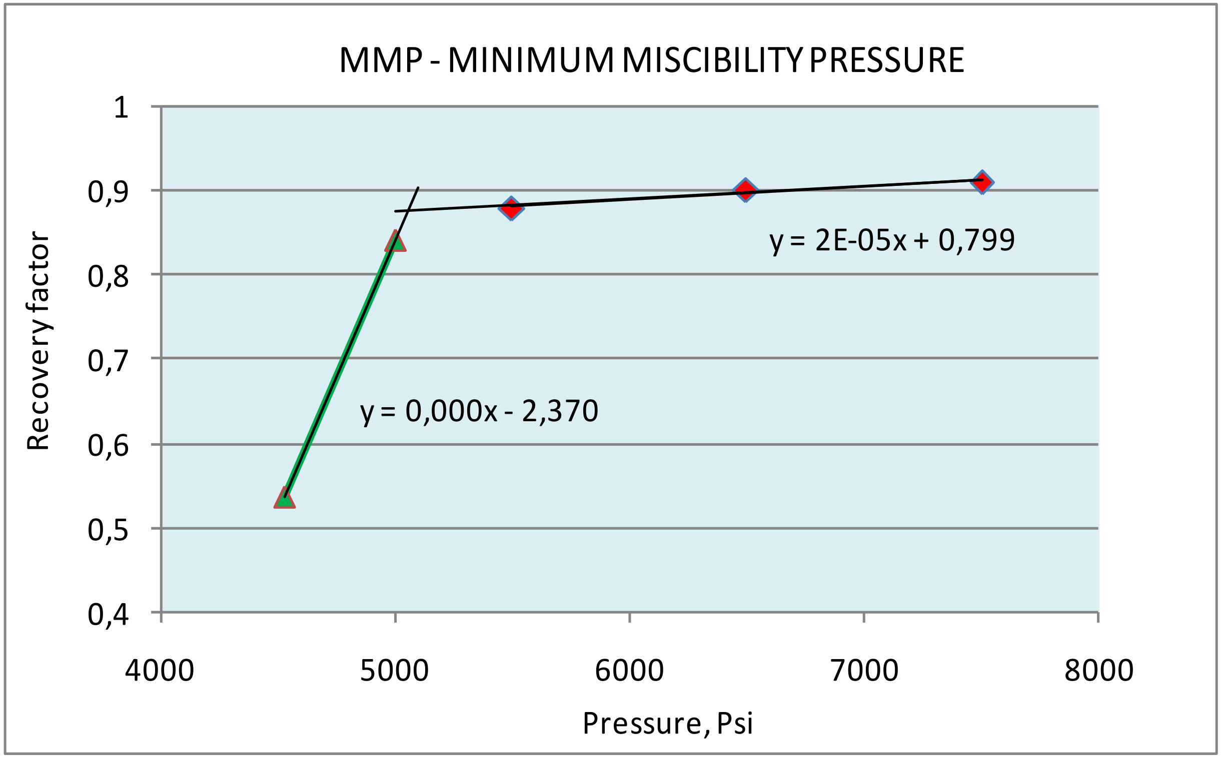
The pressure drop across the slim tube is generally small, therefore, the entire displacement process is considered to be at a single constant pressure. The slim tube effluent is flashed at the atmospheric conditions, and the rate of recovery, density and composition of produced fluids are measured. The gas break through is detected by continuously monitoring the effluent gas composition, and/or the producing gas to oil ratio.

The miscibility conditions are determined by conducting the displacement at various pressures, or injection gas enrichment levels, and monitoring the oil recovery. This can also be aided by visual observation of the flow through a sight glass placed at the tube outlet. The achievement of miscibility is expected to accompany a gradual change of colour of the flowing fluid from that of the oil to clear gas. Whereas, observing two-phase flow is indicative of an immiscible displacement.

Schematic Diagram of Slim Tube Apparatus



Original Fluid MMP Study



Source: Cupiagua South

Ecopetrol S.A.

Lumping Schemes Modelling

SEUDOCOMPONENTES				
36	15	12	10	2
N2	N2	N2	CO2	Livianos
CO2	CO2	CO2	C1-N2	Pesados
C1	C1	C1	C2	
C2	C2	C2	C3-4	
C3	C3	C3-4	C5-6	
i-C4	i-C4	C5	C7-10	
n-C4	n-C4	C6	C11-14	
i-C5	i-C5	C7-10	C15-20	
n-C5	n-C5	C11-14	C21-29	
C6	C6	C15-20	C30+	
Benzene	C7-10	C21-29		
Toluene	C11-14	C30+		
C7	C15-20			
C8	C21-29			
C9	C30+			
C10				
C11				
C12				
C13				
C14				
C15				
C16				
C17				
C18				
C19				
C20				
C21				
C22				
C23				
C24				
C25				
C26				
C27				
C28				
C29				
C30+				

Source: Ecopetrol S.A.

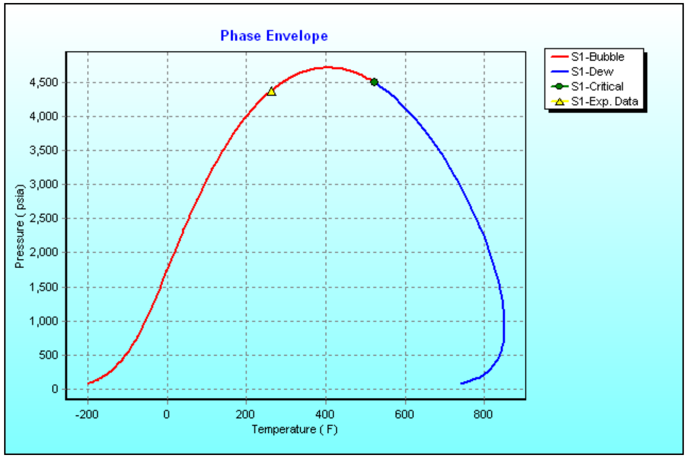
EoS's Crítical Properties - Basic PVT (10 and 12 pseudocomponents)

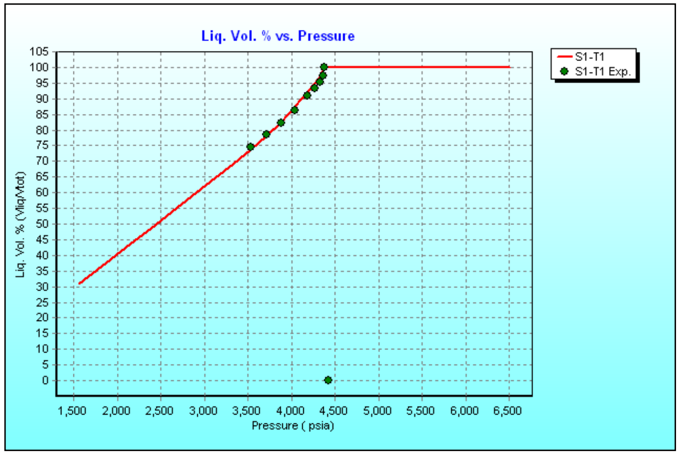
Component	MW g/mol	Critical P. psia	Critical T. F	Acentric	Critical V. cm^3/gmol	Critical Z	Tb F	Volume Trans.
CO2	44.01	1071.3	87.9	0.225	93.9	0.274246	-109.2	-0.04958
C1N2	16.11	671.4	-117.5	0.01326	99.11	0.290287	-259.2	-0.14851
C2	30.07	708.3	90.1	0.0986	148.3	0.285222	-127.4	-0.10863
C3-4	50.32	579.2	251.6	0.17436	231.12	0.280966	-8.8	-0.073239
C5-6	78.94	494	438.9	0.25983	328.29	0.2694	133	-0.033306
C7-10	117.7	396.3	509.7	0.50217	454.41	0.277291	385.9	0.127803
C11-14	167.3	311.9	621.7	0.63182	615.72	0.265075	493.8	0.303643
C15-20	237.77	258	743.1	0.80079	778	0.249148	614.5	0.175046
C21-29	339.94	225.7	885.7	1.00932	916.27	0.229493	752.4	-0.236022
C30+	550	210.8	1131.5	1.26965	1036.56	0.204954	966.7	-1.291503

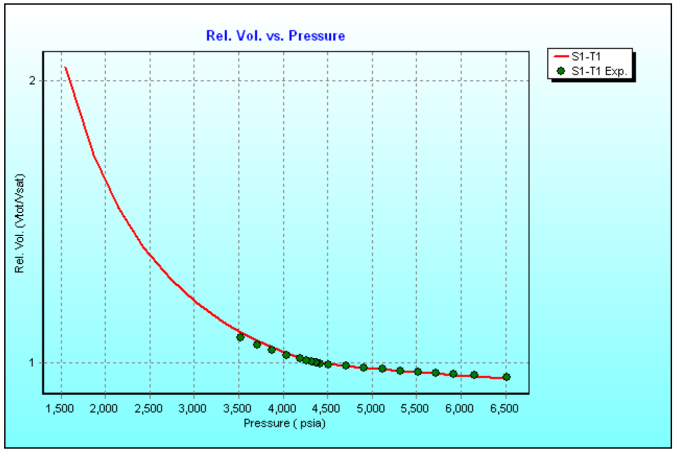
	N2	CO2	C1	C2	C3	C4	C5-C6	C7-10	C11-14	C15-20	C21-29	C30+
N2	0	-0.02	0.036	0.05	0.08	0.092	0	0.1	0.1	0.1	0.1	0.1
CO2		0	0.1	0.13	0.135	0.13	0	0.125	0.125	0.125	0.125	0.125
C1			0	0	0	0	0	0	0	0	0	0
C2				0	0	0	0	0	0	0	0	0
C3					0	0	0	0	0	0	0	0
C4						0	0	0	0	0	0	0
C5-C6							0	0	0	0	0	0
C7-10								0	0	0	0	0
C11-14									0	0	0	0
C15-20										0	0	0
C21-29											0	0
C30+												0

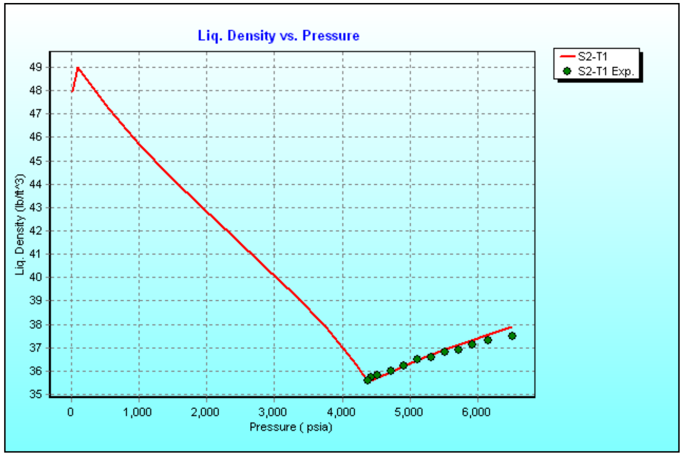
Source: Ecopetrol S.A.

EoS Basic PVT Adjustment









Source: Ecopetrol S.A.

MODELING ANALYSIS

It was found that reducing from 10 to 8 pseudocomponents failed to replicate some of the key phase behavior of the original 36-component characterization.

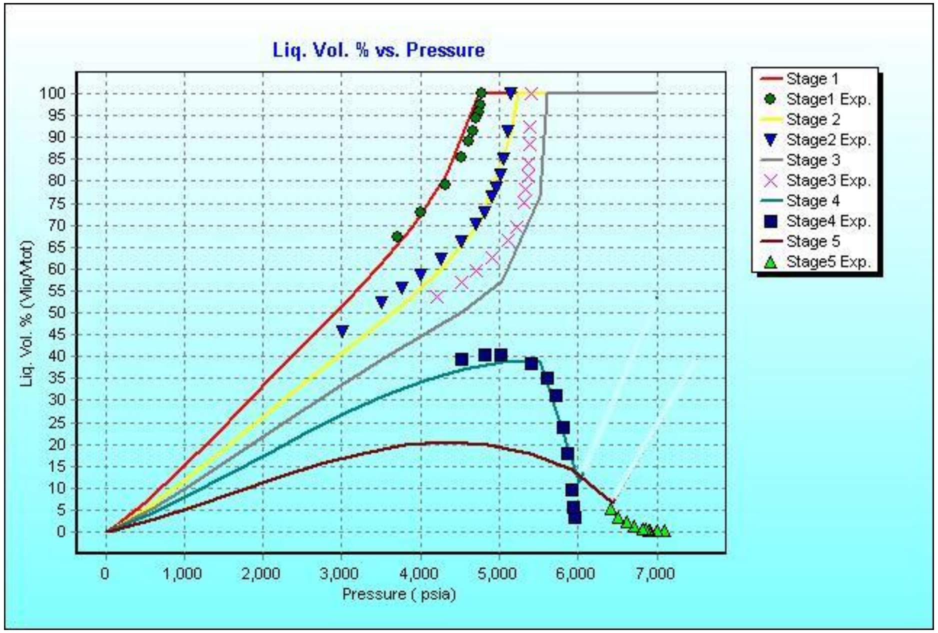
This type of detailed C_{7+} description was necessary to capture vaporization of intermediate components as high as C_{20} to C_{25} by the dense CO_2-rich phase.

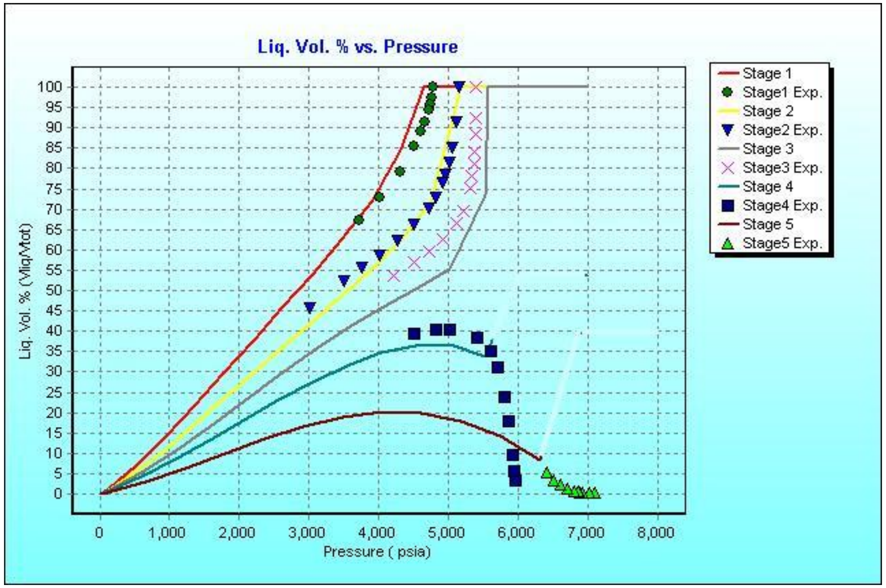
A special procedure was used to develop a fluid characterization with only ten pseudocomponents. This pseudoized characterization proved to be as accurate as the original 36-component characterization for describing standard PVT behavior, near-critical behavior, and combined vaporization/condensation effects associated with developed miscibility mechanisms.

MODELING ANALYSIS

50% CO_2 INJECTION

Swelling Test (10 comp)

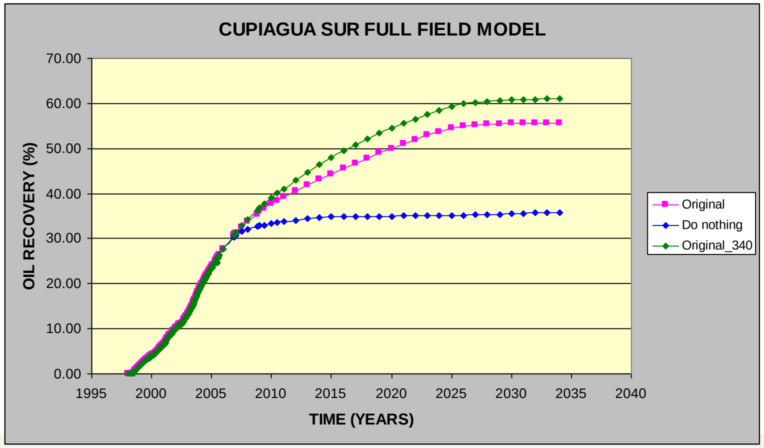




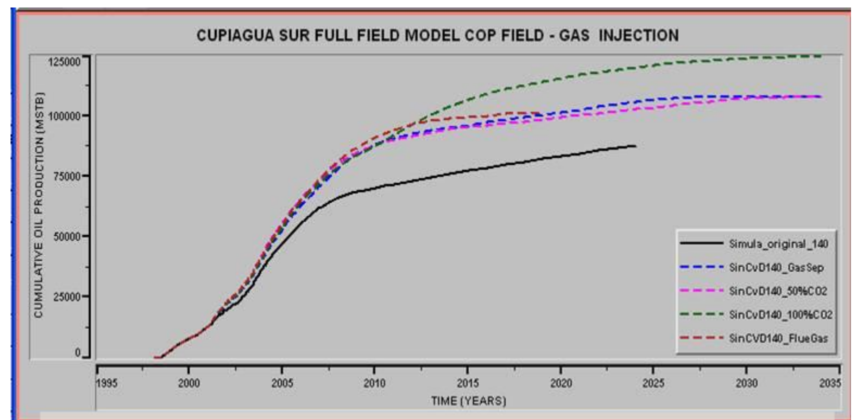
Swelling Test (12 comp)

Source: Ecopetrol S.A.

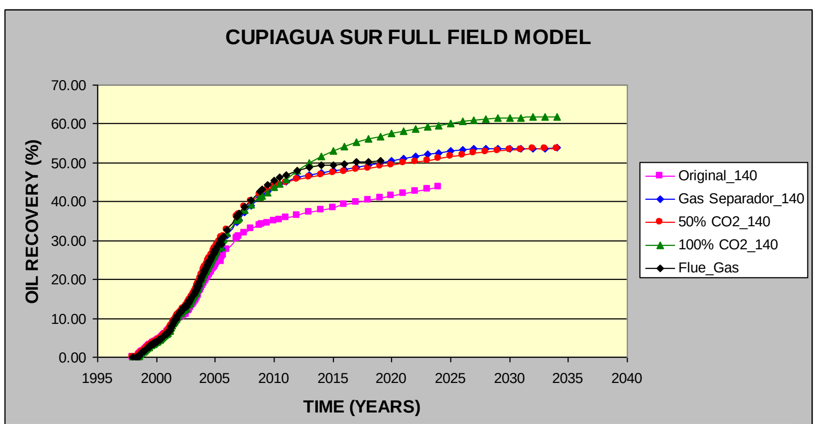
SIMULATION ANALYSIS



Comparison of the prediction of recovery factor - base case



Comparison of the prediction of the produced cumulative oil

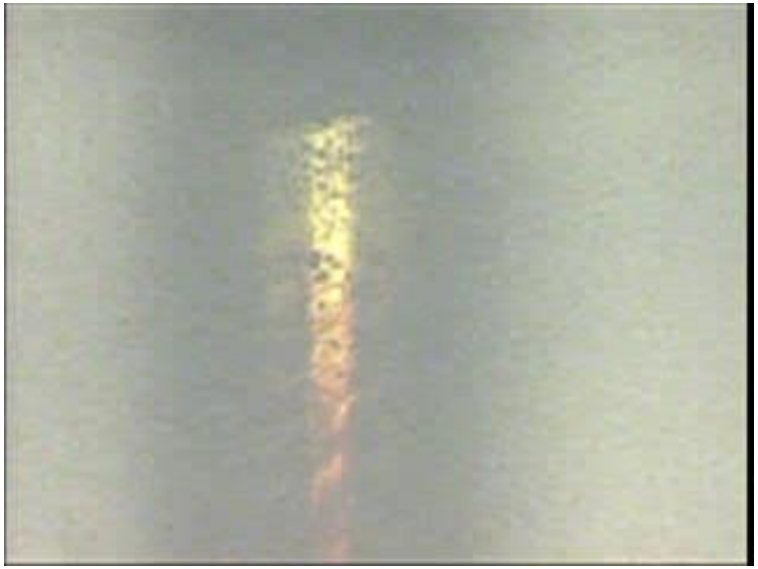


Comparison of the prediction of the recovery factor

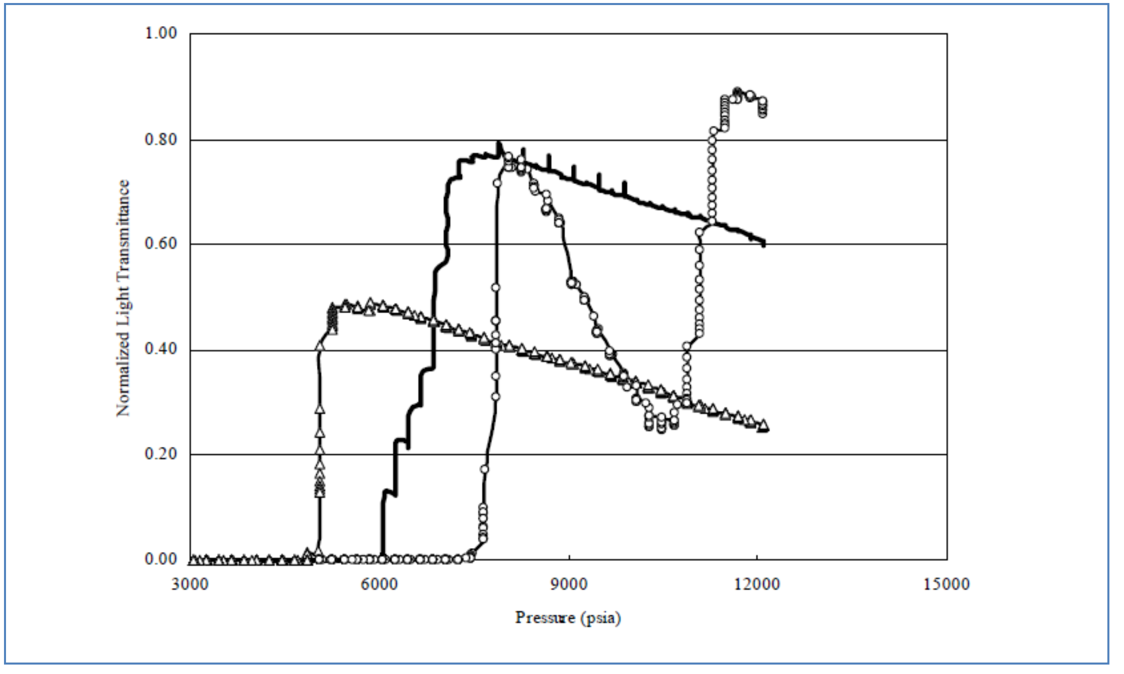
Source: Ecopetrol S.A.

EXPERIMENTAL ANALYSIS

Based on the experimental observations, during the injection processes with all the solvents, it was felt there was significant risk of solid formation in this volatile fluid study. So, it was necessary to check this precipitation and develop an “black material” formation model that could adequately predict the measured experimental data.

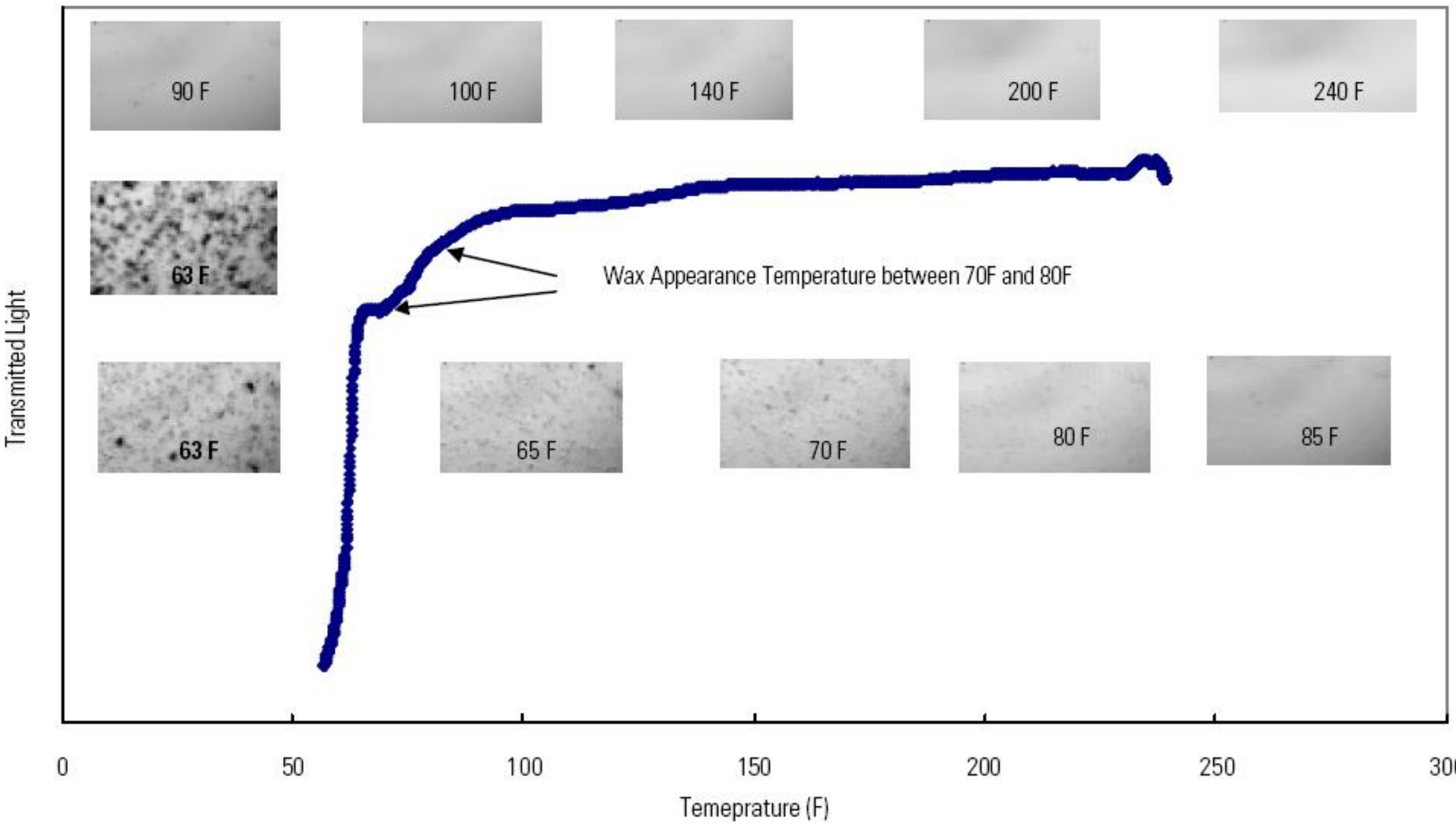


EXPERIMENTAL ANALYSIS

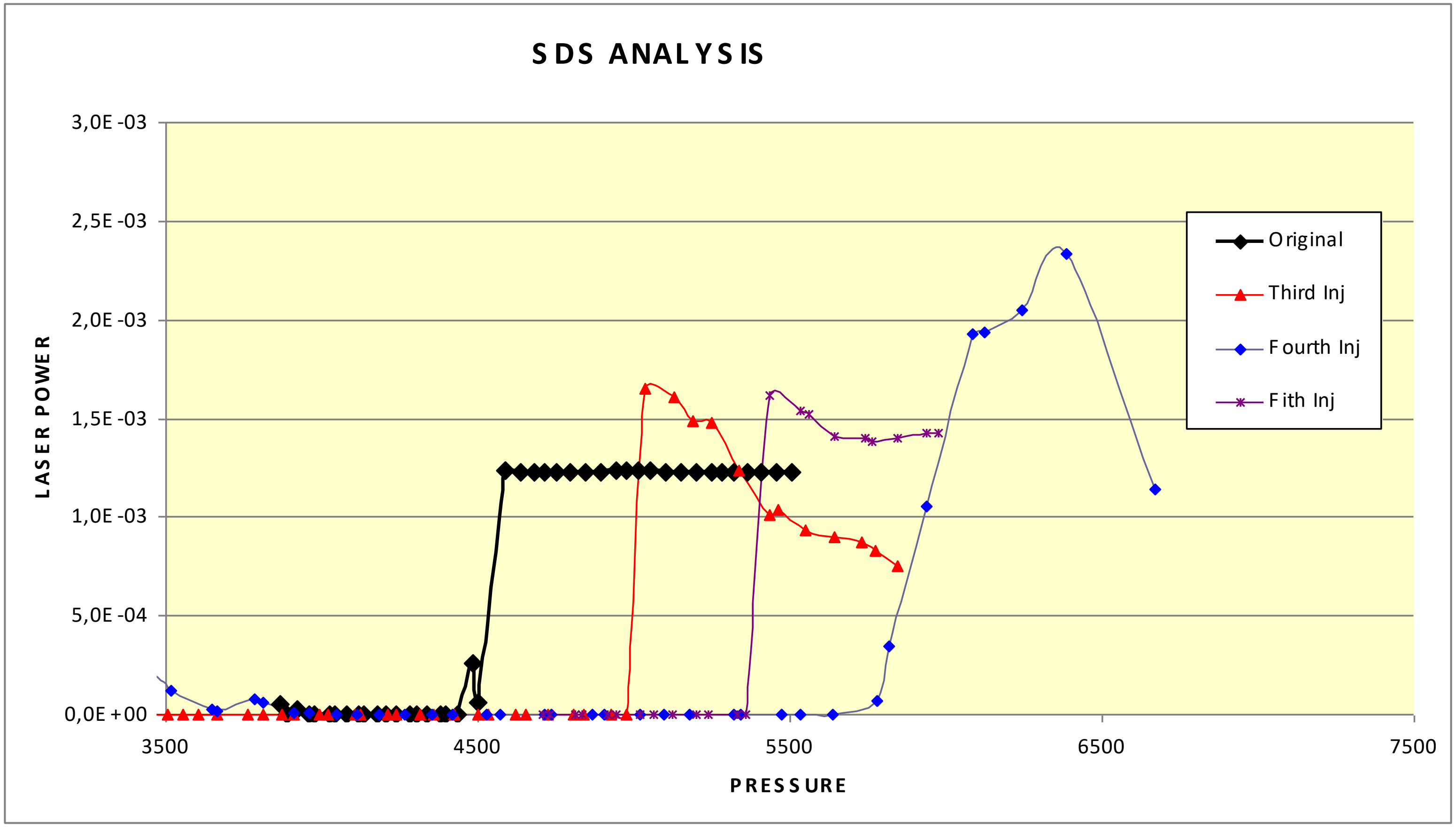


The NIR light transmittance increases with decreasing pressure. This is a result of the decrease in reservoir fluid density while in the single-phase condition. Subsequently, the NIR response shows a sudden drop in the light transmittance caused by segregation of asphaltene particles. This inflection point is defined as the onset of asphaltene precipitation (OAP).

EXPERIMENTAL ANALYSIS



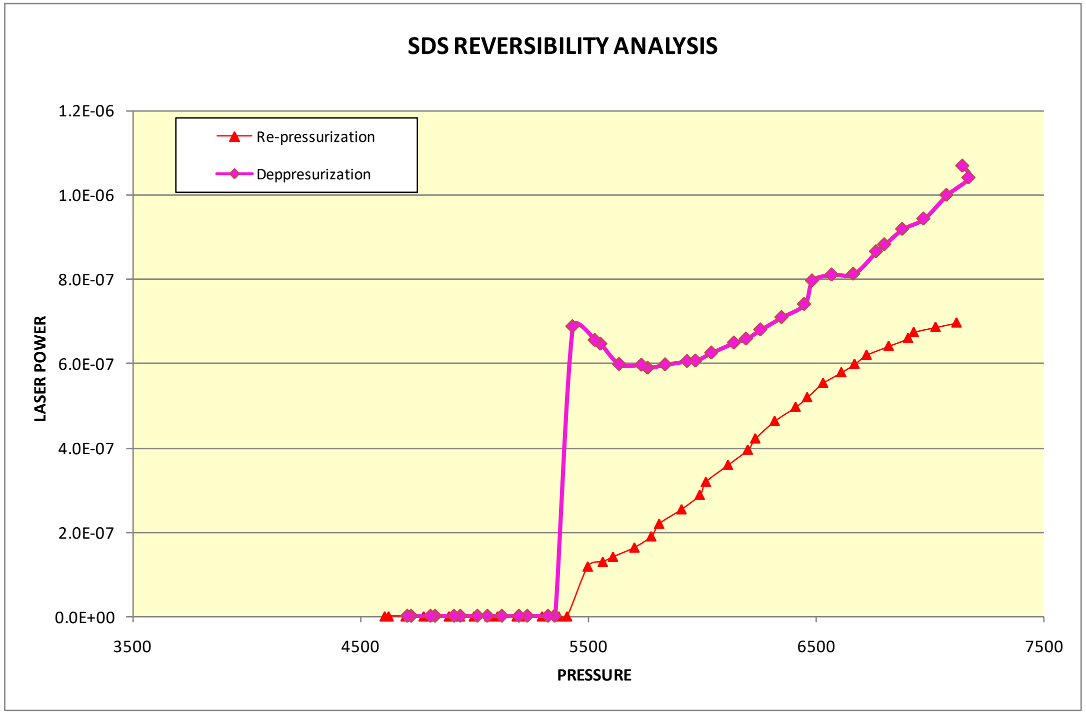
Asphaltene Precipitation during solvent injection



Source: Cupiagua South
Ecopetrol S.A. – BP Colombia

Asphaltene Precipitation during solvent injection

The asphaltene reversibility appears to be delayed. In these reversibility experiments, the initial light transmittance level is higher before the depressurization experiment than that at the end of the re-pressurization experiment. This phenomenon may be due to partial reversibility of asphaltenes, that is, some of the asphaltenes particles that have precipitated do not re-peptize during re-pressurization.



Source: Rio Chitamena

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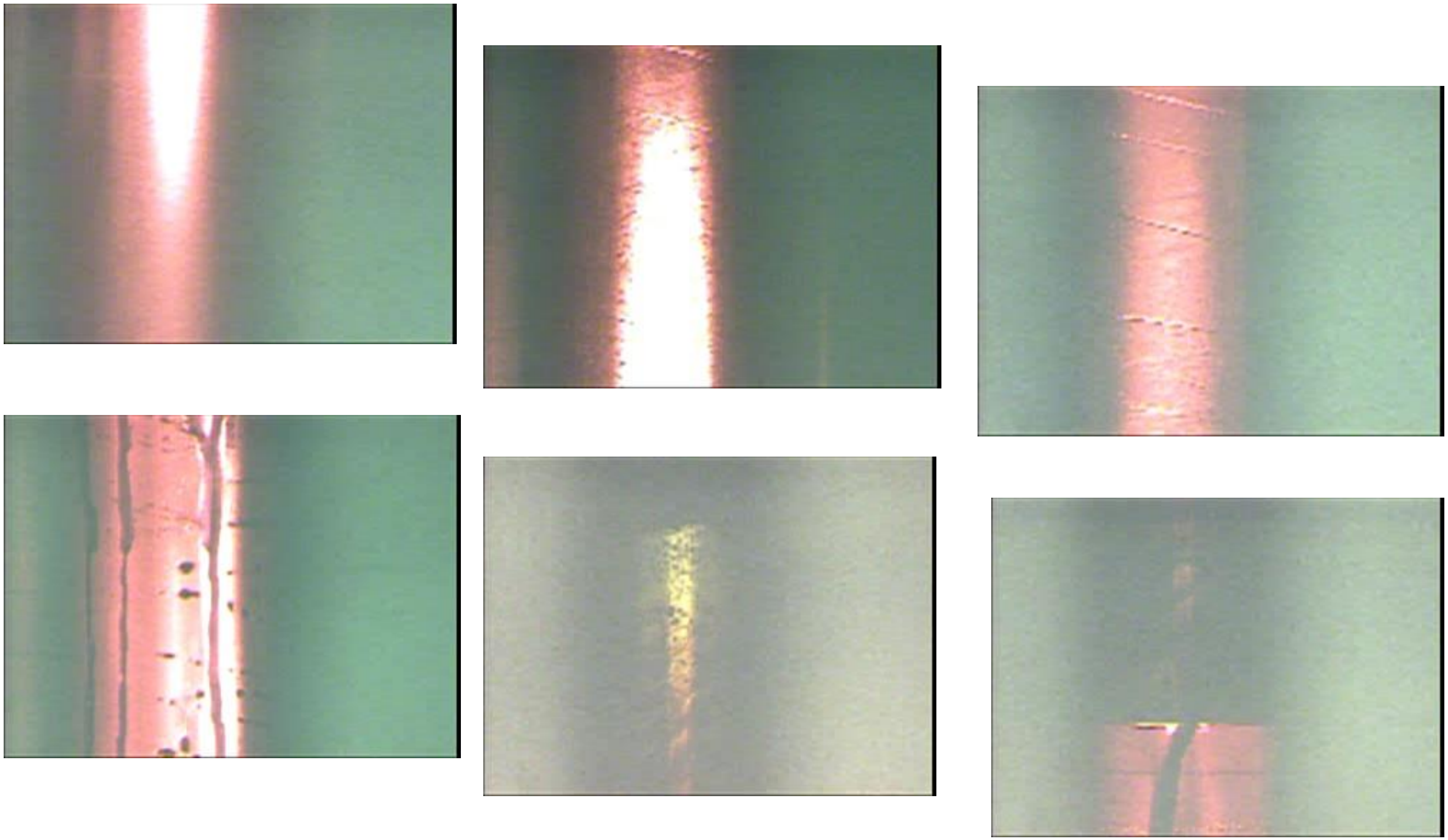
Asphaltene Precipitation



Source: Ecopetrol S.A.

SARA – Fluid Analysis

Volatile Oil		
COMPONENT	Espectroscospy	
	Reported	Normalized
SATURATES	**51.4**	70.0
AROMATICS	**19.2**	26.2
RESINS	**2.5**	3.4
ASPHALTENES	**0.4**	0.4
RECUPERATED %	73.5	100.0
Light Fraction Losses (%)	26.5	
Estability index	2.4	2.4

Source: Cupiagua South

Ecopetrol S.A. – BP Colombia

Black Material Analysis

SARA ANALYSIS	
Components	**Unit**
	% wt
SATURATES	3.9
AROMATICS	5.4
RESINS	2.6
ASPHALTENES	**88.1**
RECUPERATED %	100

Source: Cupiagua South

Ecopetrol S.A. – BP Colombia

Black Material Analysis

Formula	Name	% Weight
Saturated Hydrocarbons		
Cn.H(2n + 2)	Paraffin's	35.45
Cn.H(2n)	Monocicloparaffins	29.07
Cn.H(2n-2,4,6)	Di, Tri, Tetracicloparaffins	12.80
Total		**77.32**
Aromatic hydrocarbons		
Cn.H(2n-6, -8, -10)	Monoaromatics	18.00
Cn.H(2n-12, -14, -16)	Diaromatics	4.05
Cn.H(2n-18, -20)	Triaromatics	0.24
Cn.H(2n-22, -24, -26)	Tetraaromatics	0.06
Cn.H(2n-28, -30)	Pentaaromatics	0.00
Total		**22.34**
Sulphured Aromatics		
Cn.H(2n-10, -12-14).S	Benzotiofenos	0.27
Cn.H(2n-16, -18-20).S	Dibenzotiofenos	0.07
Cn.H(2n-22, -24-26,...., -42).S	Naftobenzotiofenos	0.00
Total		**0.34**
	Overall Aromatics	**22.68**

Fuente: Ecopetrol S.A.

Black Material Analysis

GROUPS SUMMARIZE

Reference: **Sample taken at tthe end of the Swelling Test**

Group	**% Weight**	**% Vol**	**% Mol**
Paraffin	8.992	9.765	9.646
I-Paraffins	9.840	10.556	10.001
Aromatics	6.443	5.365	5.803
Naphthenes	6.746	6.386	6.644
Olefins	0.000	0.000	0.000

CUTS TABLE

ASTM D2887 HIGH -TEMP(*)

Start (C)	**End (C)**	**% Off**
19.7	221.0	32.3
221.0	344.0	26.7
344.0	590.2	40.2

Fuente: Ecopetrol S.A.

Asphaltene Precipitation Video

Source: Cupiagua South

Ecopetrol S.A. – BP Colombia

CHARACTERIZATION ASPHALTENE MODELING

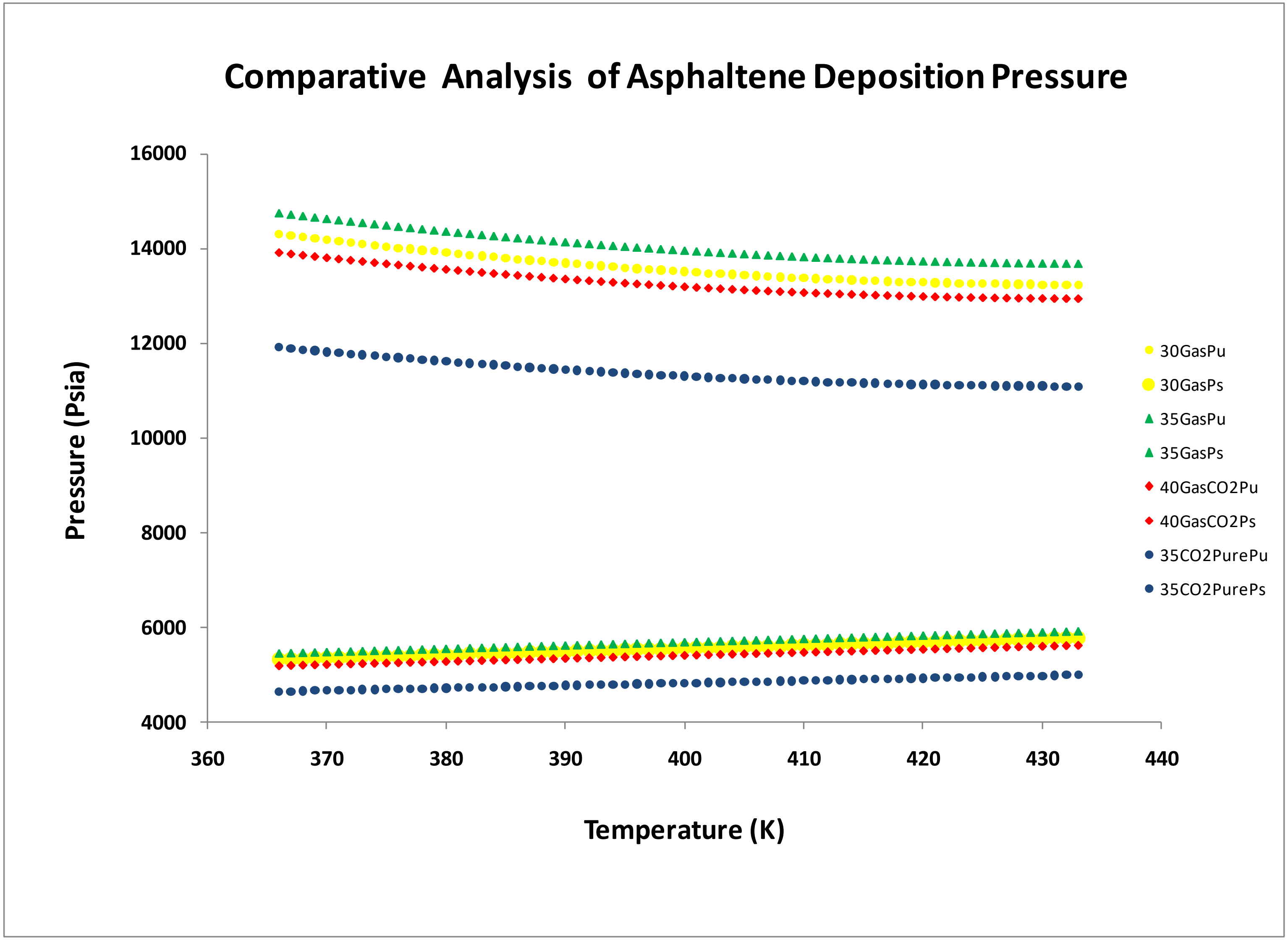
		30Gas	***35Gas***	***40Gas+CO2***	***35CO2 Pure***
COMPONENT	***MW***	***% wt***	***% wt***	***% wt***	***% wt***
N2	28.01	0.246	0.250	0.123	0.068
CO2	44.01	3.514	3.613	17.362	26.523
C1	16.04	18.310	19.135	13.824	8.783
C2	30.07	5.231	5.461	4.165	2.952
C3	44.10	5.048	5.181	4.021	2.950
IC4	58.12	1.702	1.740	1.390	1.149
nC4	58.12	2.306	2.337	2.034	1.670
IC5	75.15	1.573	1.565	1.266	1.134
nC5	72.15	1.175	1.158	1.001	0.910
C6	84.00	2.614	2.532	1.789	1.752
Molar Fraction Cn+		***15.157***	**14.190**	**12.573**	**13.775**
Calculated MW		***197.016***	**200.491**	**230.257**	**230.540**
Denstiy Cn+		***0.837***	**0.8396**	**0.8616**	**0.8621**
Experimental Density		**0.5905**	**0.5846**	**0.5968**	**0.6134**

EQUATIONS

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)} \quad EOS-SRK$$

$$f_{aspha}^{s,pure} - f_{aspha}^{feed} > 0.0 \quad \text{Stability concept}$$

ASPHALTENE MODELING



CONCLUSIONS

✓ PVT tests and SDS experiments were performed on a volatile oil under the injection of three different solvents.

✓ The experience of this study shows that if the EoS is fit to the swelling tests, with a suitable prediction of the transition in the critical point, the EoS will be able to predict phase behavior phenomenon completely.

✓Experimental evidence of asphaltene precipitation has been observed at reservoir conditions under the scenario of CO2 injection, separator gas and its mixtures in this fluid unless its low in asphaltene content (< 2 wt %).

✓Under certain reservoir conditions two liquid phases would coexist in the system. Studies with greater detail in this aspect must be made.

✓The EoS model used in this study describes the asphaltene onset behavior as a function of the amount of injected solvent.

CONCERNS

- ✓ What do you think about the second "liquid" phase formed during the swelling test which was observed in the video?
- ✓ What recommendations will you do to this experimental procedures and the modeling of this kind of injection studies?
- ✓ Which will be the best strategy to know the impact on recovery factor?