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DETERMINATION OF MISCIBILITY PRESSURE  
BY DIRECT OBSERVATION METHOD

Quarterly Report for the Period

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**MASTER**

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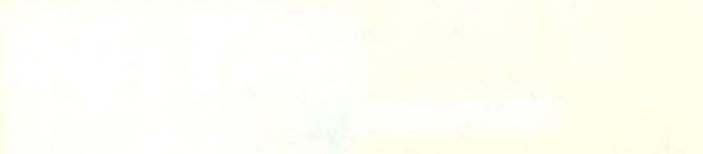
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## Background

The objective of the project is to conduct laboratory tests to:

1. develop a method for determining MMP through direct observation using a high pressure cell;
2. determine feasibility of in-situ foam generation by visual observation and microphotographic technique.

The project is presently organized and carried out in three major fronts, i.e., (1) MMP test; (2) high pressure sampling and chemical analysis; and (3) foam study and displacement test. The technical progress in each of these areas is discussed as follows:

### (A) MMP test

#### SACROC Crude Oil

Investigation of miscibility development for SACROC crude was continued at 72°F and 140°F. Volumetric and phase behavior at 140°F were very similar to that at 120°F as described in the last quarterly report. The principal difference is the higher pressures at which the CO<sub>2</sub>-rich liquid emerged and became miscible with the vapor phase. Again, we have observed that the emergence of a CO<sub>2</sub>-rich liquid phase was the key to the development of a transition zone miscible with both fresh crude oil and the driving CO<sub>2</sub>. At the forward contacts, the CO<sub>2</sub>-rich liquid becomes enriched through multiple contact until it becomes miscible with fresh crude. At the rear of the transition zone, the CO<sub>2</sub>-rich liquid phase becomes miscible with the driving CO<sub>2</sub> at a pressure equivalent to MMP. It is also clear that the regeneration of the CO<sub>2</sub>-rich phase is necessary to maintain a miscible displacement and the absence of CO<sub>2</sub>-rich phase would result in an immiscible type displacement.

For the 72°F experiment, there was no distinguished CO<sub>2</sub>-rich phase as was observed at 120°F and 140°F runs. This is because that as soon as the CO<sub>2</sub>-rich phase was formed, it immediately mixed with the liquid CO<sub>2</sub>. This enriched liquid CO<sub>2</sub> was observed to be miscible with fresh CO<sub>2</sub> but immiscible with the stripped crude. In the later multiple contact experiment, the liquid CO<sub>2</sub> was continuously enriched through contact with drops of fresh crude and finally became completely miscible with crude oil.

This experiment tends to show that for low temperature reservoirs, miscibility could be developed between the liquid CO<sub>2</sub> and crude oil through multiple contact process. The CO<sub>2</sub>-rich liquid phase may be obscured as opposed to those at higher temperatures.

#### Penn-Grade Oil

MMP experiments were conducted on Penn-Grade oil at 84°F, 120°, and 140°F. The CO<sub>2</sub>-rich liquid appeared at 1157 psig and became miscible with vapor phase at 1400 psig in the experiment at 120°F. At 140°F, the pressure at which CO<sub>2</sub>-rich phase emerged and became miscible with the vapor phase were 1300 psig and 1481 psig, respectively.

### Slaughter Estate Crude Oil

Experiments conducted on Slaughter Estate at 72°F, 120°F, and 140°F produced volumetric behavior similar to that exhibited by SACROC oil. The key difference was that the pressures at which the CO<sub>2</sub>-rich phase emerged and became miscible with CO<sub>2</sub> vapor were higher. Also, the amount of asphaltic precipitation that fell out of this oil were so great that a large part of the sight glass was obscured.

### Rock Creek Oil

Experiments conducted on Rock Creek oil at 70°F, 120°F, and 140°F produced results very similar to those of Penn-Grade crude oil. Both crudes exhibited large swelling factors from 1.7 to 1.8 at 120°F and 140°F. The amount of CO<sub>2</sub>-rich liquid generated was much greater in the experiments at 120°F and 140°F.

Special attention was given to the experiment conducted on Rock Creek oil at 70°F, its true reservoir temperature. Swelling of the crude oil phase began at approximately 515 psig and continued up to 880 psig to reach its maximum swelling factor of 1.4. At this point, the CO<sub>2</sub> began to enter the system in liquid phase and the crude oil phase was observed to shrink, indicating that the major extraction of hydrocarbons by liquid CO<sub>2</sub> had begun. As described earlier in the SACROC experiment, it was almost impossible to identify a distinct CO<sub>2</sub>-rich liquid column due to the mixing nature of CO<sub>2</sub>-rich phase and liquid CO<sub>2</sub>. When fresh crude oil was charged, it liquid CO<sub>2</sub> was further enriched and changed its color from misty-white to yellow and then became miscible with crude oil.

### Gilbertown Crude Oil

Gilbertown crude oil is a 17° API from southwest Alabama. A swelling factor of 1.3 was observed at 120°F as compared to 1.13 and 1.1 at 140°F and 74°F.

In the experiment at 120°F and 140°F, only a thin layer of CO<sub>2</sub>-rich liquid was generated at approximately 1250 psi and became miscible with vapor at 1400 psi and 1550 psi in the 120°F and 140°F experiments, respectively. Because of the scanty amount of CO<sub>2</sub>-rich liquid, miscible condition with the crude oil was never observed.

The effects of temperature on MMP and appearance of CO<sub>2</sub>-rich phase for each of the four crude oils tested are plotted on Figures 1-5. The MMP is the pressure at which the CO<sub>2</sub>-rich phase becomes miscible with CO<sub>2</sub> vapor.

### Comparison with Other MMP Techniques

In order to verify the results from the study, comparisons have been made with published Yellig and Metcalf correlations. In Figure 6, the observed MMP are superimposed on the correlation curve. While the majority of MMPs determined by direct observation fall within the limits of the



correlation, our data appear to show slightly low MMP at higher temperatures. This would be expected since they used recombined reservoir oil rather than stock tank oil in their displacement tests. The MMP would be higher to obtain a comparable recovery for a recombined reservoir oil than for a stock tank oil because of methane content.

Comparison of MMP was also made with Maljamar crude oil. The MMP of stock tank Maljamar crude determined by slim tube displacement tests at the New Mexico Petroleum Recovery Research Center (NMPRRC) was 1200 psi at 90°F. The direct observation study at our laboratory indicates that an upper CO<sub>2</sub>-rich liquid phase emerged at 1025 psi and became miscible with CO<sub>2</sub> vapor at 1181 psi. This compares favorably with NMPRRC's results.

#### (B) Sampling and Chemical Analysis

The Hewlet-Packard 5880-A gas chromatograph has been tested and a BASIC program has been incorporated with the unit to determine C<sub>5</sub> to C<sub>36</sub>. The results of analysis for the four crude oils tested are shown in Figure 7. It is obvious that the SACROC crude oil is the richest in C<sub>5</sub> to C<sub>20</sub> components, followed by Penn-Grade, Slaughter Estate and Gilberttown crude oils. The deficiency of C<sub>5</sub> to C<sub>20</sub> in the Gilberttown oil may explain why no miscibility between the CO<sub>2</sub>-rich liquid and crude oil was observed. As previously stated that the richness of C<sub>5</sub> to C<sub>20</sub> components is the key factor for determining the quality and stability of the miscible transition zone.

#### (C) Foam Displacement Test

##### Apparatus and Procedure

The high pressure foam testing unit has been revised as shown in Figure 8. The system has a working pressure of 3000 psi at 140°F. The foam generator was constructed using a 3-inch piece of 1/8-inch stainless tubing for the body, and glass wool as the packing material; two small metal screens were placed at the two ends to prevent glass wool being flushed out. Preliminary testing of the packing materials indicated that the glass wool is more effective in generating foam than glass beads for a practical CO<sub>2</sub> injection rate of approximately 8 cc/hr; this can be explained as glass wool's greater surface area promotes more mixing between CO<sub>2</sub> and surfactant solution. The generator has porosity and permeability of approximately 70% and 8 darcies respectively.

The observation cell is a Jerguson liquid level indicator with a linear scale attached to the outside of the glass window. A conversion factor of 3.79 cc/cm was calculated for this cell to convert from height into volume.

Surfactant solution is supplied by an adjustable rate pump made by Milton Roy Co.. Carbon dioxide is supplied by a custom made rod-cell; the CO<sub>2</sub> rate is controlled by a Ruska positive displacement pump pumping water into the lower part of the cell to move a rod connected piston separating the two fluid chambers, the upward moving piston displaces CO<sub>2</sub> into the foam generator, and the rod indicates the relative position of the piston.

The surfactant solution used in the test was prepared by adding Alipal CD-128 into distilled water to a concentration of 0.5% by volume.

The system is first charged with liquid CO<sub>2</sub>, and the heater is then turned on to bring it to the desired temperature. After the temperature is stabilized, the outlet pressure is set by adjusting the CO<sub>2</sub> pressure and the back pressure regulator. The CO<sub>2</sub> pump and the surfactant pump are then turned on to begin the injection of these two fluids into the foam generator. It will take approximately one hour before the foam first appears in the observation cell. The foam level in the observation cell, CO<sub>2</sub> and surfactant injection pressure, system pressure and the surfactant level in the reservoir are recorded at this instant. The system is left to continue without altering the running condition and readings are taken again after one hour interval. The increase in foam level and the surfactant level are determined which are then used to calculate foam quality.

The CO<sub>2</sub> rate was kept constant at 8.1 cc/hr for every run. Different surfactant rates were tested to study the effect on foam quality and foam quantity at a particular temperature-pressure condition. The process was repeated to study the effect of pressure on foam properties by generating foam at different system pressures: 1000, 1500 and 2000 psi. Tests at different temperatures of 75, 120 and 140°F were also performed.

### Results and Discussion

Because the densities of carbon dioxide are changed with temperatures and pressures, CO<sub>2</sub> mass flow rates were calculated to provide the basis for analysis. The surfactant/CO<sub>2</sub> ratio relative to foam quality and foam quantity are presented in Table 1 and plotted in Figures 9 to 14.

Figures 9, 10 and 11 show the foam qualities increased as the surfactant rates are decreased. At 75°F, the foam quality increases as the pressure is decreased whereas the reverse is true for temperature at 120°F. The reversal in behavior could be true since CO<sub>2</sub> is existed at 75°F in liquid phase and in gas phase at 120°F. For CO<sub>2</sub> injection rate of 8.1 cc/hr, foam did not appear at 1000 psi-120°F, 1000 psi-140°F and 1500 psi-140°F.

Figures 12, 13 and 14 show foam generating rate increase with increasing surfactant/CO<sub>2</sub> ratio. High temperatures tend to lower the rate and high pressures tend to increase the rate at 120°F but to decrease at 75°F. Foam quality was found to be affected more by surfactant/CO<sub>2</sub> ratio, and to a lesser degree by pressures and temperatures. For a specific foam quality and gaseous CO<sub>2</sub>, more foam would be generated at higher pressures, however, the reverse is true whereas the CO<sub>2</sub> is liquid.

More testings are being planned to study the effects of foam properties in relation to brine and crude oil before conclusions can be drawn to which surfactant /CO<sub>2</sub> ratio is the best for later uses in foam flooding tests.



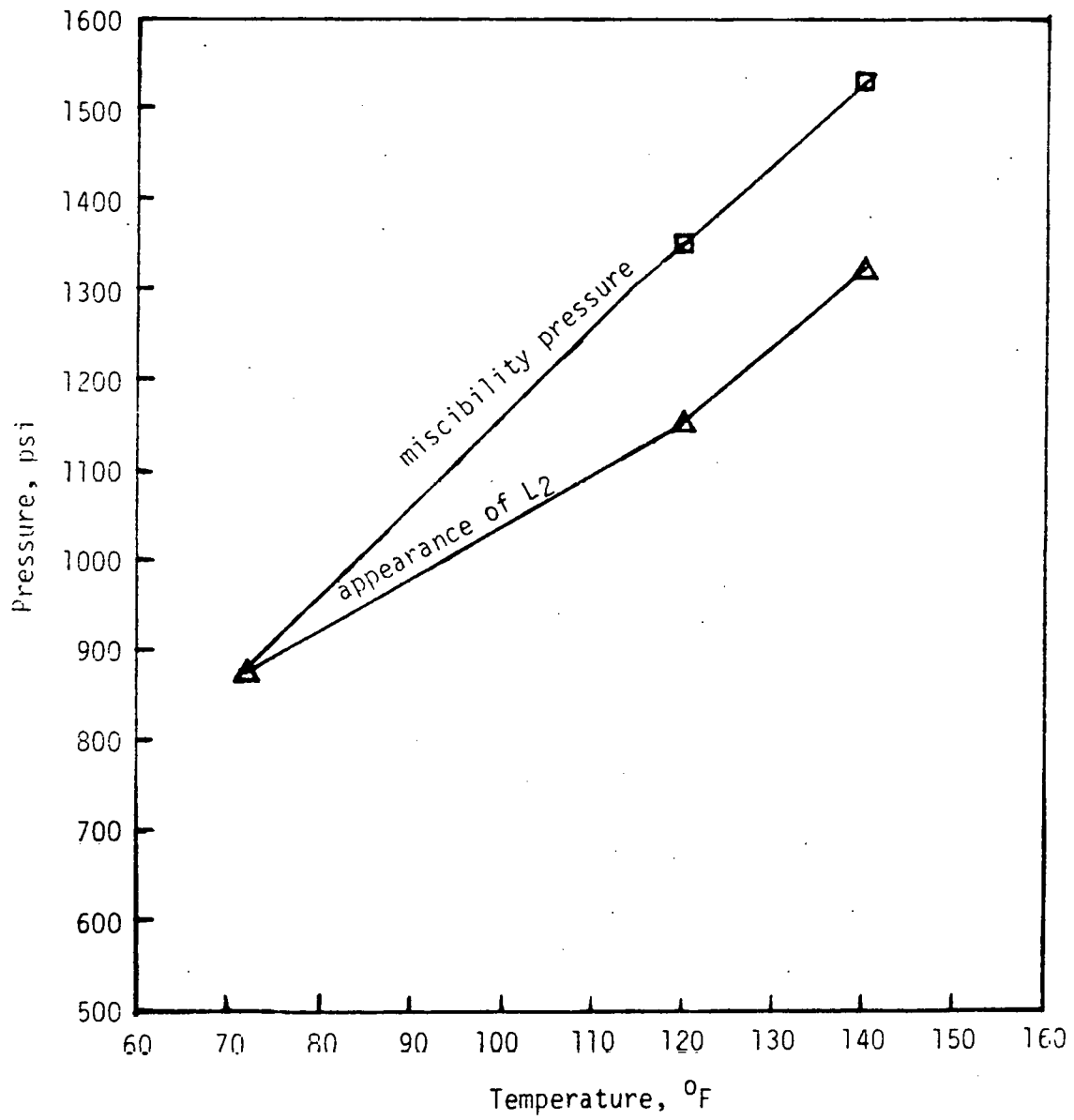


Figure 1. SACROC Crude Oil-CO<sub>2</sub>  
MMP vs. Temperature

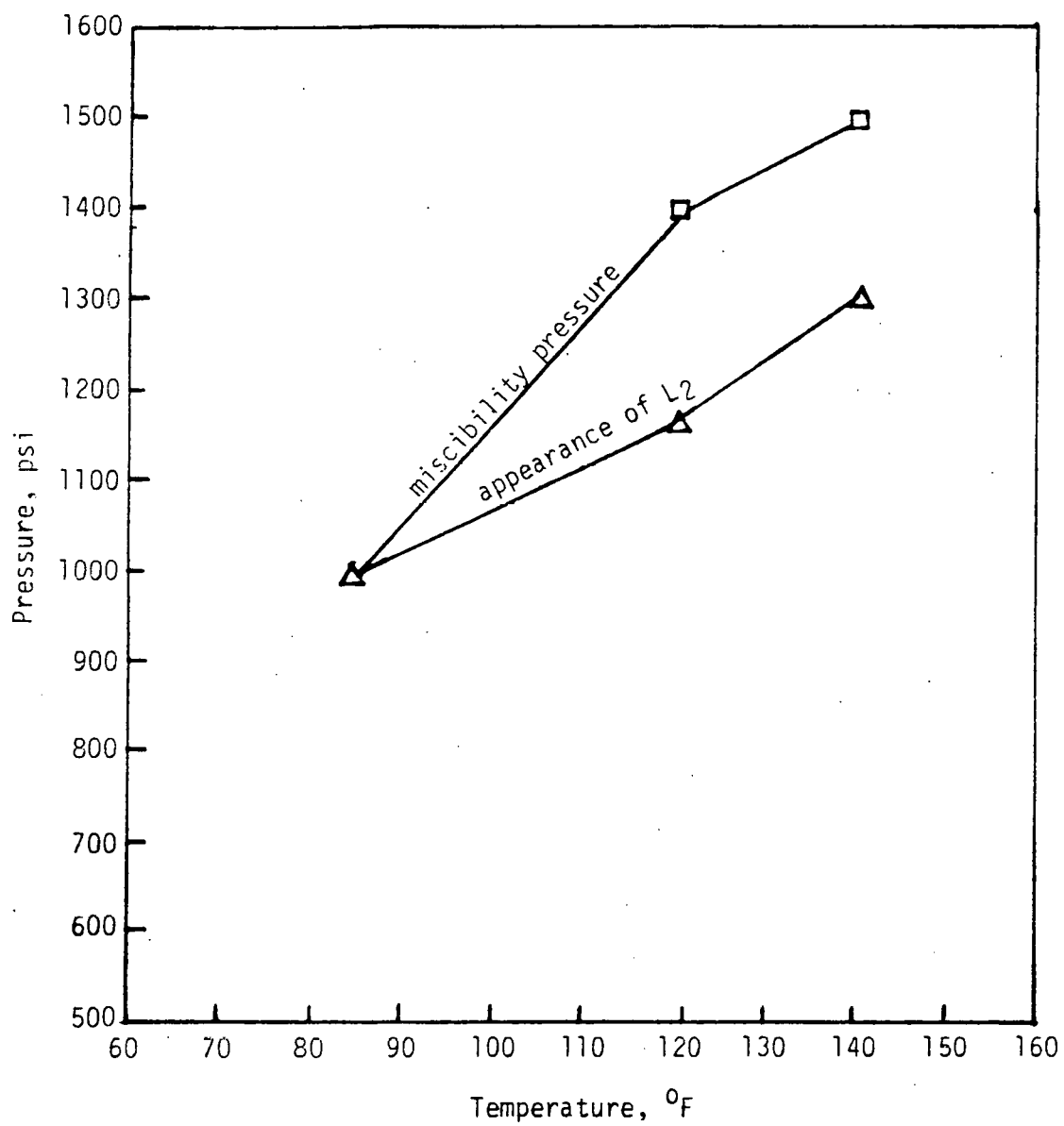


Figure 2 . Penn-Grade Crude Oil MMP vs. Temperature

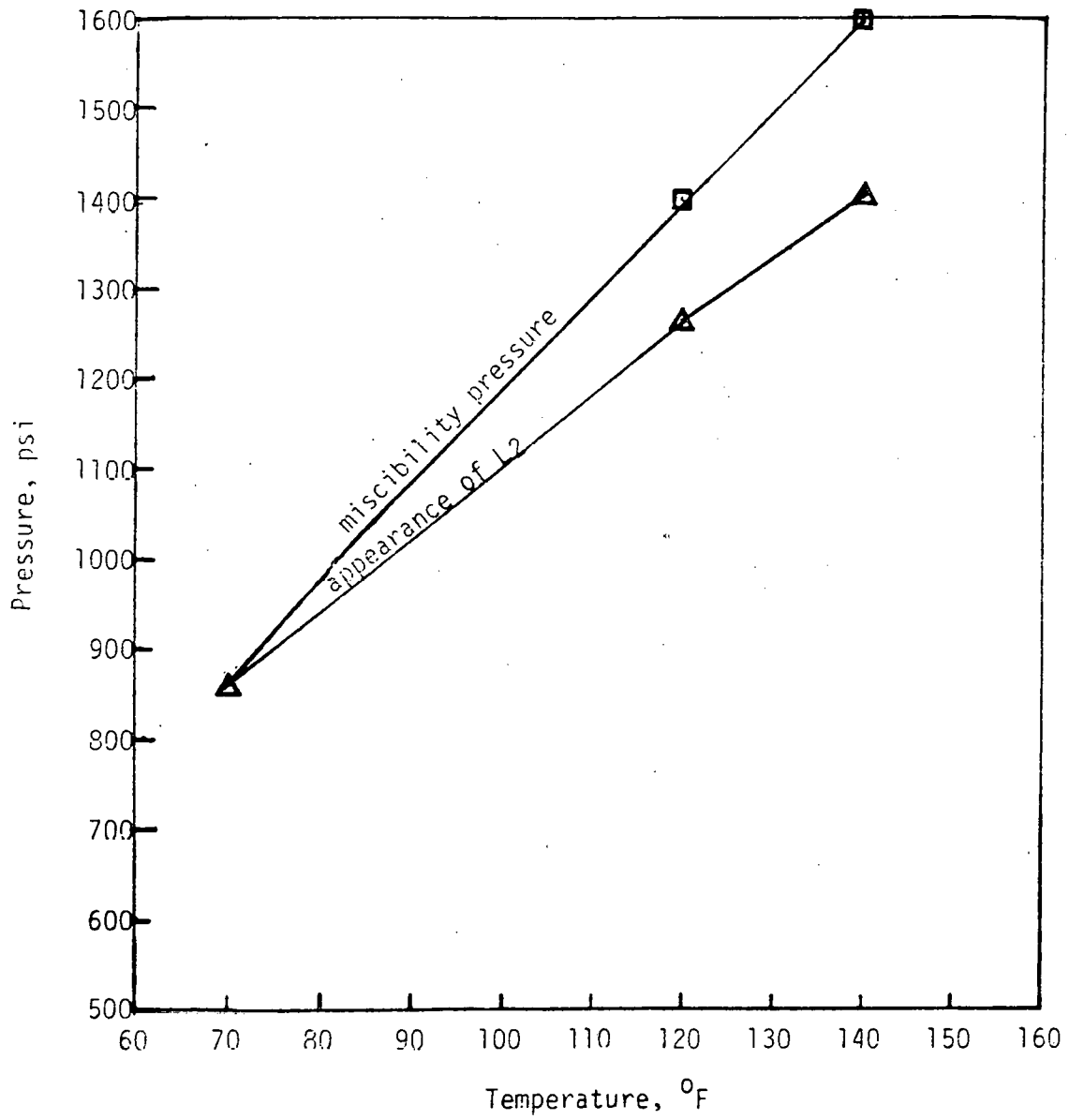


Figure 3 . Slaughter Estate Crude Oil  
MMP vs. Temperature

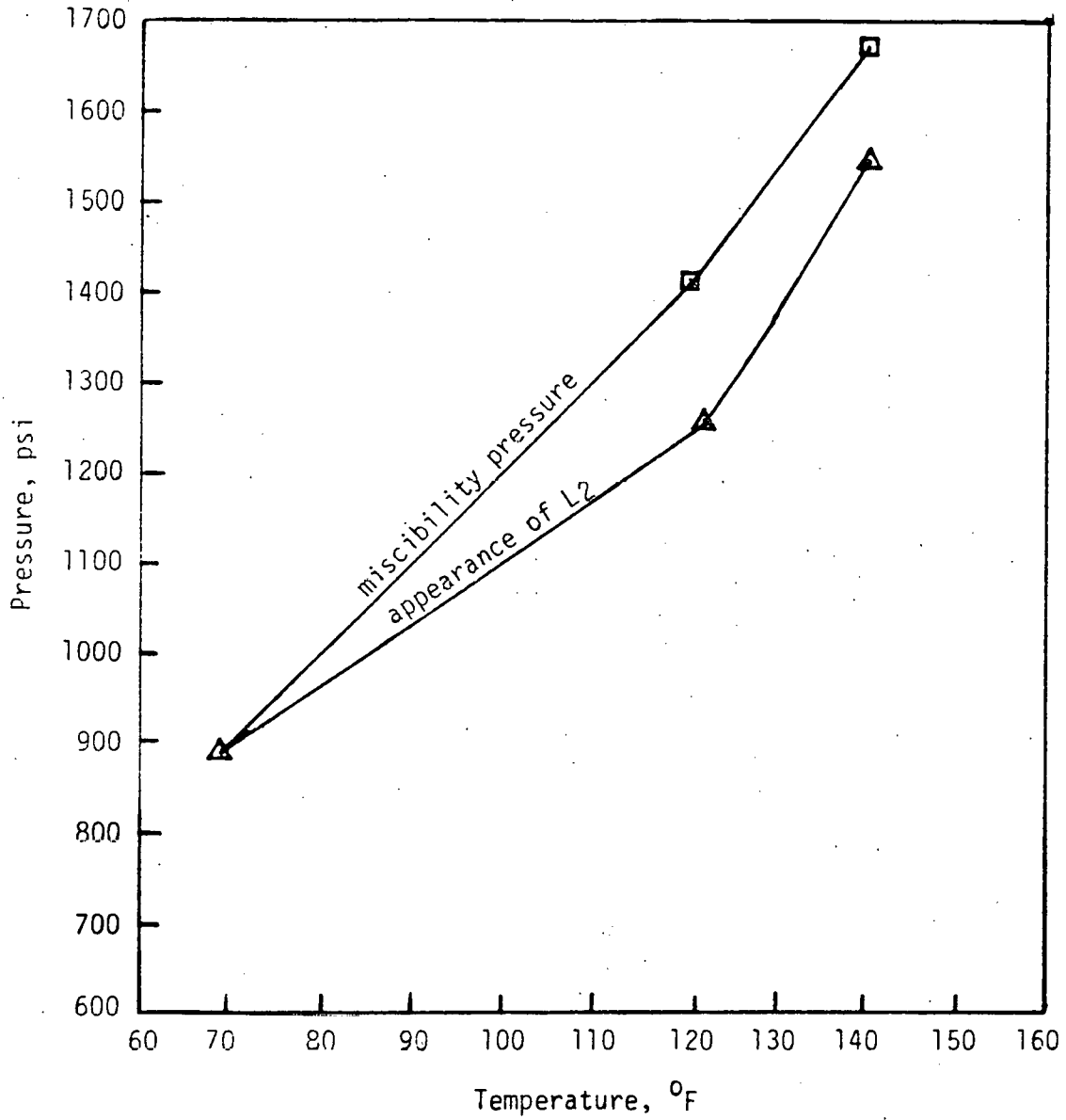


Figure 4 . Rock Creek Crude Oil MMP vs. Temperature

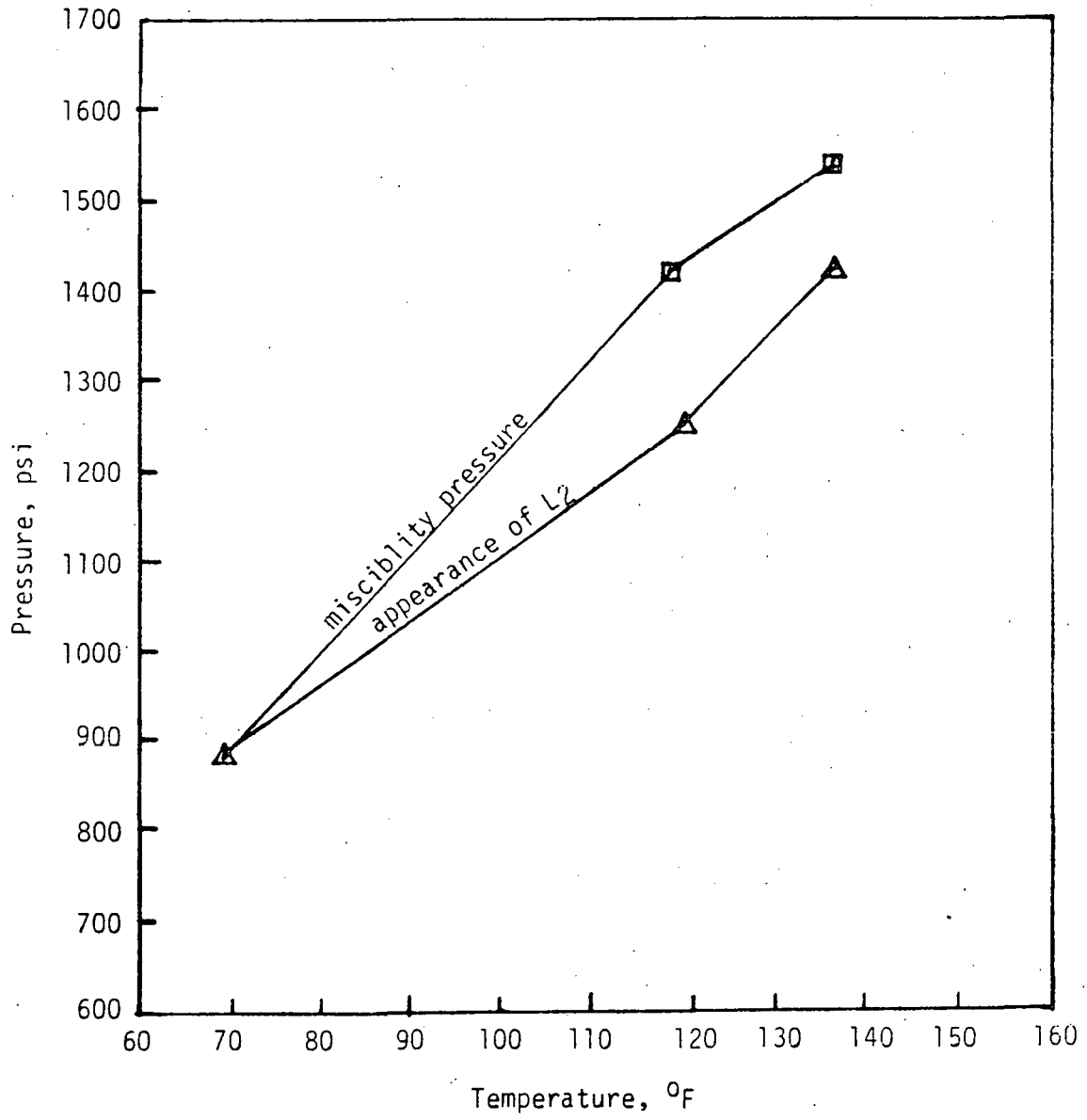


Figure 5 . Gilberttown Crude Oil MMP vs. Temperature

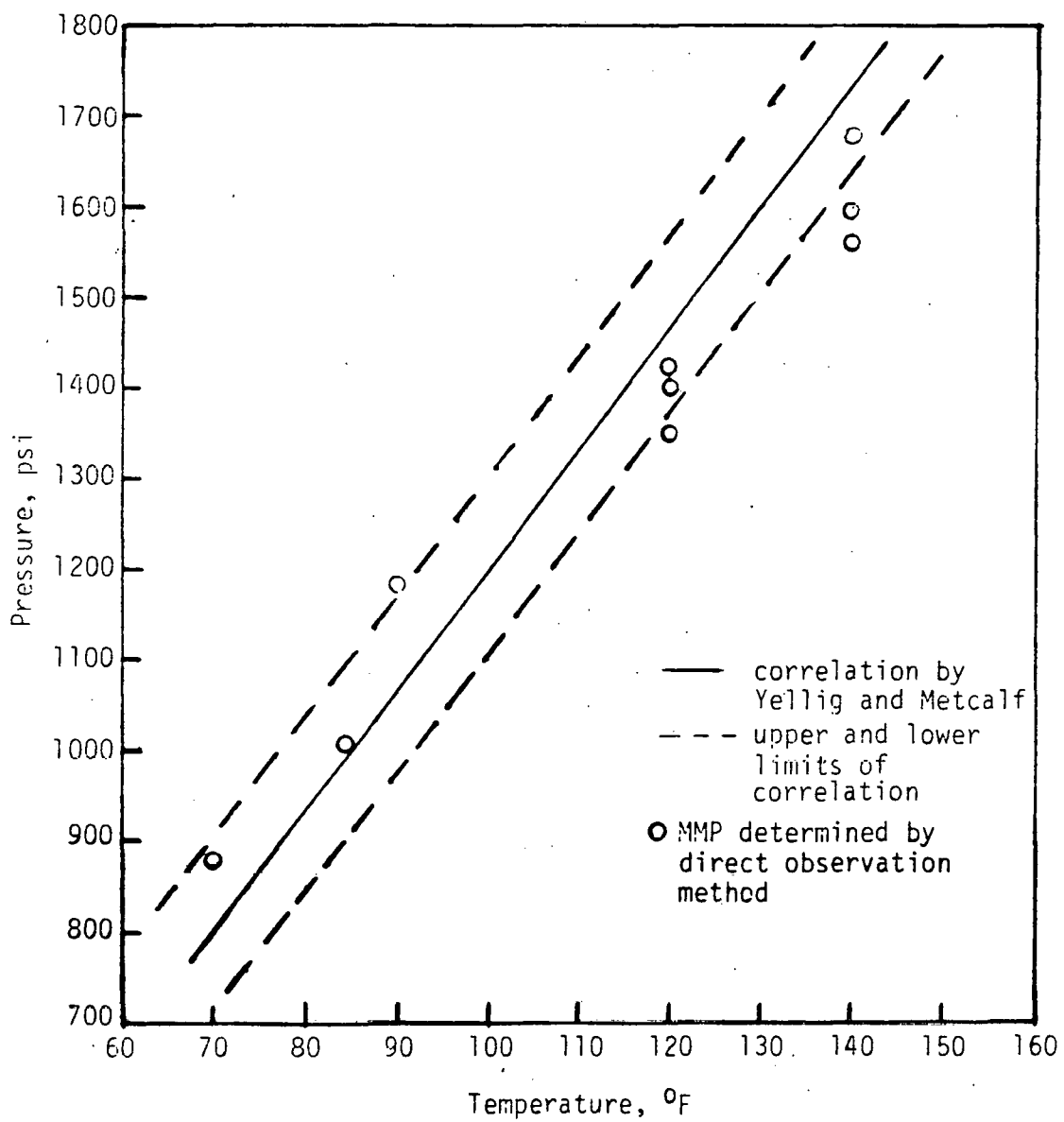


Figure 6 . CO<sub>2</sub>-Crude Oil MMP Correlation  
Developed by Yellig and Metcalf

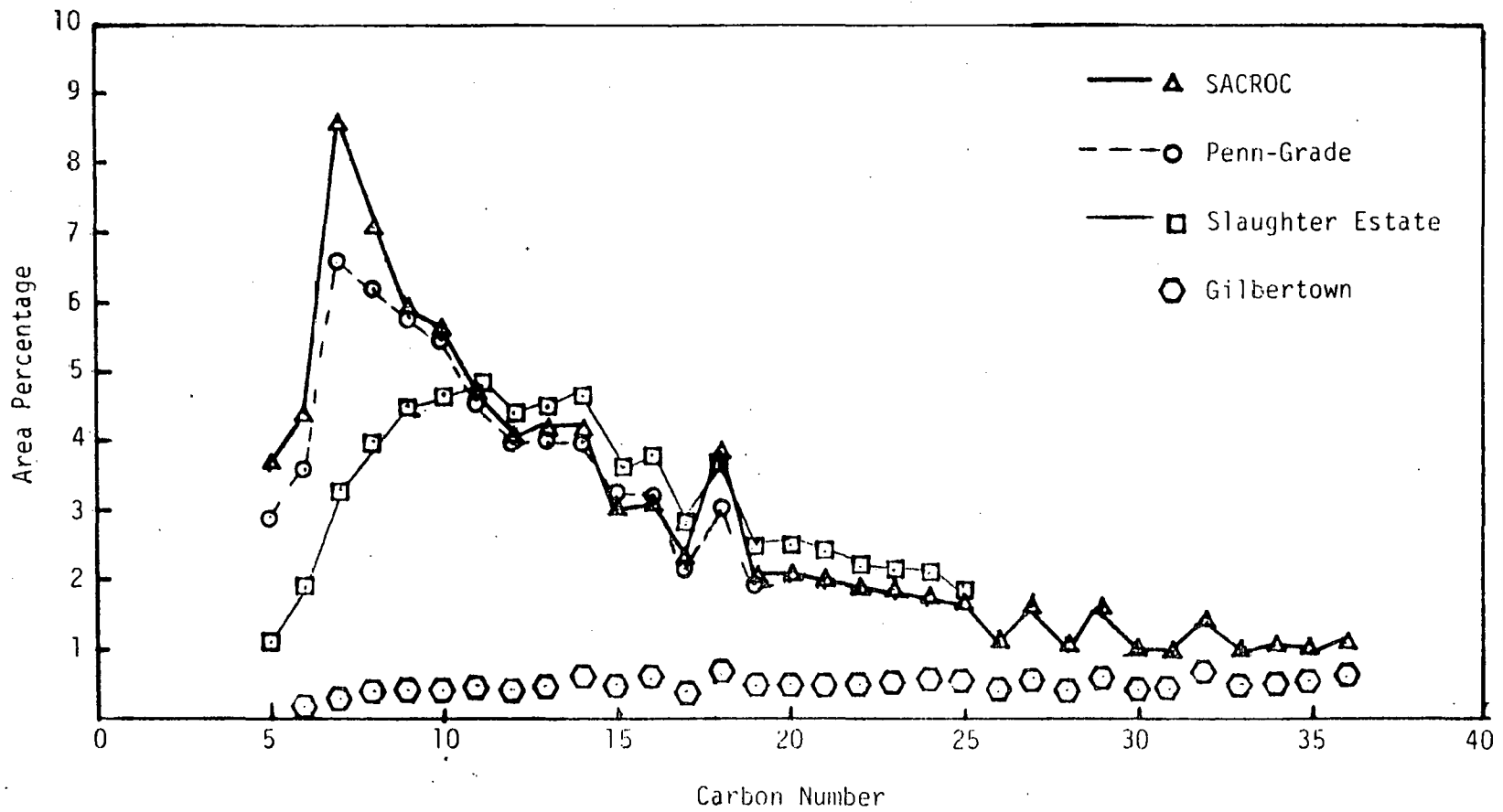
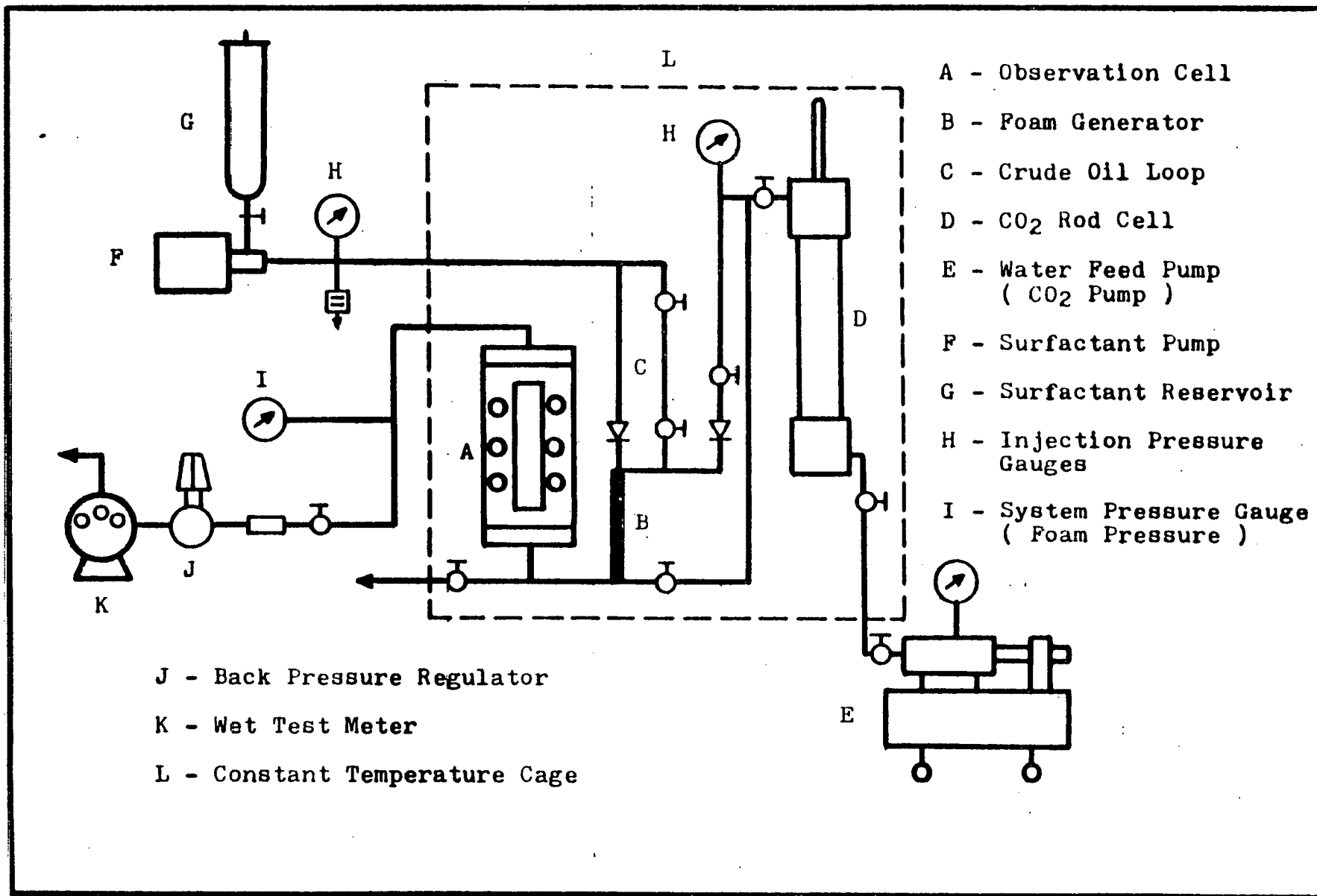


Figure 7 . Component Area Percentage vs. Carbon Number  
for Crude Oils Studied



Figure 8 - Laboratory Set-Up for CO<sub>2</sub>-Surfactant Foam Generating.



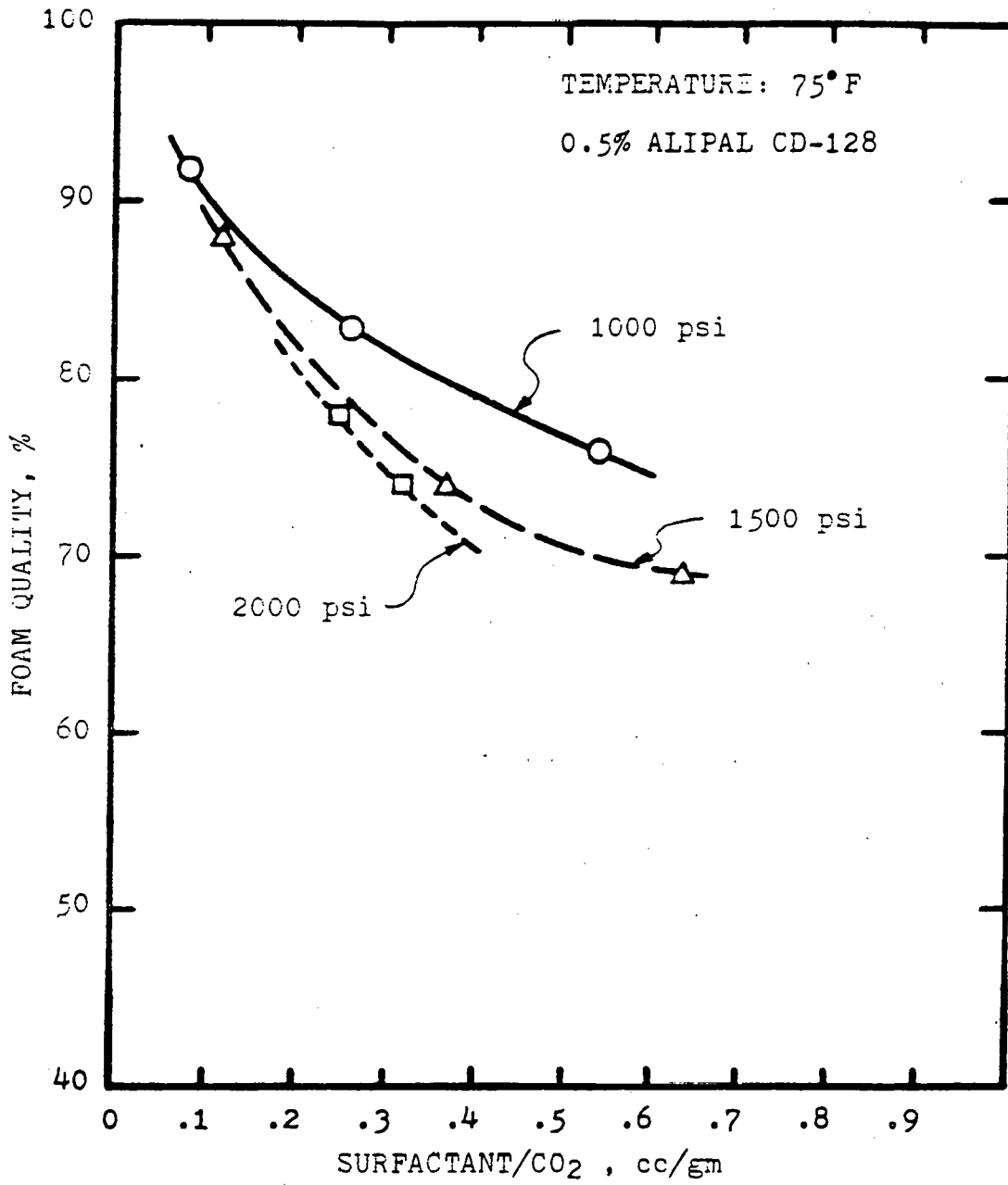


Figure 9 - Effect of Surfactant/CO<sub>2</sub> ratio on Foam Quality at 75°F.

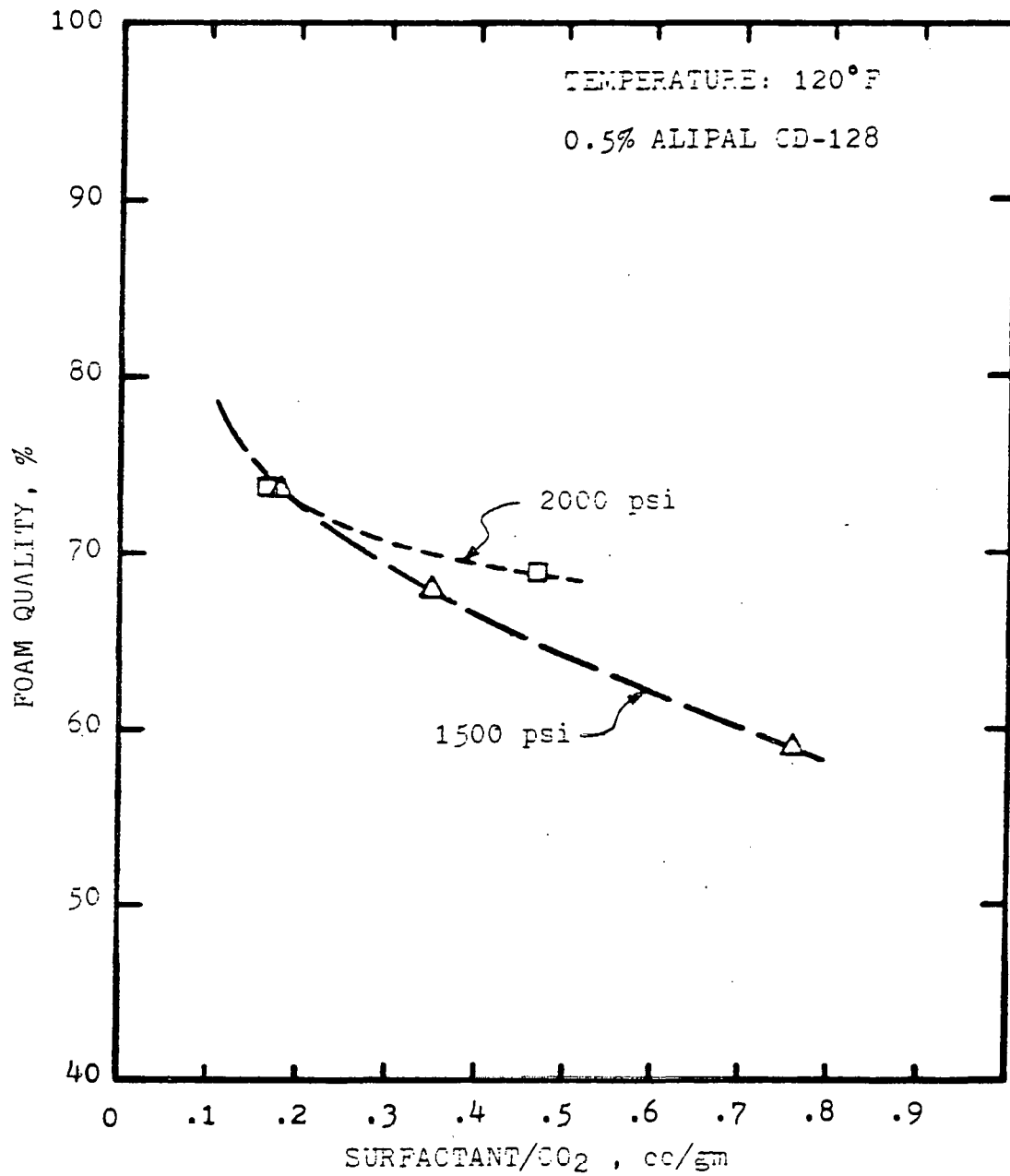


Figure 10 - Effect of Surfactant/CO<sub>2</sub> ratio on Foam Quality at 120°F.

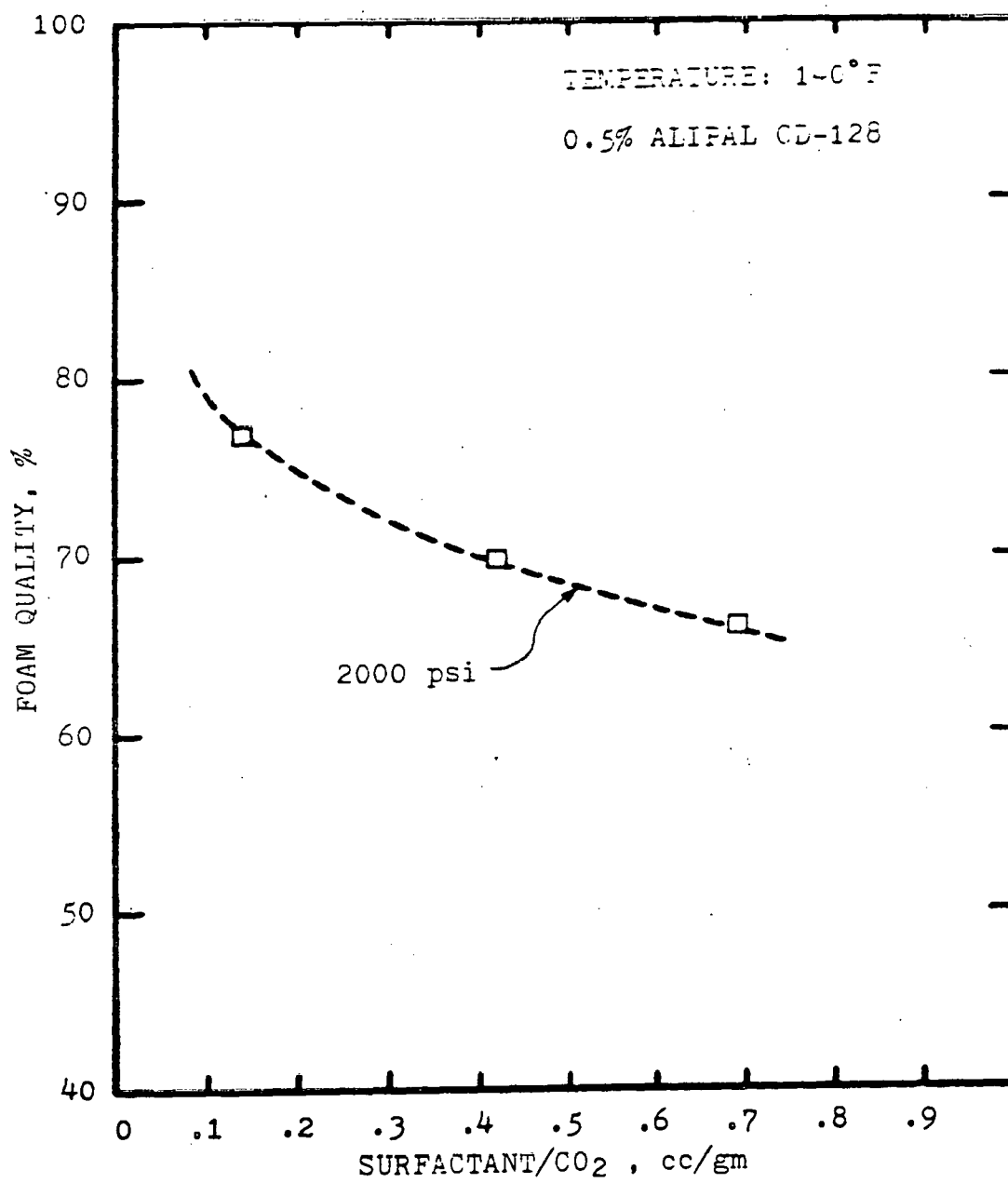


Figure 11 - Effect of Surfactant/CO<sub>2</sub> ratio on Foam Quality at 140°F.

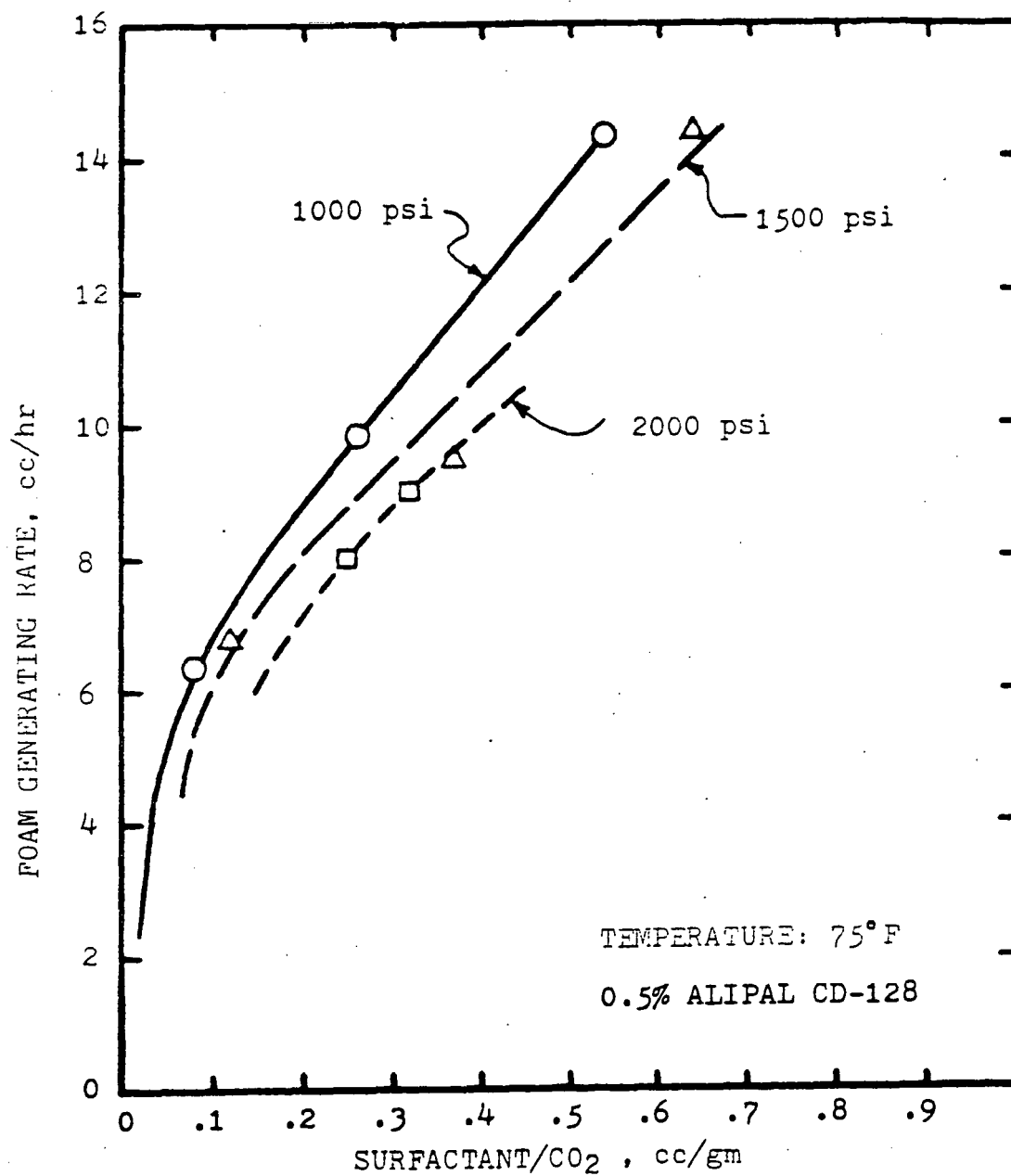


Figure 12 - Effect of Surfactant/CO<sub>2</sub> ratio on Foam Quantity at 75°F.

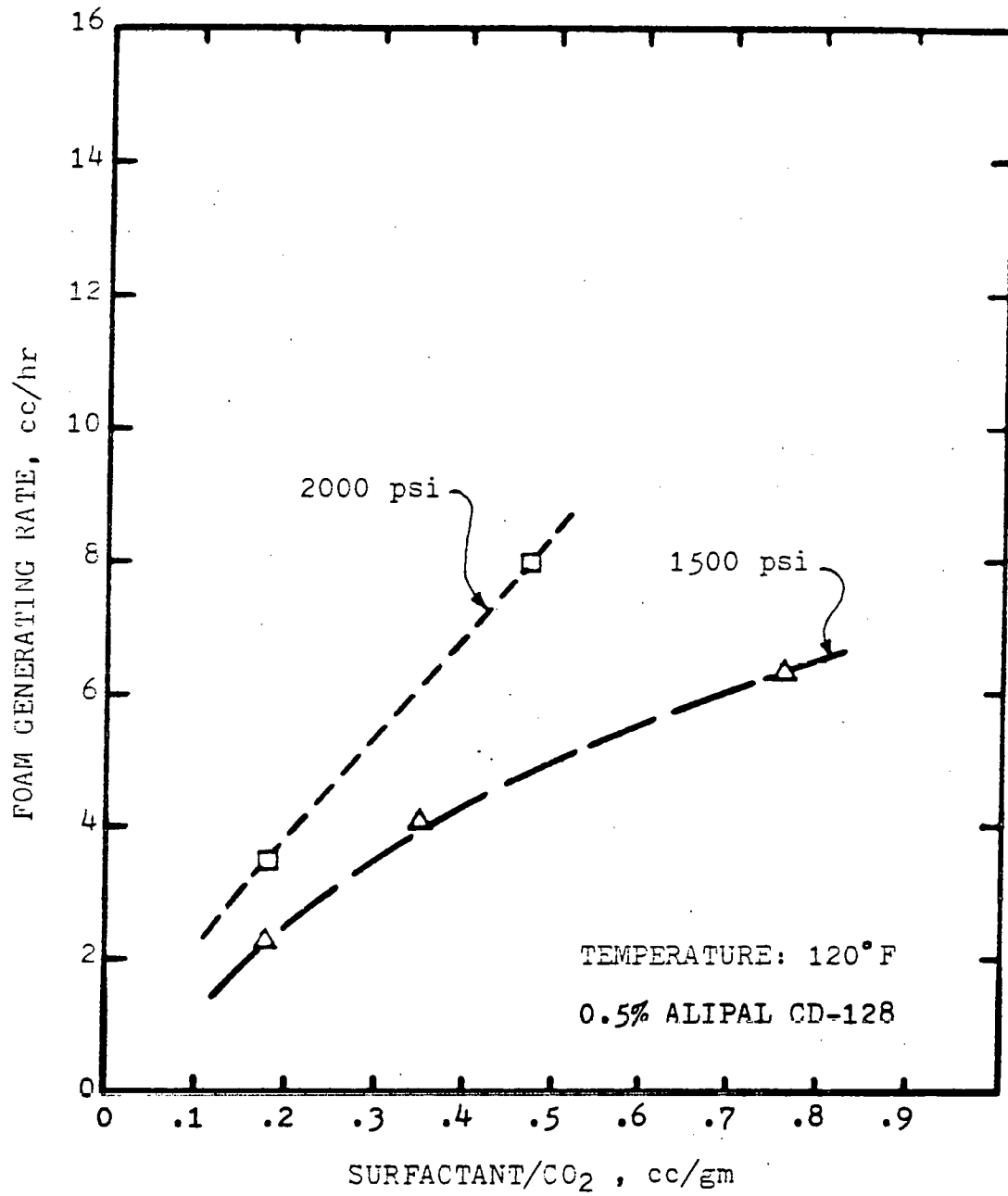


Figure 13 - Effect of Surfactant/CO<sub>2</sub> ratio on Foam Quantity at 120°F.

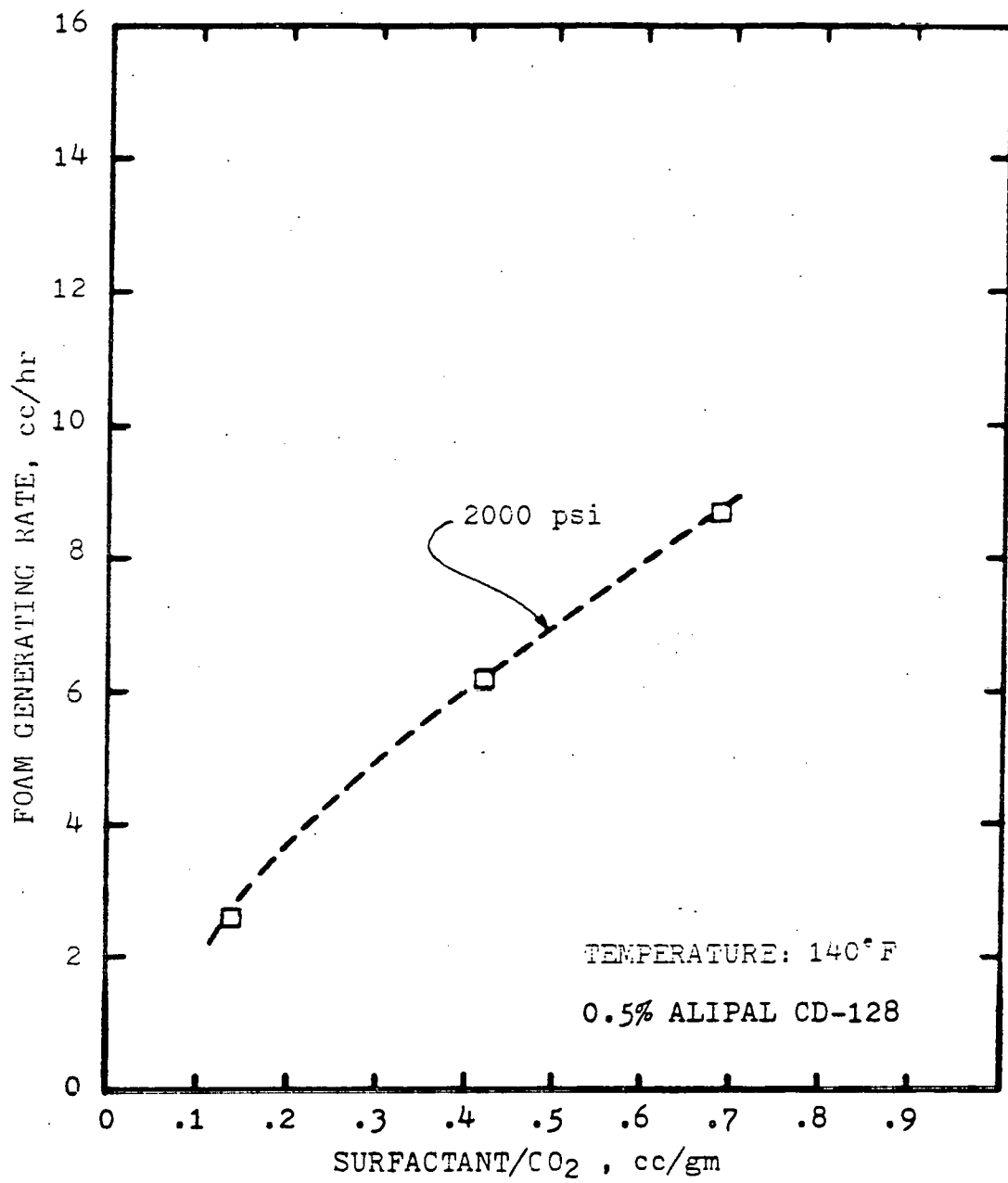


Figure 14 - Effect of Surfactant/CO<sub>2</sub> ratio on Foam Quantity at 140°F.



Run #	Foam Pressure (psi)	Foam Temperature (°F)	Injection Pressure (psi)	CO <sub>2</sub> Inj. Rate (cc/hr)	Surfactant Inj. Rate (cc/hr)	Foam Gen. Rate (cc/hr)	Foam Quality (%)	CO <sub>2</sub> Mass Flow Rate (gm/hr)	Surfactant/CO <sub>2</sub> (cc/gm)
0308M	1000	75	1200	8.1	1.7	9.8	83	6.49	0.26
0309A	990	75	1235	8.1	3.5	14.4	76	6.51	0.54
0310M	1000	76	1090	8.1	0.5	6.4	92	6.35	0.08
0304P	1500	75	1620	8.1	2.5	9.5	74	6.83	0.37
0305A	1490	75	1590	8.1	0.8	6.8	88	6.81	0.12
0310P	1465	75	1640	8.1	4.4	14.4	69	6.84	0.64
0225M	2000	76	2190	8.1	2.3	8.8	74	7.14	0.32
0302P	2005	75	2115	8.1	1.8	8.0	78	7.09	0.25
0311A	1500	121	1645	8.1	1.3	4.1	68	3.68	0.35
0315A	1480	121	1575	8.1	2.6	6.4	59	3.44	0.76
0315P	1495	121	1570	8.1	0.6	2.3	74	3.43	0.18
0316A	2000	120	2135	8.1	2.5	8.0	69	5.28	0.47
0316P	1980	120	2100	8.1	0.9	3.4	74	5.26	0.17
0319M	2005	139	2095	8.1	1.8	6.1	70	4.28	0.42
0322A	2000	140	2080	8.1	0.6	2.6	77	4.26	0.14
0322P	2030	140	2150	8.1	3.0	8.7	66	4.35	0.69

Table 1 - Summary of Test Results for CO<sub>2</sub>-Surfactant Foam Generating.