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Study of temperature effect on asphaltene precipitation by visual and quantitative methods

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Asphaltene precipitation is one of conventional problem in crude oil production and refining process. Changes in temperature, pressure and composition are the main factors causing asphaltene instability. Pressure effect is studied in many literatures but temperature effect remains obscure yet. The onset pressure for asphaltene precipitation can be obtained by spectroscopy techniques such as transferring near infrared lights (NIR) through crude oil or by magnifier visual apparatus (HPM). The objective of the study was to evaluate the asphaltene instability in the reservoir fluid samples from one of southwest Iranian wells (Fahlyian Layers 2 and 3) at various temperatures of various visual methods. The main point in this work is studying temperature effect on initiation of asphaltene nuclei formation.

Key words: Asphaltene precipitation process, temperature effect, NIR method, HPM (high pressure microscopy) method.

INTRODUCTION

Occurrence of asphaltene deposition in producing formation constitutes one of the most serious problems currently encountered in the petroleum industry in many areas of the world (Shedid, 2005). Heavy molecules such as asphaltene may separate from the mixture, resulting in deposition problems. Severe asphaltene aggregation problems are faced in both upstream and downstream production operations. It is highly important to predict where and when in the production system such problems may arise, to prevent the consequences of unexpected asphaltene deposition (Hemanta, 2001). They are destabilized and start to precipitate when the pressure, temperature and/or composition changes occur during primary production (Hirscberg et al., 1984). The precipitated asphaltene particles will then grow in size and may start to deposit onto the production string and/or flow lines, causing operational problems (Jamaluddin et al., 2001). Asphaltene is defined as the large benzenic

material precipitated from the crude and heavy oils upon addition of n-pentane or n-heptane at a dilution ratio of 40 volumes of solvent per volume of petroleum sample as introduced by Speight et al. (1948). One of the best ways to detect onset point (the first pressure of asphaltene precipitation) is visual technique such as NIR and HPM. In order to have a better understanding of results obtained by NIR and HPM methods, a detailed description of these two methods looks necessary.

METHODOLOGY

Near-infrared spectroscopy (NIR)

The principle behind the measurement is based on the transmittance of a laser light in the NIR wavelength through the test fluid undergoing temperature, pressure or the fluid composition changes. The NIR spectroscopic region of the electromagnetic spectrum extends from 780 to 2500 nm (12820 to 4000 cm^{-1}) (Narve et al., 2002). In this region the system with asphaltene aggregates can undergo electronic transitions as well as vibration overtone transitions. But the region generally used is between 1100 and 2500 nm (9090 to 4000 cm^{-1}). The NIR region is attractive for hydrocarbon analysis because many of the absorption bands

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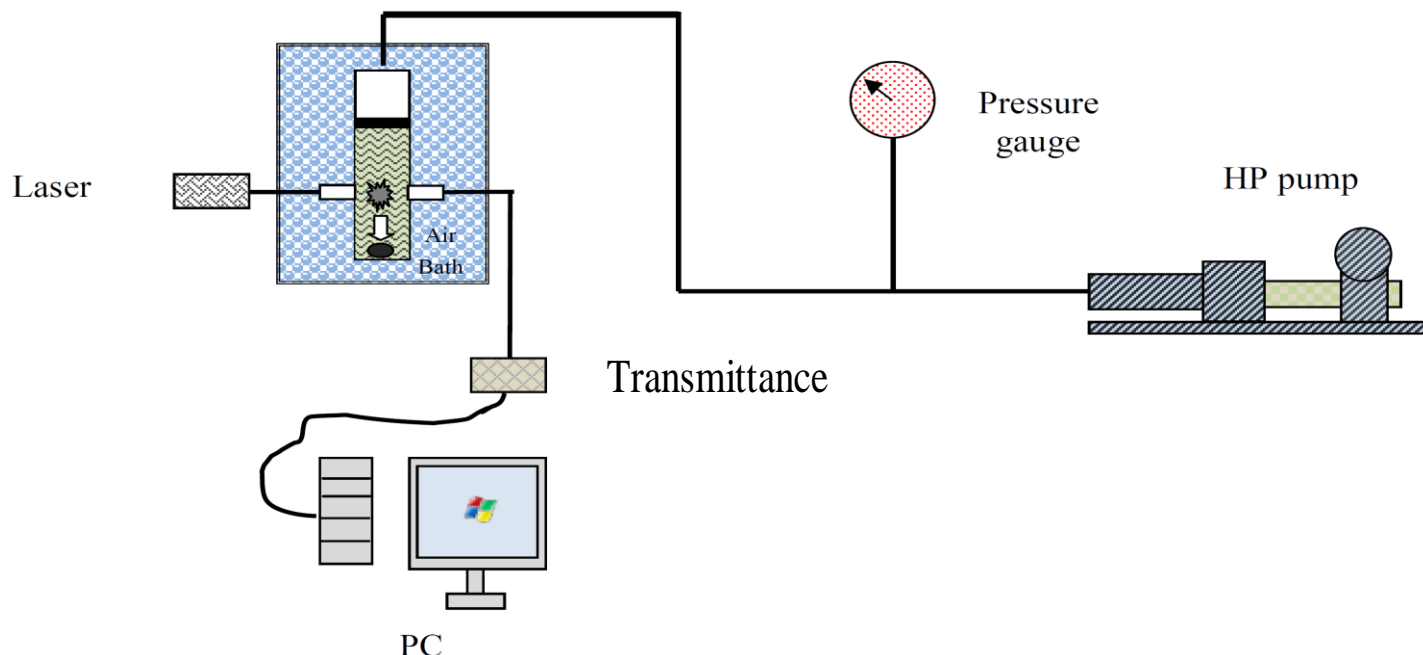
Figure 1. A schematic of NIR apparatus.

observed in this region arise from overtones or combinations of carbon-hydrogen stretching vibrations. Functional groups such as methylenic, olefinic, or aromatic C-H give rise to various C-H stretching vibrations that are mainly independent of the rest of the molecule. Asphaltenes, being large aromatic fused- ring systems, also display π π* and n π * electronic transitions in the near-infrared region. In addition to attenuation of the transmitted light by absorbance, light scattering by asphaltene nucleus aggregates in hydrocarbon solutions contributes to the light attenuation. For slightly lossy dielectric particles in the Rayleigh limit the light attenuation is a sum of the absorbance and scattering contribution.

The ratio of scattering to absorption scales with r^3 (radius of particle), indicating the importance of particle size on the total light attenuation. The influence of scattering increases extensively with increasing diameter of the particles, the particles being asphaltene aggregates in this case (Narve et al., 2002). In NIR, the light transmittance characteristics are linked to precipitation of solids (asphaltene) based on the observations that the light transmittance (i) increases when the fluid density decreases, (ii) increases when pressure decreases to P_b (that is, the starting pressure must be above P_b), (iii) decreases when the particles size increases, and (iv) decreases when the nucleation density of solids increases (Hemanta, 2001). The process variables (that is, temperature, pressure, solvent volume, time and transmitted light power level) are recorded and displayed from the detector. The fibber optic light transmittance system detects the conditions of onsets of hydrocarbon solids nucleation is termed as the light scattering technology using NIR (Jamaluddin, 2000).

High pressure microscopy (HPM)

HPM set up is composed of a high-pressure high-temperature cell with sapphire walls that is used for the measurements. The cell thickness is 300 mm and the diameter of the sapphire is 3 mm. However, the cell thickness can be adjusted according to requirements. A high magnification (x100) camera is used in conjunction to observe the changes that the fluid undergoes (Dalia et al., 2010). (Jamaluddin, 2000) the cell temperature is controlled by a circulation bath whereas the fluid pressure inside the cell is maintained using a displacement pump. The camera monitors the fluid continuously during the isothermal depressurization tests and photographs at distinct steps are taken for comparison. Each time the solid particles by 0.01 μm is formed the microscope can detect it. Schematic of this apparatus is depicted in Figure 1.

RESULTS AND DISCUSSION

Fluids preparation, characterization and analysis

Monophasic wellhead samples were collected from one of Southern Iranian oil well (Fahlyian Layer-A and B). The well, formation, and reservoir conditions data are summarized in Table 1. After receipt at laboratory, the opening pressures for samples were measured. Subsequently, these samples were restored and homogenized at the reservoir temperature of 145.72 and 143°C, respectively, above reservoir pressure. A sub-sample from cylinders was used to conduct preliminary analyses to validate the samples. The bubble point pressures at the reservoir temperature of 145.72 and 143°C were measured. The constant volume composition test conducted was to measure the main PVT characteristics of oil sample such as GOR, relative volume, compressibility and so on. For this purpose the reservoir fluid was flashed from reservoir to ambient condition. Thus, it was expected that the stock-tank oil

Table 1. Fluid properties for samples A and B.

Property	Sample A	Sample B		Property	Sample A	Sample B
$T_{reservoir}$ (°C)	145.722	142.77		P_b (Mpa)	33.39	29.53
P_i (Mpa)	63.30077	63.2249		$MW_{reservoir\ fluid}$	66.69	69.82
Compressibility at Pi Mpa^{-1}	0.002176	0.001798		MW_{C12+}	304.51	310.20
Specific gravity $_{reservoir\ oil}$	0.542	0.603		Specific gravity $_{C12+}$	0.873	0.877
Specific gravity $_{residual\ oil}$	0.8565	0.8476		Specific gravity $_{gas}$	0.839	0.875
API	33.71	35.44		Viscosity at P_b (Kg/m.s)	0.0020	0.0020
Viscosity at P_i (Kg/m.s)	0.00028	0.0030				
At initial static pressure						
Bo (m^3/m^3)	2.356	2.254		$\rho_{reservoir\ oil}$ (Kg/m^3)	595	603
At bubble point pressure						
Bo (m^3/m^3)	2.586	2.505		R_s (m^3/m^3)	314.78	286.73

would retain all the solids present in the reservoir fluid. The stock-tank oil from constant volume composition test was used to measure its properties such as density, wax and sulfur content and main hydrocarbon contents include saturates aromatics, resins and asphaltene (SARA) analyses. The constant volume composition test result to various asphaltene content for each sample. The results of this test and SARA analyses are summarized in Tables 2 and 3.

Asphaltenes pose the potential to destabilize, flocculate and precipitate out of the reservoir fluid when subjected to pressure, temperature or compositional changes. Screening criteria are used to evaluate the propensy of asphaltene to precipitate out. There are four plots for screening the tendency of asphaltene precipitation, namely de Boer Plot, Asphaltene-Resin ratio, colloidal instability index (Baker Petrolite) and the asphaltene stability index (Oilphase-Schlumberger). The data required for the screening were PVT properties such as density at bubble point pressure and the reservoir pressure, etc and SARA contents of the stock-tank oil. Results from the stability screening suggested that there is the potential for severe asphaltene problems for both samples. Hence, detailed measurements were conducted to measure onset of asphaltene destabilization and the amount of precipitated asphaltene at various temperatures. For this purpose, visual NIR and HPM methods are used.

Study of temperature effect on asphaltene precipitation by visual methods

The first study includes the onset of asphaltene destabilization pressure at various temperatures one samples by NIR methods. These measurements were conducted by measuring the light transmittance through the reservoir fluid samples undergoing isothermal depressurization. The light source was an optimized single wavelength beam of 1600 nm (NIR region). The

isothermal depressurization was conducted at three temperatures ranging from the reservoir temperature of 145.72°C to the lowest temperature feasible. The lowest temperature for measurements was selected based on the reported static temperature gradient profile from reservoir to surface. Sub-samples of the reservoir fluid were used for each measurement. The fluids were charged to the PVT cells and stabilized at the specified temperature. Subsequently, the fluid was isothermally depressurized from 82.74 to 3.447 MPa and the light transmittance through the fluid was measured for each sample. An abrupt change in the light transmittance is expected when phase change occurs. The light transmittance characteristics for reservoir fluid at three temperatures (145.72, 143, and 90°C) are presented in Figures 2, 3 and 4, respectively. At all the three temperatures, the light transmittance increases due to decrease in fluid density as a result of decreasing pressure till the bubble point pressure is reached. Then the light transmittance drops sharply due to the evolution of gas bubbles.

The onset of asphaltene destabilization or asphaltene onset pressure (AOP) above the bubble point is indicated by a change in slope of the increasing light transmittance curve. As such, asphaltene destabilization is observed in the reservoir fluid at 145.72, 143 and 90°C. The results of NIR method show that decrease in temperature, increases the onset of asphaltene destabilization pressure above the bubble point pressure. Another visual method to obtain confirmation of the asphaltene destabilization and to better understand the morphological behaviour of the asphaltene material is HPM Method. An isothermal depressurization was conducted in the HPM cell at the reservoir temperature. A sub-sample of the fluid from cylinder was transferred at 82.74 MPa to the HPM cell that was stabilized at the reservoir temperature. A few solid particles were observed at this pressure by HPM (Figures 5 to 7); however these particles showed no size growth during depressurization. Hence, the photograph at 82.74 MPa is

Table 2. Reservoir fluid analysis (reservoir condition).

Component	Monophasic fluid mole % sample B	Monophasic fluid mole % sample A
N_2	0.04	0.02
CO_2	2.23	2.76
H_2S	0.25	0.51
C_1	50.74	54.92
C_2	8.59	7.55
C_3	5.66	4.90
$I - C_4$	1.06	0.96
$N - C_4$	2.94	2.61
$I - C_5$	1.21	1.08
$N - C_5$	1.67	1.50
pseudo C_6H_{14}	2.27	2.07
M-C-Pentane	0.32	0.27
Benzene	0.29	0.22
Cyclohexane	0.32	0.12
pseudo C_7H_{16}	1.6	1.37
M-C-Hexane	0.48	0.35
Toluene	0.82	0.74
pseudo C_8H_{18}	1.6	1.26
E-Benzene	0.24	0.29
M/P-Xylene	0.45	0.17
O-Xylene	0.17	0.00
pseudo C_9H_{20}	1.72	1.55
pseudo $C_{10}H_{22}$	2.17	1.73
pseudo $C_{11}H_{24}$	1.69	1.38
C_{12+}	11.48	11.65
Total	100	100.00
MW	69.82	66.69

Table 3. Sara analysis for two sample oil A and B.

Sample	Saturates (wt%)	Aromatics (wt%)	Resins (wt%)	Asphaltenes (wt%)
A	74.81	21.59	2.63	0.97
B	70.88	24.21	3.87	1.04

considered as a baseline reference for comparative purposes. The fluid was depressurized in discrete steps until at a pressure of 48.95 MPa, drops of solid started to form (Figure 6). With further decrease in pressure, the quantity of solids forming slightly increased. The evolution of gas bubbles was also observed with a decrease in pressure below the bubble point pressure.

The particle growth was measured at each pressure step up to 0.14 microns at 34.47 MPa (Figure 7). Re-performing the experiment by HPM method show that decrease in temperature, increases the onset of asphaltene destabilization pressure above the bubble point pressure. The onset of Asphaltene precipitation at reservoir temperature from the fixed wavelength NIR technique was in good agreement with the pressure at which a growth in solids quantity was observed with the HPM. Thus visual confirmation was obtained for the onset of asphaltene destabilization. The Asphaltene Deposition Envelope (ADE) characterise limits of asphaltene region in pressure-temperature graph of fluid. In Figure 8 the ADE of oil sample by visual method is depicted. The main result of this method is decreasing solid precipitation by increasing temperature as discussed. According to results from visual method, precipitation process start by establishment of initial solid nuclei and growth in solid nuclei size so that solid particles precipitate out of the liquid phase. In this process, a deflection occurs in the NIR curve as solid nuclei that have a diameter less than 0.05 µm are created. This deflection point is known as onset point.
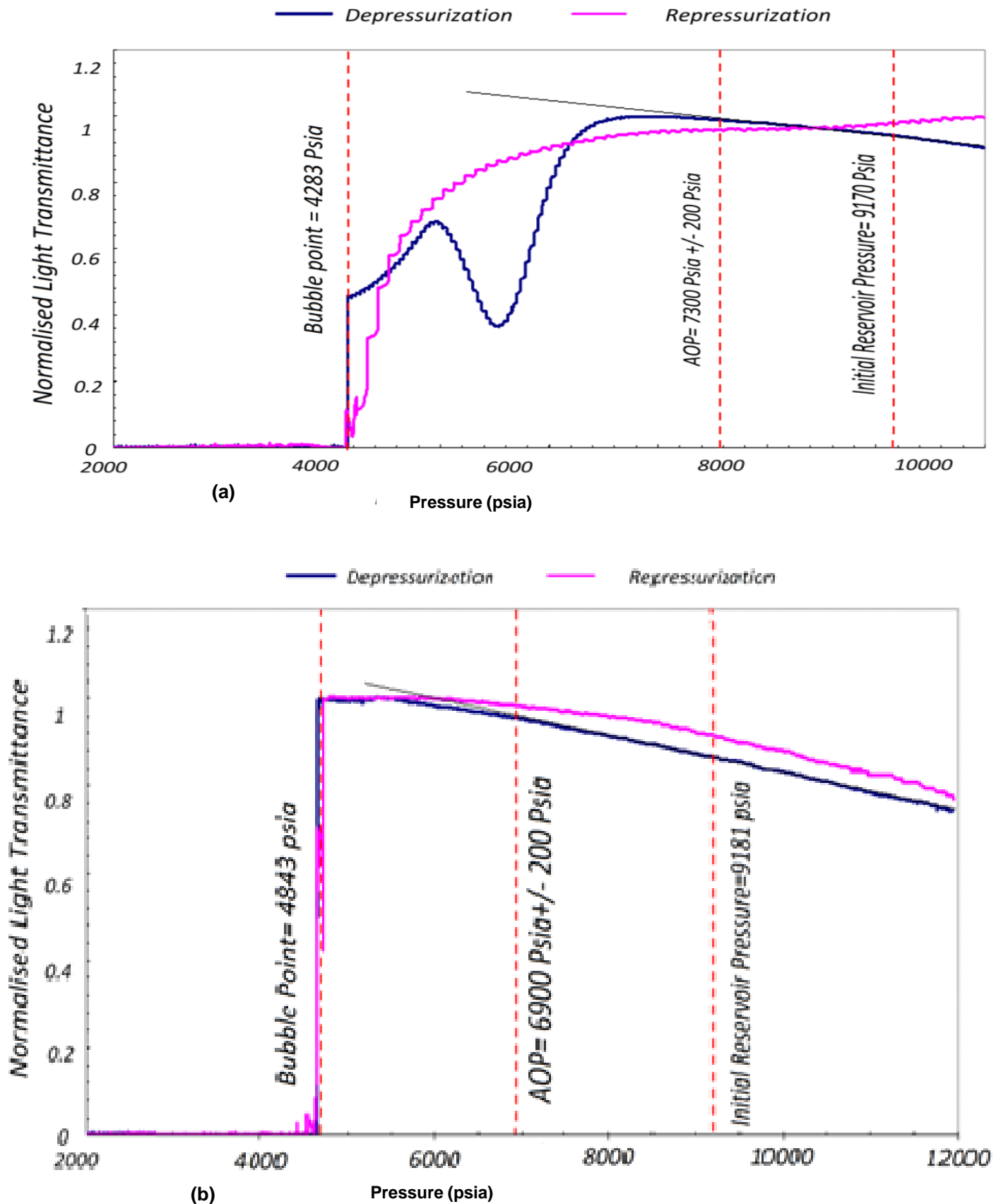
Figure 2. Normalized light transmittance curve at 289.4°F for (a) Sample B and (b) Sample A.
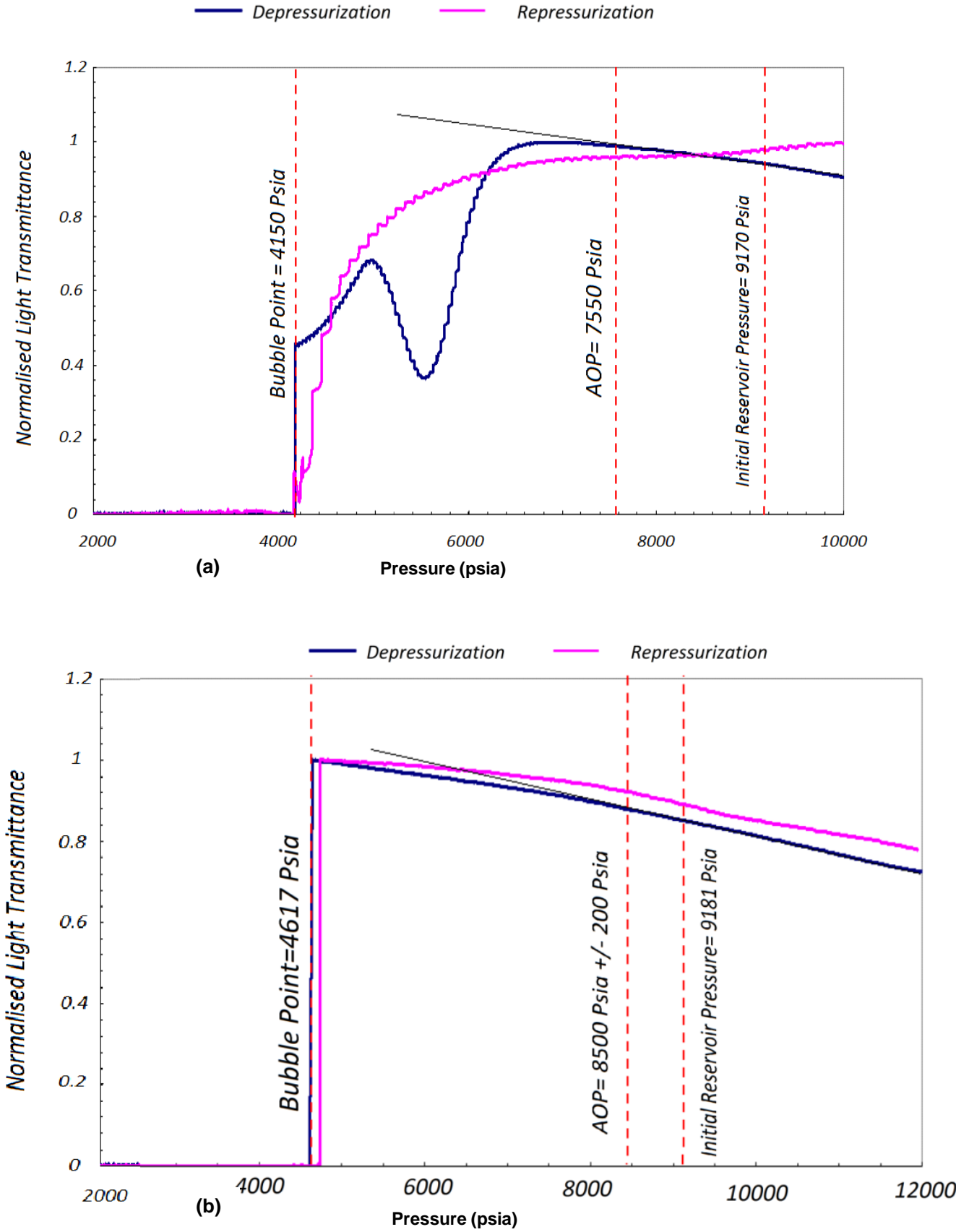
Figure 3. Normalized light transmittance curve at 248°F for (a) Sample B and (b) Sample A.
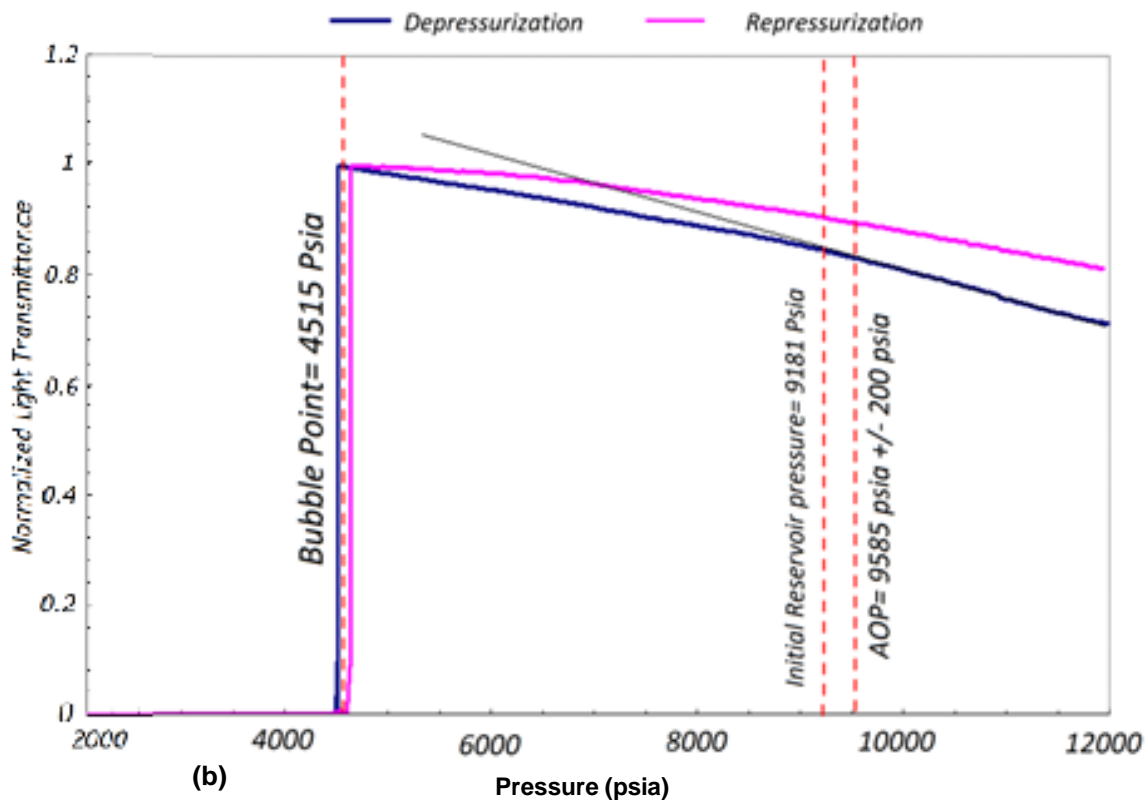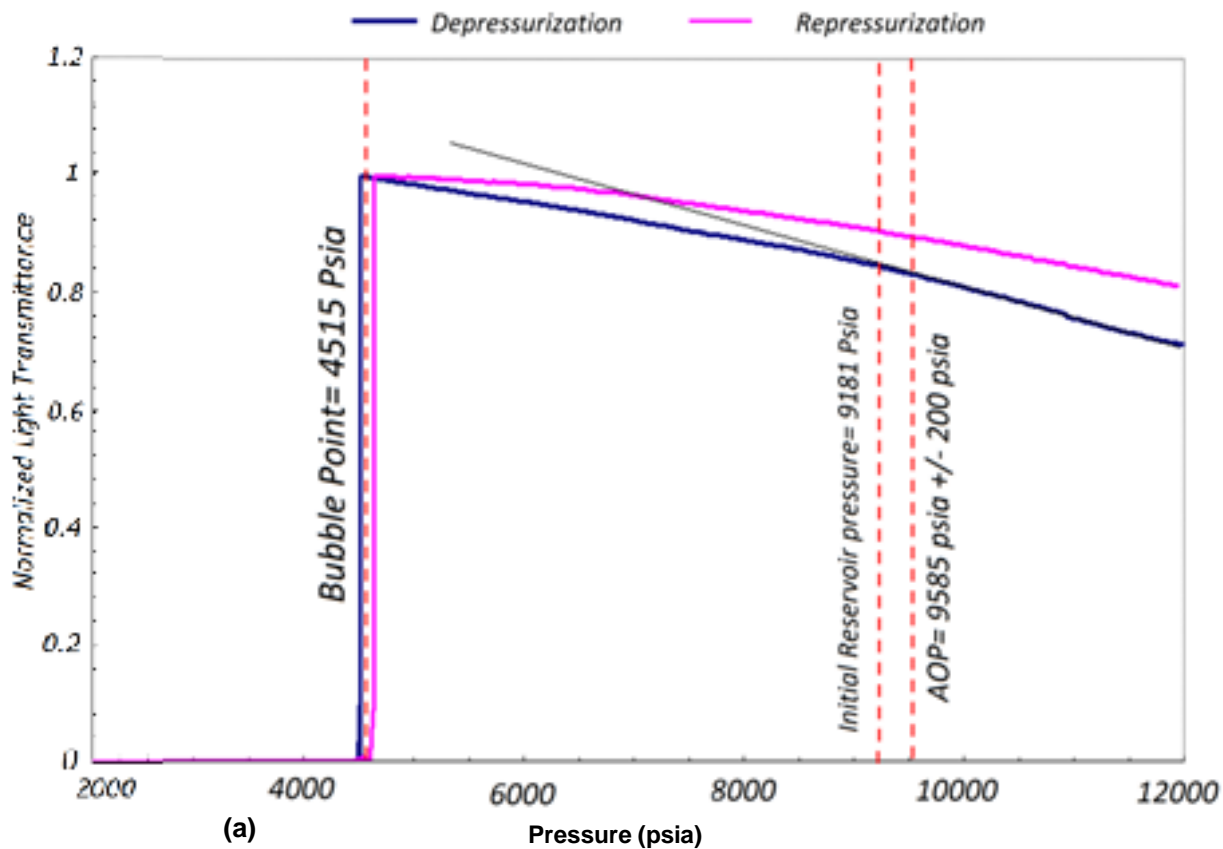
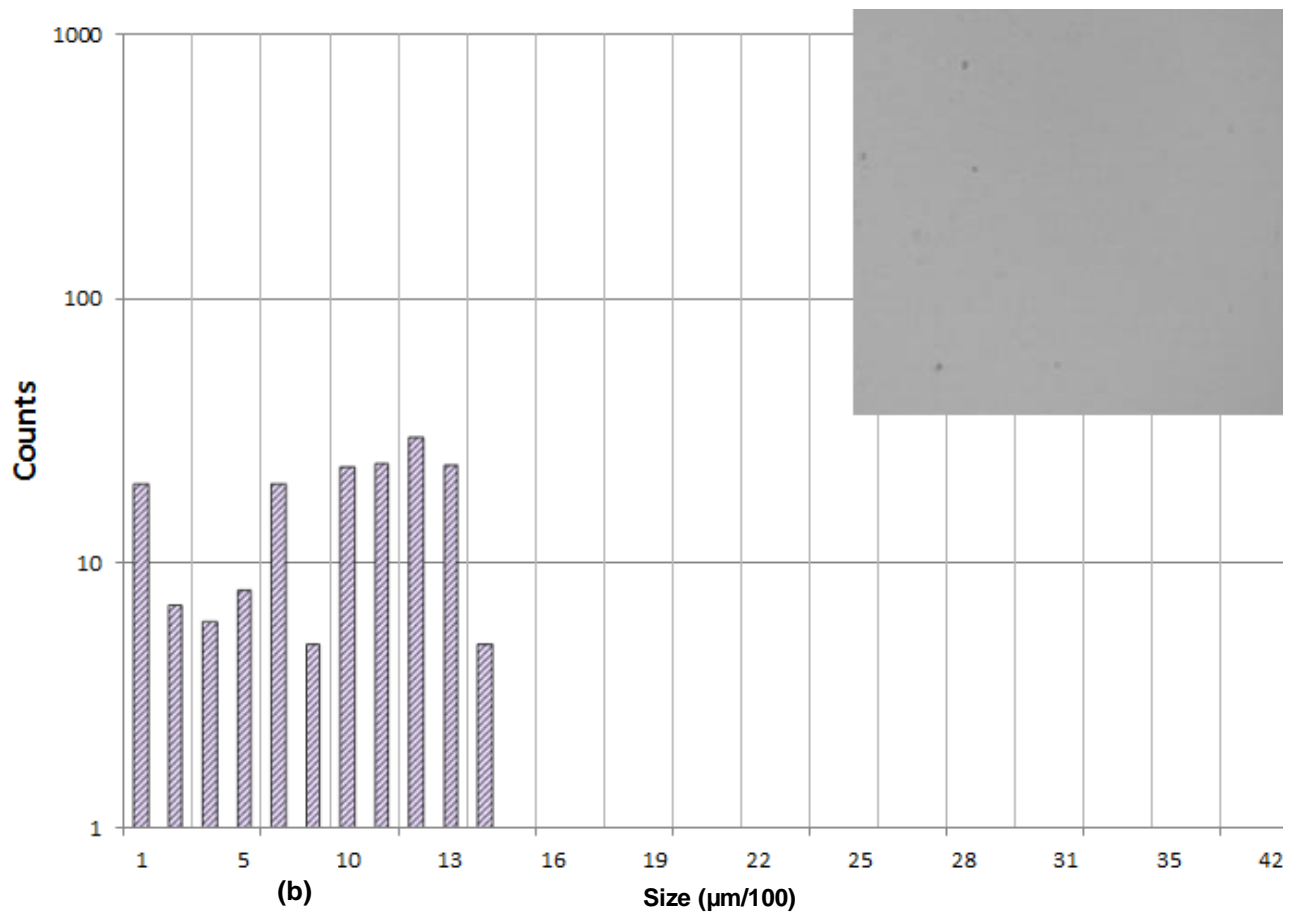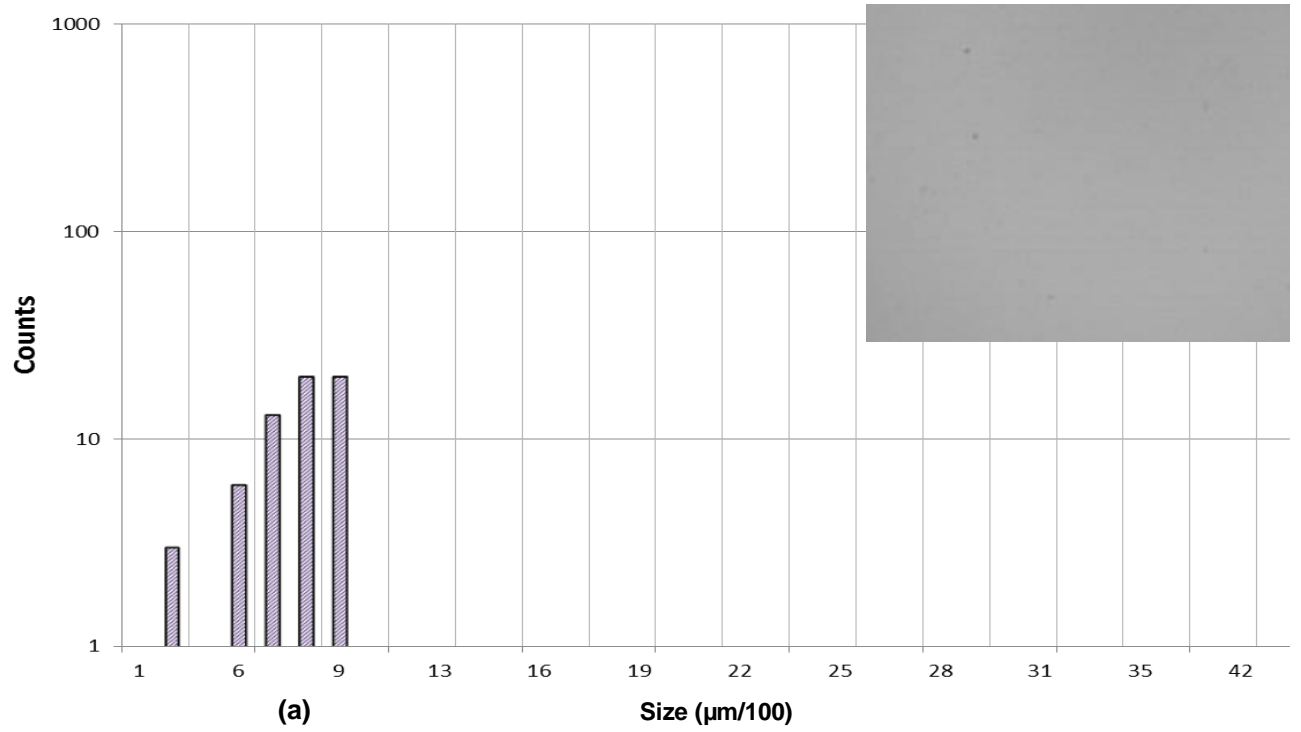**Figure 4.** Normalized light transmittance curve at 194°F for (a) Sample B and (b) Sample A.

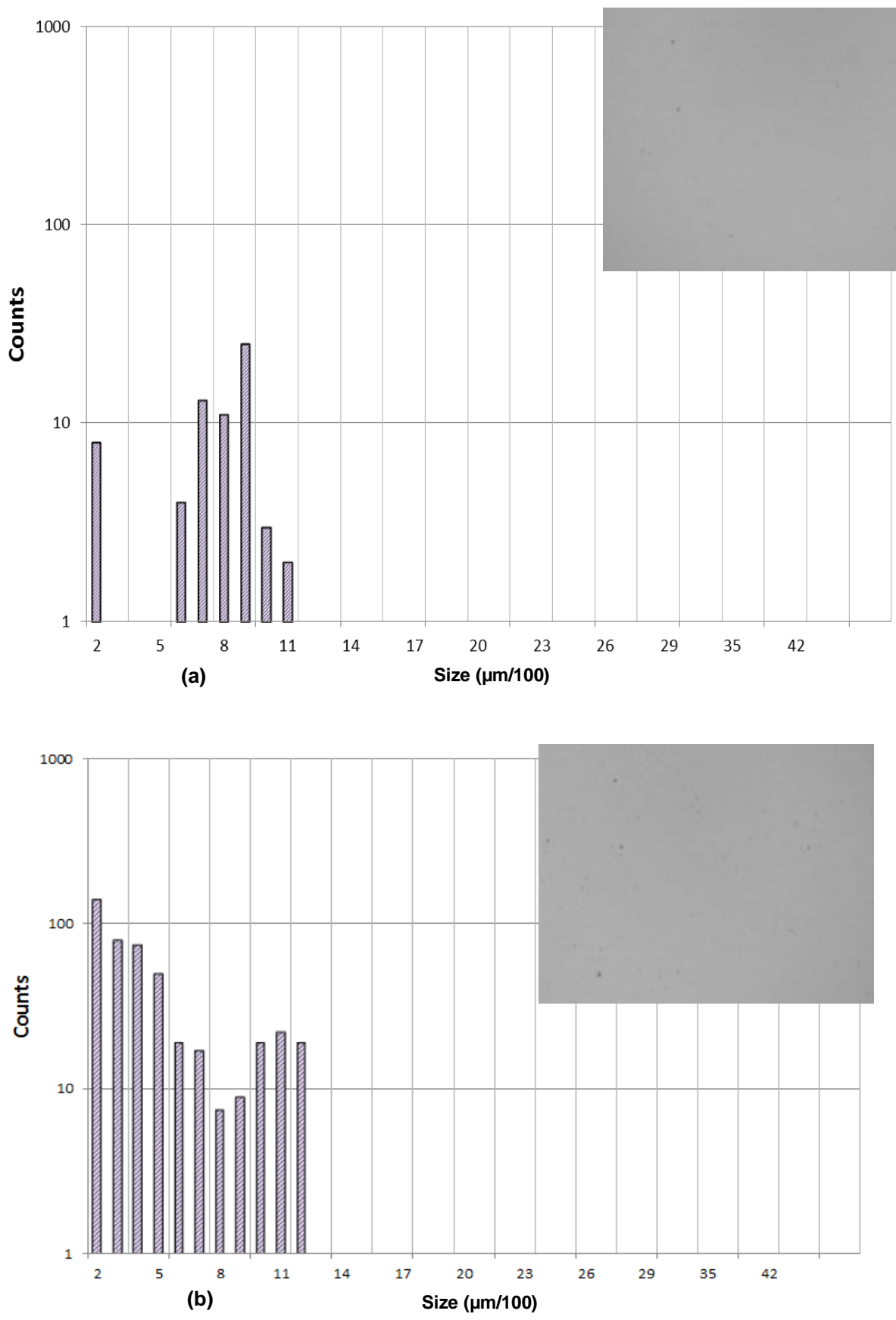**Figure 5.** Particle size analysis at 12000 Psia and 294.3°F for (a) Sample B and (b) Sample A.

Figure 6. Particle size analysis at 7100 Psia and 294.3°F for (a) Sample B and (b) Sample A.
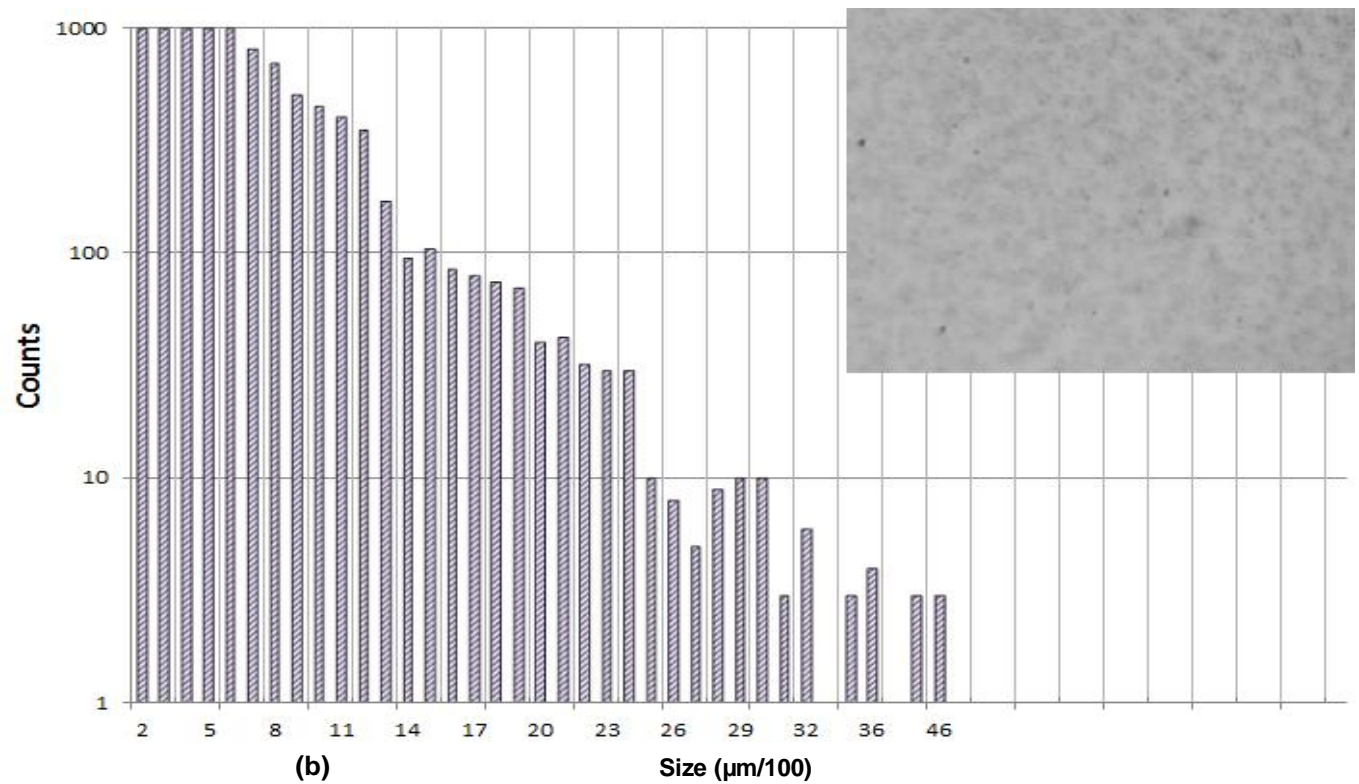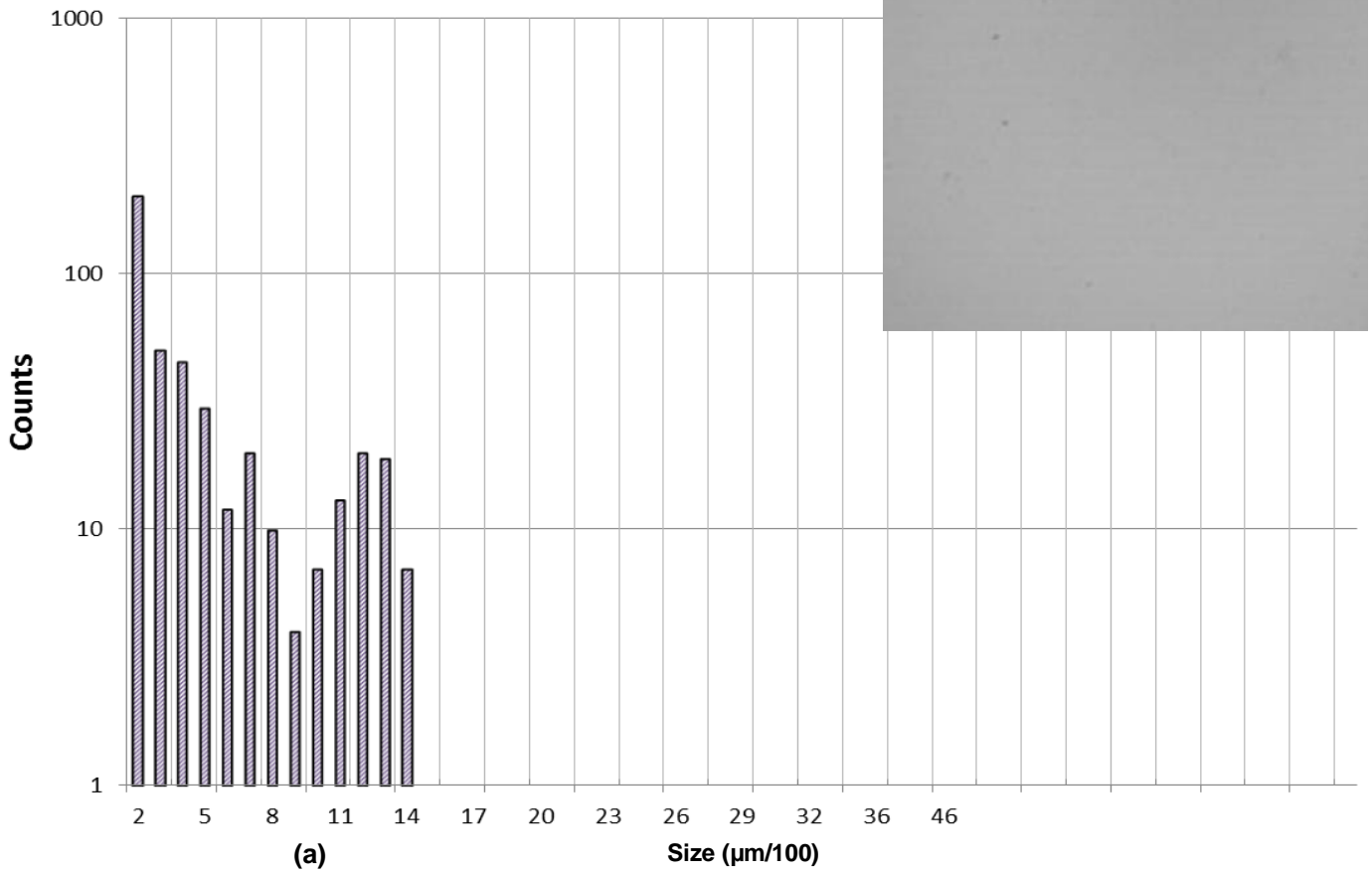
(a)

(b)

Figure 7. Particle size analysis at 5000 Psia and 294.3°F for (a) Sample B and (b) Sample A.
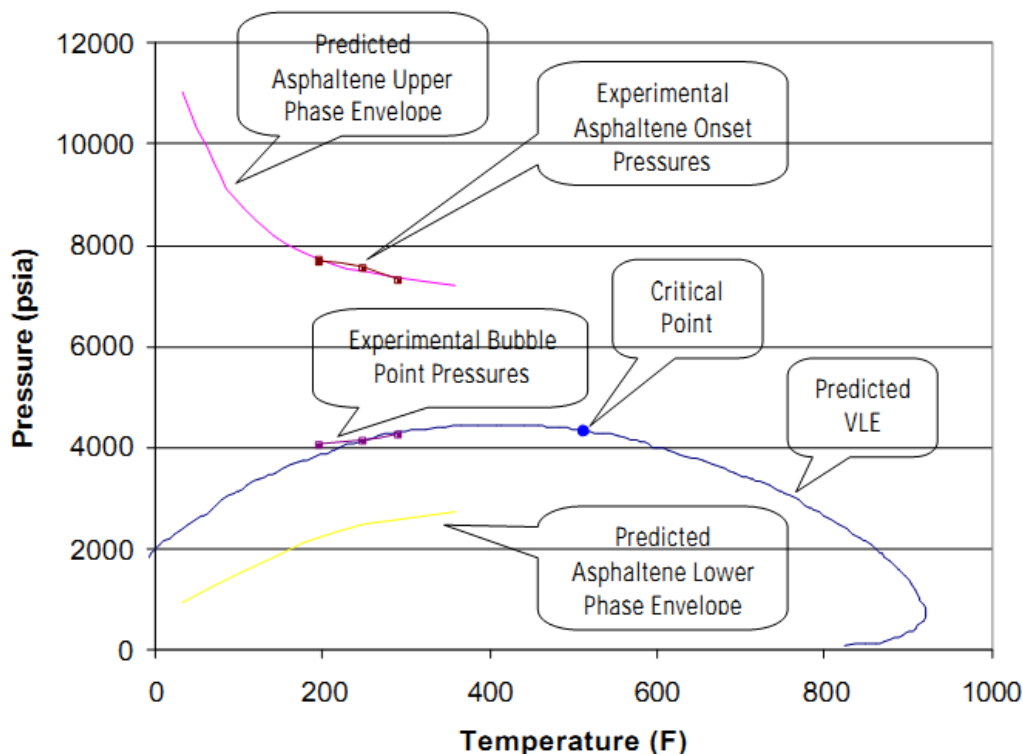
Figure 8. Phase diagram of reservoir fluid and ADE.

Increase in temperature results in fewer numbers and these nuclei are creating at a lower pressure.

Conclusion

The following conclusions were made and they are as follows:

1. By NIR spectroscopy techniques, formation of initial nuclei cusses deflection in normalised light transmittance curve; this is the key point for solid nucleation detection.
2. By visual method (NIR and HPM), increase in temperature results in Asphaltene nucleation to occur in lower pressure.
3. HPM is a more reliable method for studying Asphaltene precipitation problem between visual and quantitative methods.
4. By using visual methods result for as Asphaltene deposition envelope, the maximum precipitation occurred in bubble point pressure.

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