THE EFFECTS OF PETROLEUM RESERVOIR CONDITIONS ON
OIL RECOVERY BY CARBON DIOXIDE INJECTION

By

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by

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ABSTRACT

Several petroleum reservoir conditions were evaluated to determine their effects on oil recovery by CO₂ injection. The conditions studied were reservoir temperature, reservoir pressure, and CO₂ slug injection size. With constant pressure, the reservoir temperature was varied from 75° to 130°F, and optimum oil recovery was obtained at a temperature near the critical temperature of CO₂ (87.8°F). When the temperature was held constant and the reservoir pressure varied from 650 to 1800 psi, it was found that miscibility pressure may be above but close to 1800 psi.

The CO₂ slug injection size has been varied from 3 percent to over 40 percent PV to determine if oil recovery would increase with increase of CO₂ slug size. Graphic representation of the results show that a maximum slope is reached between 12 and 15 percent PV. Above 15 percent the slope becomes smaller. It is concluded that optimum oil recovery lies between 12 and 15 percent PV, and the additional oil recovered, above a 15 percent PV CO₂ slug, would not warrant the increased cost of the CO₂.

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INTRODUCTION

Background

Over the many years that the petroleum industry has been producing oil from petroleum reservoirs, only 20 to 40 percent of the original oil-in-place has been recovered. Primary production by pressure release or pumping recovers from 20 to 30 percent, and secondary production (waterflooding) increases that recovery to about 40 percent of the original oil-in-place. This leaves 60 percent of that original oil in the reservoir which the petroleum industry has considered to be unrecoverable by established commercial methods. The recovery of half of this remaining oil can make our country independent of foreign oil imports.

Many investigations have been made to develop methods by which a significant part of this remaining oil can be recovered. Carbon dioxide flooding has been found to be a meaningful oil recovery process which, in most cases, can increase the oil recovered from 40 to 70 percent or more of the original oil. Also, special improved carbon dioxide methods can increase that oil recovery to almost 89 percent (1).

The use of carbon dioxide injection has been studied as a secondary (2-6) and as a tertiary (7,8) oil recovery method. Its use as a tertiary method is limited to those oil reservoirs that can be effectively and economically waterflooded. While in reservoirs where waterflooding is not effective (for example the Appalachian area), carbon dioxide as a secondary recovery method can be used for substantial oil recovery. A past, present, and future outlook for CO₂ flooding has been presented by Stalkup (9).

Objectives

The Enhanced Oil Recovery laboratories of the Morgantown Energy Technology Center of Morgantown, West Virginia, have been investigating ways of improving the carbon dioxide flooding method and also determine mechanisms by which carbon dioxide can recover oil from oil-bearing rock strata. The effects of some of the conditions that govern oil recovery are the petroleum reservoir conditions over which we can exercise little or no control. These include reservoir temperature, pressure, permeability and oil viscosity, oil hydrocarbon composition, etc. One of the few conditions we can control is the CO₂ slug injection size. To maximize oil recovery, these conditions are being studied.

The present report is concerned with the effects of pressure, temperature, and CO₂ slug injection size. Each reservoir has the distinction of having (among other conditions) certain pressure and temperature ranges which are quite narrow. Both these conditions depend upon the depth of the reservoir. The temperature, which may have slight variations, is fixed, so we cannot change that without sending huge amounts of heat down the reservoir at a tremendous cost. The pressure can be varied within limits, either by applying a back pressure to the production well to increase pressure or by pumping the production well to decrease the pressure. Decreasing the pressure would, of course, incur higher costs but may shorten production time. On the other hand, increasing the pressure would be a simple matter of applying a back pressure. But there are limits on increasing the pressure, and the main consideration is not to exceed the overburden pressure.

One of the most important factors in the use of liquid carbon dioxide is the slug size for one injection followed by flooding with brine. Alternating slugs of CO₂ and brine is only briefly discussed and should be the subject for another report. In this report the whole CO₂ slug is injected at one time. The importance of studying the CO₂ slug size is the optimum recovery of oil and the associated cost of the CO₂. As the CO₂ slug size is increased, the cost of CO₂ increases as do the transportation and equipment and design costs. Therefore, the increased revenue from additional oil recovery must be greater than the increased costs. The purpose of this study was to determine the optimum CO₂ slug size that would provide maximum oil recovery at a reasonable cost.

EXPERIMENTAL PROCEDURE

Core Testing -- Apparatus

Table 1 presents the specifications of a typical core used in these tests. Also listed are the chemicals and solutions. The core preparation and testing equipment used are shown in Figures 1 and 2. Figure 1 shows a typical Berea sandstone core which had been obtained from quarries in Ohio. Eight (8) inches long and 1 1/2 inches in diameter cores were used. They were brushed free of loose particles and dried in an oven at 230°F. The core was ensheathed in heat-shrinking plastic tubing. Stainless steel end plates, grooved on the inner surface to prevent particle blockage, and carrying lengths of 1/8-inch I.D. stainless steel tubing were placed at each end of the core. Heat was applied to the plastic tubing with a heat gun to cause the tubing to shrink tightly over the core and to overlap over the end plates. A small amount of epoxy was applied over the end plates which was overlaid by the shrinkable tubing. A complete water-tight seal at each end was thus effected by the epoxy resin.

The encased core was placed in a stainless steel core holder which is 2 inches in diameter and 12 inches in length. The 1/8-inch tubing attached to the end plates extends out of each end of the core holder through stainless steel fittings which were sealed with tubing nuts and ferrules. The core holder was filled with aqueous ethylene glycol or other hydraulic fluid and placed under pressure with a hand-operated hydraulic jack which is shown in Figure 1. The pressure used was at least 300 psi above the operating pressure of the test or internal pressure of the core.

The test apparatus used for this study is shown in Figure 2. The pump used for brine, oil, and isopropyl alcohol is a piston-type, positive displacement unit measured in milliliters and provides a constant flow. Flow rates may be varied from 0.8 to 200 ml/hr with increments of 0.008 ml/hr in the low region and 2.0 ml/hr in the high region. All tubing, needle valves, and fittings are 1/8-inch stainless steel, type 316. The coil containing the liquid CO₂ is made of 1/8-inch stainless steel tubing which has been calibrated and has a needle valve at each end. Two 6-inch, dial-type pressure gauges (at inlet and outlet) indicate the pressure of the system. The pressure is controlled by back pressure (pressure relief valve) at the outlet of the system.

Temperature is controlled by a heating mantle and a temperature controller. For tests above 75°F the apparatus was modified for heating the core and for introduction of gaseous and liquid additives and is shown in Figure 2. A sleeve-type heating jacket was put around the core holder to heat the core

TABLE 1

<u>Core and Materials</u>	
Core Used:	Berea Type Sandstone
Diameter:	3.8 cm
Length:	20.0 cm
Porosity:	21.9 percent
Permeability:	Ko = 62 md (effective for Hilly Upland oil) Ka = 72 md (absolute with 2.0 percent NaCl brine)
Pore Volume:	50 ml
Oil Used:	Hilly Upland Crude oil, viscosity = 3.64 cps
Brine Used:	2 percent NaCl in distilled water
Alcohol Used:	Commercial-grade isopropanol
CO ₂ Used:	Commercial-grade cylinder with outlet tube reaching to bottom of inside cylinder
Oil Slug Used:	Hilly Upland oil, viscosity = 3.7 cps

FIGURE 1 - PREPARATION OF CORE

FIGURE 2 - CORE TESTING EQUIPMENT

to the desired temperature. A thermocouple-type probe was inserted between the heating jacket and the core holder to measure the temperature. The heating jacket and the probe were connected to an on-off type, indicating temperature controller. The time necessary for the heat to pass through the core was determined by drilling a hole halfway through the center of a core and inserting a thermocouple. The core was then placed in a water bath at the desired temperature and the time for the thermocouple to reach that temperature was measured. The temperatures and corresponding times are listed below.

<u>Temperature (°F)</u>	<u>Time (Minutes)</u>
86	6
100	10
130	11
160	12
190	16

Core Testing -- Procedure

The core is evacuated for at least 4 hours by a vacuum pump to remove all trapped air. A 2 percent brine solution (sodium chloride in water at a pH 10) is then forced into the core to fill all of the pore space from the direct reading metering pump which when the core is filled provides a measure of its pore volume (PV). The valve at the outlet end of the core is then opened to a receiver and several PVs of brine is passed through the core to insure complete brine saturation. Four (4) to 5 PVs of oil is then injected into the core by means of the positive displacement pump, and the brine is displaced to irreducible water (brine) saturation or maximum oil saturation (S_o). Flow rates for the brine and oil saturations are 40 ml/hr or 12.4 ft/day. For secondary oil recovery tests, the CO_2 would then be injected followed by brine.

For tertiary tests the core would be waterflooded by the injection of 4 to 5 PVs of the brine solution. Any residual oil remaining in the core is immobile oil and usually represents over 60 percent of the original oil in the core. Flow rates of about 40 ml/hr are used in all these operations. The oil recovered by the waterflood gives the measure of the mobile or recoverable oil (ΔS_o). The difference between it and the oil produced during the waterflood gives the volume of the residual oil. The residual oil saturation, S_{or} , is obtained by dividing the former by the pore volume of the core. Waterflooding would be followed by the introduction of the CO_2 into the core followed by brine at a flow rate of 20 ml/hr (6.2 ft/day) for the tertiary tests.

For the different temperatures and pressures used in this study, a number of calibrated sample CO_2 coils (1/8-inch O.D. SS tubing) were made to accommodate the desired pore volumes. Each coil was preweighed, then filled with liquid CO_2 and reweighed. The difference in weights gave the weight of the liquid CO_2 slug. The temperature at the CO_2 cylinder provided the density correction for the volume of liquid CO_2 in the coil. This liquid volume was then calculated for the pore volume. Back calculations were made to determine the amount of liquid CO_2 which would provide the desired volume of vapor, liquid, or gaseous CO_2 for each pressure and corresponding temperature.

Tests were made at temperatures of 75°, 86°, 100°, and 130°F. For temperatures of 75° and 86°F, pressures of 650, 850, 1000, 1155, 1300, 1500, and 1800 psia were used; and at the temperatures of 100° and 130°F, the pressures used were 1000, 1155, 1300, 1500, and 1800 psia.

Secondary flooding tests were made by heating and pressurizing the displacement system to the desired temperature and pressure. The CO₂ slug was then permitted to flow into the oil/brine saturated core. This was followed by one pore volume of 2 percent brine at a flow rate of 20 ml/hr. "Blow down" was then initiated by lowering the pressure in steps until atmospheric pressure was reached. At this point the test was terminated. Tertiary tests were performed by following the same procedure after the brine/oil saturated core had been waterflooded. Upon completion of each test, the core was cleaned with 4 pore volumes of isopropanol followed by resaturation with brine and oil. The core was then ready for a new test. New cores were prepared when leaks developed or the results became erratic.

The products of oil and brine were collected and measured in a graduated burette-type receiver and recorded as a function of time. The results were reported as percent of pore volume and percent of original oil-in-place of oil recovered.

RESULTS AND DISCUSSION

The Effect of Temperature

The results of all tests made are listed in Table 2. The bulk of these tests were made to show the effect of supercritical CO₂ on oil recovery. All tests were made at a constant pressure of 1150 psi so that only temperature could effect any changes.

Most tests were made at 100°F (CO₂ as a gas) and compared to tests made at 75°F (CO₂ as a liquid). They were made using tertiary and secondary methods and the size of the CO₂ slug varied. Several tests are listed in Table 2 to show the effect of light and heavy oil slugs injected with the CO₂ slugs. Also, there are two tests in which nitrogen was pre-injected. Near the end of the table are several tests made at 86° and 130°F.

The effects of temperature and CO₂ slug size are presented in Table 3. The amount of recovered oil is given as pore volume (PV) and volume percent of original oil-in-place. Both results are given because secondary tests cannot be compared to tertiary in pore volume but can be compared as percent of oil-in-place. Also, CO₂ slug size is presented as pore volume of the liquid CO₂ and as a gaseous CO₂. This is presented because the CO₂ slug was obtained as a liquid and then calculated for its volume as a gas at the desired temperature. The column "Oil, So" refers to the oil saturation at the time the CO₂ slug was introduced into the system. In secondary tests this is the initial oil saturation. In tertiary tests this is the oil left in the core after waterflooding.

The first seven tests were made at 100°F and they compare secondary to tertiary flooding and also the change in CO₂ slug size. Comparing secondary (E-59-1) to tertiary (E-59-3) and using the same slug size of CO₂, the secondary test

TABLE 2

Oil Recovery Results from Core Tests by CO₂ Injection

Test No.	Core Temp. °F	Pore Volume (Percent)									Residual Oil	Remarks
		CO ₂ Slug		Oil Saturation	Water Flood	Recovered Oil			Total (Corr.)			
		Liquid	Gas			Displacement	Blow Down	Oil Slug (Corr.)				
E-59-3	100	6.1	15.2	68.1	30.2	3.4	14.9	--	48.5	19.6	Tertiary	
E-19-2	100	15.4	38.5	62.0	21.2	14.0	9.6	--	44.8	17.2	Tertiary	
E-19-3	100	14.0	35.0	62.0	23.2	8.4	11.2	--	42.8	19.2	Tertiary	
E-19-5	100	14.5	36.2	62.0	24.8	6.8	11.6	--	43.2	18.8	Tertiary	
E-19-9	100	15.8	39.5	63.0	23.2	9.2	8.8	--	41.2	21.8	Tertiary	
E-59-1	100	5.6	14.0	70.2	--	24.7	15.3	--	40.0	30.2	Secondary	
E-19-6	100	15.3	38.2	63.0	--	29.2	9.6	--	38.8	24.2	Secondary	
E-19-10	100	16.1	40.2	61.0	22.8	12.0	8.8	--	43.6	17.4	Tertiary	
E-19-14	100	10.8	27.0	64.0	23.2	7.6	10.4	--	41.2	22.8	Tertiary	
E-19-15	100	18.8	47.0	64.0	22.0	11.6	7.2	--	40.8	23.2	Tertiary	
E-19-8	75	14.6	--	64.0	21.2	8.0	11.6	--	40.8	23.2	Tertiary	
E-19-7	75	15.0	--	62.0	--	24.4	11.2	--	35.6	26.4	Secondary	
E-19-11	75	15.4	--	64.0	22.4	10.0	12.0	--	44.4	19.6	Tertiary	
E-19-16	75	10.9	--	64.0	20.8	7.2	12.4	--	40.4	23.6	Tertiary	
E-19-17	75	19.4	--	62.0	26.0	8.8	9.6	--	44.4	17.6	Tertiary	
E-14-1	75	18.2	--	66.3	25.7	14.8	11.7	(-) 5.4	46.8	19.5	Tertiary (Oil Slug)	
E-14-2	75	17.5	--	58.3	25.7	12.2	13.0	(-) 4.8	46.1	12.2	Tertiary (Oil Slug)	
E-14-5	75	13.0	--	63.0	25.6	5.9	15.2	(-) 4.3	41.7	21.3	Tertiary (Oil Slug)	
E-14-3	75	14.0	--	65.2	24.8	6.5	13.5	--	44.8	20.4	Tertiary	
E-14-4	75	12.9	--	66.3	--	18.7	17.8	--	36.5	29.8	Secondary	
E-19-12	100	16.2	40.5	62.0	23.2	8.4	10.4	--	42.0	20.0	Tertiary (Air Slug)	
E-19-18	100	15.3	38.2	61.0	26.0	9.2	9.2	--	44.4	16.6	Tertiary (Air Slug)	
E-19-20	100	17.9	44.7	63.0	26.0	12.0	8.6	(-) 4.6	42.0	21.0	Tertiary (Oil Slug)	
E-19-21	100	18.4	46.0	62.0	25.2	7.8	13.4	(-) 5.4	41.0	21.0	Tertiary (Oil Slug)	
E-19-24	100	16.8	42.0	62.0	--	30.8	12.4	(-) 5.8	37.4	24.6	Secondary (Oil Slug)	
E-19-25	86	17.5	21.9	62.0	--	24.0	15.2	--	39.2	22.8	Secondary	
E-19-26	130	17.7	68.1	64.0	--	28.8	6.8	--	35.6	28.4	Secondary	
E-59-8	86	13.7	17.1	66.0	--	26.8	17.0	--	43.8	22.2	Secondary	
E-79-1	130	4.5	17.3	70.4	--	20.9	9.8	--	30.7	39.7	Secondary	

TABLE 3

The Effect of Temperature, CO₂ Slug Size,
and Recovery Method on Oil Yields

Run No.	Recovery Method	Flow Rate (ml/hr)	Core Temp (°F)	Oil So (PV)	CO ₂ Slug (pore volume)		Recovered Oil	
					Liquid	Gas	(pv)	oil-in-place
E-59-1	Secondary	20	100	.702	.056	.143	.400	.570
E-19-6	Secondary	20	100	.630	.153	.395	.388	.616
E-59-3	Tertiary	20	100	.379	.061	.156	.183	.483
E-19-14	Tertiary	20	100	.408	.108	.276	.180	.441
E-19-3 E-19-5	Tertiary	20	100	.380	.143	.364	.190	.500
E-19-15	Tertiary	20	100	.420	.188	.477	.188	.448
E-19-7	Secondary	20	75	.620	.150	-	.356	.574
E-19-16	Tertiary	20	75	.432	.109	-	.196	.454
E-19-8 E-14-3	Tertiary	20	75	.416	.143	-	.198	.477
E-19-17	Tertiary	20	75	.360	.194	-	.184	.511

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recovered about 9 percent more oil as oil-in-place. This was also found to be true when the CO₂ slug size was more than doubled. The secondary (E-19-6) gave about 11 percent more oil than the corresponding tertiary test (E-19-3, 5).

When the tertiary tests at 100°F (E-59-3, E-19-14, E-19-3, E-19-5, and E-19-15) are compared using an increasing CO₂ slug size from .156 to .477 PV, the recovered oil as pore volume was essentially the same with only small differences as percent of oil-in-place. Therefore, increasing the CO₂ slug size at 100°F does not noticeably increase the oil recovered when it is used for tertiary recovery.

When using the same CO₂ slug sizes and comparing a secondary test (E-59-1) at 100°F to a secondary (E-19-7) at 75°F, the oil recovered as pore volume favors the 100°F (.400 and .356 PV). When the oil saturations (S_o) are adjusted, the recovery for both are about the same as shown by the percent of oil-in-place (.570 and .574).

Increasing the temperature from 75°F to 100°F for tertiary tests (E-19-8 and E-14-3) at 75°F and (E-59-3) at 100°F gave a small decrease in oil recovery as pore volume (.198 and .183) but about the same as oil-in-place (.477 and .483).

Although the use of CO₂ as a gas at 100°F could disperse better and make contact with more oil, it is equally true that the gas moves at a faster rate and, therefore, most of it does not remain in solution with the oil. The amount of CO₂ gas left in the oil decreases with increase of temperature, while the liquid increased. Therefore, this might explain why gaseous CO₂ cannot recover more oil than liquid CO₂.

The effect of flow rate and liquid or gaseous additives on oil recoveries are presented in Table 4. Decreasing the flow rate from 20 to 10 ml/hr for tertiary tests at 100°F gave corresponding oil yields of 50.0 percent and 54.4 percent of oil-in-place. Thus, this effected a 4.4 percent increase in oil (Test Runs E-19-3, 5 and E-19-10). Similar results were obtained at 75°F on Test Runs E-19-11 and E-19-8, 3 which gave oil yields of 47.7 percent and 52.9 percent for an increase of 5.2 percent of oil-in-place.

The reasoning for changing the flow rate was that slower flow rates may provide more time for gaseous or liquid CO₂ to make contact with the oil. It appears to hold true according to the above results, but it also appears to limit the increase in oil recovery.

Oil in a porous medium (in tertiary recovery) is considered to be deposited as unconsolidated droplets which are probably surrounded by brine. Therefore, in order to recover this oil, the droplets must be moved together to form a consolidated front (oil bank). Many researchers have suggested the injection of an oil slug could develop this oil bank. The use of a light oil slug would help to solubilize the trapped oil droplets, while the use of a heavy oil slug might act as a piston in the movement of the trapped oil droplets and also slow down the flow of the CO₂.

In tertiary tests, both light and heavy oil slugs were used followed by CO₂ slugs. These results are compared in Table 4. Test E-14-1 using a light oil slug followed by a CO₂ slug gave an oil recovery of .518 oil-in-place.

TABLE 4

The Effect of Flow Rate and Liquid
or Gaseous Additives on Oil Yields

Run No.	Recovery Method	Flow Rate (ml/hr)	Core Temp (°F)	Oil So (PV)	CO ₂ Slug (pore Volume) Liquid Gas	Oil* or Air Slug (PV)	Recovered Oil oil-in- place (PV)
E-19-10	Tertiary	10	100	.382	.161 .425	-	.208 .544
E-19-3 E-19-5	Tertiary	20	100	.380	.143 .364	-	.190 .500
E-19-11	Tertiary	10	75	.416	.154 -	-	.220 .529
E-19-8 E-14-3	Tertiary	20	75	.416	.143 -	-	.198 .477
E-19-17	Tertiary	20	75	.360	.194 -	-	.184 .511
E-14-1	Tertiary	20	75	.407	.182 -	.054 Hilly Upland	.211 .518
E-19-20 E-19-21	Tertiary	20	100	.369	.180 .457	.050 Drakeol #10	.159 .431
E-19-15	Tertiary	20	100	.420	.188 .477	-	.188 .448
E-19-24	Secondary	20	100	.620	.170 .430	.060 Drakeol #10	.374 .603
E-19-6	Secondary	20	100	.630	.153 .395	-	.388 .616
E-19-12	Tertiary	20	100	.388	.162 .424	.100 Air	.188 .484
E-19-3 E-19-5	Tertiary	20	100	.380	.143 .364	-	.190 .500

* Hilly Upland crude oil, viscosity 3.6 cps
Drakeol #10 oil (distillate cut) viscosity 27.0 cps

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Test E-19-17 using the same size CO₂ slug with no oil slug yielded .511 oil-in-place. Therefore, the light oil slug did not yield any additional oil.

Tests E-19-20, 21 use a heavy oil slug followed by a CO₂ slug and gave an oil yield of .431 oil-in-place, while Test E-19-15 used the same size CO₂ slug with no oil slug and yielded .448 oil-in-place. Therefore, the use of a heavy oil slug did not increase oil recovery. A secondary test (E-19-24) was also tried with a heavy oil slug and gave an oil yield of .603 oil-in-place. When compared with Test E-19-6 (yield of .616 oil-in-place), there was no definite increase in oil recovery.

Nitrogen or air has been suggested as a possible pre-injection gas followed by CO₂. Tests E-19-12 (with .10 PV of pre-injected N₂) and E-19-3, 5 (no pre-injection of N₂) were compared and gave corresponding yields of .484 and .500 oil-in-place. The pre-injected N₂ did not increase oil recovery, but gave a small decrease which was not significant.

The results from Table 3, at 100°F, had shown secondary tests to give higher oil yields than those obtained in tertiary tests. Those results consider only the oil obtained by CO₂ and not the oil obtained from waterflooding for the tertiary tests. When total oil yields are considered, the tertiary tests recovered more oil than the secondary tests. These results are presented in Table 5 for two different slug sizes of CO₂. Decreasing the CO₂ slug size to less than half had no effect on the oil yields from tertiary tests (4.6 percent). Overall oil yields for the tertiary tests were almost 10 percent higher than the secondary tests.

It has been shown that raising the temperature to 100°F had no noticeable effect on increasing or decreasing the oil recoveries. Therefore, it was decided to try temperatures below and above to determine if the vapor CO₂ or the gaseous CO₂ at a higher temperature could improve oil recoveries. Secondary tests were made at 86°F, which is very close to the critical temperature of CO₂; therefore, CO₂ probably exists as a liquid and vapor. Tests were also made at 130°F. Although reservoir pressure would increase at these temperatures, the pressure for these tests were kept constant at 1,150 psig to study the effect of temperature only. The results of these tests are presented in Table 6.

The first four tests were made so that the pore volume occupied by the CO₂ would be the same, regardless of temperature. Going from CO₂ as a liquid at 75°F (E-19-7) to CO₂ as a mixture of liquid and vapor at 86°F (E-59-2) gave a definite increase of 9 percent in oil recovery with corresponding yields of .574 and .664 oil-in-place. When the temperature was increased to 100°F (E-59-1), there was a corresponding decrease of over 9 percent with an oil yield of .570 oil-in-place. An additional increase in temperature to 130°F (E-79-1) gave an additional decrease of 13.4 percent for an oil yield of .436 oil-in-place which gave an overall decrease from the 86°F test of 22.8 percent. Figure 3 presents a graphic representation of the effect of temperature on oil recovery as percent of oil-in-place.

It would appear that 86°F is the optimum temperature for CO₂, at least at a pressure of 1,150 psig. It is possible that CO₂ as a vapor can make better contact with the oil than CO₂ as a gas. Additional supporting evidence of this to be true is found in the pore volumes of oil recovered by displacement

TABLE 5

Comparison of Oil Yields From CO₂ Injections
With and Without Pre-Water Flooding

Run No.	Recovery Method	Flow Rate (ml/hr)	Core Temp (°F)	Oil So (PV)	CO ₂ Slug (pore volume)		Recovered Oil	
					Liquid	Gas	(PV)	oil-in-place
E-19-3 E-19-5	Tertiary	20	100	.620	.143	.364	.430	.694
E-19-6	Secondary	20	100	.630	.153	.395	.388	.616
E-59-3	Tertiary	20	100	.681	.061	.156	.485	.712
E-59-1	Secondary	20	100	.702	.056	.143	.400	.570

:jj:526c

TABLE 6

The Effect of Temperature on Secondary
Recovery of Oil

Run No.	Flow Rate (ml.hr)	Core Temp (°F)	CO ₂ Slug (pore volume)		Oil So (PV)	Recovered Oil			Percent oil-in- place
			Liquid	Gas		Displ. (PV)	Blow down (PV)	Total (PV)	
E-19-7	20	75	.150	-	.620	.244	.112	.356	.574
E-59-2	20	86	.137	.163	.660	.268	.170	.438	.664
E-59-1	20	100	.056	.143	.702	.247	.153	.400	.570
E-79-1	20	130	.045	.179	.704	.209	.098	.307	.436
E-19-7	20	75	.150	-	.620	.244	.112	.356	.574
E-19-25	20	86	.175	.205	.620	.240	.152	.392	.632
E-19-6	20	100	.153	.395	.630	.308	.124	.388	.616
E-19-26	20	130	.177	.691	.640	.288	.068	.356	.556

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FIGURE 3 - THE EFFECT OF TEMPERATURE ON OIL RECOVERY
FROM CO₂ INJECTION

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and by blow down. Both values gave the same peak or optimum at 86°F for recovered oil and then decrease with increasing temperature. This effect of temperature on oil recovery by displacement and blow down is shown in Figure 4.

The second set of tests (E-19-7, 25, 6, 26) in Table 6 were made under the same set of conditions except the pore volume of the CO₂ slug was increased. The weight of the CO₂ slugs were about the same, but the pore volumes were much larger due to the expansion at higher temperatures, e.g., at a temperature of 130°F, the CO₂ slug amounted to 69 percent PV. The oil yields showed the same trend as with the first set of tests, i.e., an optimum at 86°F. Although the oil yields at 100°F and 130°F increased, probably due to the high pore volumes of CO₂, they still showed a gradual decrease in oil yields with increasing temperature. This trend is shown in Figure 5.

The Effect of Pressure

The results of all of the displacement tests are listed in Table 7. The number of tests made for each temperature and pressure were determined according to the results of the initial tests. Tests were repeated where necessary to verify the results. In a few cases more than two tests were made because a test gave unreliable results or to establish a base for comparison. In three tests (E-19-7, F-35-6A, and F-35-22) the initial oil saturations were much too low, therefore, their results could be incorrect.

Where possible, the results are given as pore volume to provide a reasonable basis of comparison. The total oil recovery is also given as percent of original oil-in-place because a number of researchers have presented their results in that manner. Care must be taken in evaluating results as percent of original oil-in-place because these values depend on initial oil saturations which can vary. An example of this is the results of tests F-35-6A and F-35-6B. The corresponding oil recovery results as pore volume are .472 and .481. Their corresponding percent of original oil-in-place are 80.8 and 65.1, which gives a false interpretation of the results.

Two values for CO₂ slug size are given in pore volume. The first value indicates the pore volume of that CO₂ slug as a liquid at room temperature of 75°F and at a pressure of 1155 psia. The second value is the decreased or increased pore volume for the corresponding temperature and/or pressure. The second values are of the vapor, liquid, or gas states that CO₂ is in at that temperature and/or pressure for that test. The preferred CO₂ slug size was 15 percent pore volume, but in several tests these values were slightly higher or lower.

The values given for residual oil must be considered as being unreliable. No true measurement can be made of this value. They are derived as the differences between initial oil saturation and the product oil. The values for the product oil can be considered as being a source of fairly reliable values because these are actual measured values of oil produced from the core.

The results of oil recovery yields from the displacement tests are reported in Table 8 as a function of pressure. Duplicate tests have been averaged and these values are reported. No values are listed for temperatures of 100° and

FIGURE 4 - THE EFFECT OF TEMPERATURE ON THE STEPS IN OIL RECOVERY

TABLE 7

The Effects of Pressure and Temperature on Oil Recovery by
CO₂ Displacement of Crude Oil from Berea Sandstone Cores

Test No.	Temperature °F	Pressure psi	Pore Volume						Total ^(b) Oil% OOIP	Residual Oil Pore Volume	Gas ^(c) Break- through PV
			CO ₂ Slag ^(a)		Oil Saturation	Recovered Oil					
			Liquid	Vapor or Gas		Displaced	Blow Down	Total			
E-19-7	75	1155	.150	.150	.620	.244	.112	.356	57.4	.264	.192
E-89-6	75	1155	.160	.160	.696	.226	.230	.456	65.5	.240	.135
E-89-4	75	1000	.163	.171	.696	.235	.234	.469	67.4	.227	.169
E-89-5	75	1000	.150	.158	.696	.231	.230	.469	66.2	.235	.143
E-89-1	75	850	.169	.412	.696	.261	.144	.405	58.2	.291	.161
E-89-2	75	650	.156	1.114	.685	.239	.174	.413	60.3	.272	.256
E-89-7	75	650	.169	1.207	.696	.278	.172	.450	64.7	.246	.174
E-96-3	75	550	.194	1.617	.727	.364	.059	.423	58.2	.304	.291
F-35-1	75	1155	.134	.134	.679	.328	.142	.470	69.5	.209	.276
F-35-2	75	1155	.084	.084	.679	.324	.174	.498	73.3	.181	.243
F-35-3	75	1155	.149	.149	.702	.314	.133	.447	63.7	.255	.267
F-35-23	75	1155	.157	.157	.738	.405	.115	.519	70.3	.219	.262
F-35-16	75	1000	.146	.154	.714	.362	.133	.495	69.3	.219	.205
F-35-15	75	850	.063	.154	.738	.343	.150	.493	66.8	.245	.609
F-35-14	75	650	.022	.157	.750	.310	.130	.443	59.0	.307	.367
F-35-24	75	650	.022	.157	.690	.343	.083	.426	61.7	.264	.228
F-35-28	75	650	.027	.193	.750	.357	.095	.452	60.3	.298	.128
F-35-12	75	1300	.140	.136	.750	.371	.124	.495	66.0	.255	.214
F-35-13	75	1500	.144	.136	.750	.410	.114	.524	69.8	.226	.219
F-35-25	75	1500	.168	.159	.702	.385	.117	.502	71.5	.200	.195
F-35-17	75	1800	.174	.160	.750	.362	.128	.490	65.4	.260	.186
F-35-26	75	1800	.158	.145	.726	.391	.121	.512	70.5	.214	.162
F-35-4	86	650	.133	1.025	.655	.443	.029	.472	72.0	.183	.309
F-35-5	86	850	.133	.633	.738	.395	.081	.476	64.5	.262	.243
F-35-6A	86	1000	.131	.234	.583	.329	.143	.472	80.8	.111	.262
F-35-6B	86	1000	.131	.234	.738	.371	.110	.481	65.1	.257	.255
F-35-19	86	1155	.129	.161	.726	.395	.091	.486	66.9	.240	.238
F-35-18	86	1155	.127	.159	.738	.391	.114	.505	68.4	.233	.214
F-35-7	86	1300	.135	.144	.679	.352	.129	.481	70.9	.198	.062
F-35-29	86	1300	.148	.157	.690	.395	.090	.485	70.3	.205	.214

(a) CO₂ slug is obtained as a liquid-vapor or gas. Slug is calculated according to pressure and temperature.

(b) Total oil recovered as a percent of original oil-in-place.

(c) Gas breakthrough of CO₂.

TABLE 7
(Continued)

The Effects of Pressure and Temperature on Oil Recovery by
CO₂ Displacement of Crude Oil from Berea Sandstone Cores

Test No.	Temperature °F	Pressure psi	Pore Volume						Total ^(b) Oil% OOIP	Residual Oil Pore Volume	Gas ^(c) Break- through PV
			CO ₂ Slag ^(a)		Oil Saturation	Recovered Oil					
			Liquid	Vapor or Gas		Displaced	Blow Down	Total			
F-35-8	86	1500	.129	.130	.750	.376	.129	.504	67.3	.246	.162
F-35-20	86	1500	.145	.146	.738	.400	.119	.519	70.3	.219	.195
F-35-21	86	1800	.149	.143	.738	.405	.114	.519	70.3	.219	.238
F-35-22	86	1800	.159	.153	.607	.400	.090	.490	80.8	.117	.224
F-35-27	86	1800	.157	.150	.714	.357	.119	.476	66.7	.238	.176
F-35-30	100	1000	.037	.149	.750	.357	.129	.486	64.8	.264	.138
F-35-31	100	1155	.066	.165	.750	.371	.138	.509	67.9	.241	.295
F-35-9	100	1300	.066	.092	.738	.319	.133	.452	61.3	.286	.128
F-35-10	100	1500	.066	.079	.750	.329	.138	.467	62.2	.283	
F-35-32	100	1500	.133	.153	.750	.376	.100	.476	63.5	.274	.248
F-35-11	100	1800	.070	.073	.750	.386	.095	.481	64.1	.269	.252
-19- F-35-33	100	1800	.146	.152	.750	.386	.066	.452	60.3	.298	.262
F-35-35	100	1800	.142	.148	.714	.352	.067	.419	58.7	.295	.205
F-35-43	100	1155	.055	.138	.690	.362	.102	.464	67.2	.226	.305
F-35-42	130	1000	.025	.125	.726	.357	.048	.405	55.7	.321	.376
F-35-40	130	1155	.042	.160	.690	.352	.086	.438	63.4	.252	.305
F-35-39	130	1300	.054	.164	.714	.362	.090	.452	63.3	.262	.300
F-35-38	130	1500	.070	.152	.690	.371	.105	.476	69.0	.214	.262
F-35-44	130	1800	.102	.148	.726	.381	.059	.440	60.7	.286	.233
F-35-45	130	1800	.099	.143	.690	.386	.079	.464	67.2	.226	.248
F-35-46	100	1300	.105	.146	.702	.390	.086	.476	67.8	.226	.186
F-35-47	100	1155	.067	.167	.702	.386	.071	.457	65.1	.245	.371
F-35-48	100	1000	.040	.160	.738	.352	.100	.452	61.3	.286	.181

(a) CO₂ slug is obtained as a liquid-vapor or gas. Slug is calculated according to pressure and temperature.

(b) Total oil recovered as a percent of original oil-in-place.

(c) Gas breakthrough of CO₂.

FIGURE 5 - OIL RECOVERY FROM THE EXPANSION OF GASEOUS CO₂ SLUGS AT HIGHER TEMPERATURES

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130°F at pressures of 650 and 850 psia because these values would be unrealistic and, therefore, no tests were made. The values in Table 8 for an individual temperature showed little change in the oil yields when the pressure is varied over a range from 650 to 1800 psi. In the case of yields at a temperature of 75°F, the biggest change was from 650 to 850 psi. This change might be due to CO₂ being a vapor at 650 psi and it being a mixture of vapor and liquid at 850 psi, because it is close to the vapor pressure of 909 psi for a temperature of 75°F. The small increases in oil recoveries resulting from increasing the pressure from 850 to 1800 psi could be due to test errors and, therefore, are not significant. The oil yields obtained at 86°F for the range of pressures used showed little changes or small increases as they did at 75°F. These results, theoretically, should be what can be expected, because the CO₂ is in the liquid state and cannot be compressed by increasing the pressure. Therefore, no significant changes in oil recovery yields should be expected.

TABLE 8

Oil Recovery by CO₂ Flooding as a Function of Pressure

Pressure psia	75°F	Oil Recovery (Percent PV)		
		86°F	100°F	130°F
650	44.0	47.2		
850	49.3	47.6		
1000	49.5	48.1	46.9	40.5
1155	49.6	49.6	47.2	43.8
1300	49.5	48.3	46.4	45.2
1500	51.3	51.2	47.2	47.6
1800	50.1	50.2	48.1	46.4

It was expected that a definite trend would be shown over a pressure range of 1000 to 1800 psi at temperatures of 100° and 130°F. At a temperature of 100°F there appears to be no definite pattern. Oil yields at 1000 and 1800 show no change, but there is a sudden drop at 1300 psi. This is followed by a definite increase as pressure is increased from 1500 to 1800 psi. It is possible that at pressures above 1800 psi this increase in oil yield may continue until a "miscibility pressure" is reached. This is a possible conclusion since at a temperature of 100°F the CO₂ is in a gaseous state and can be compressed to make better contact with the oil.

The oil recovery yields obtained at a temperature of 130°F for the same pressure range gave a similar view except there is no drop in oil yield at 1300 psi. There is an increasing oil yield with increasing pressure. Here again a "miscibility pressure" may be encountered at a pressure above 1800 psi, although at

1800 psi there is a small decrease in oil yield. A generally acceptable definition for "miscibility pressure" as applied to CO₂ flooding is the minimum CO₂ injection pressure required to ensure a satisfactory level of oil recovery. Although it may be impossible to reach this pressure because the overburden pressure may be lower than the "miscibility pressure," it is my opinion that the above definition might be reworded. Miscibility means to mix, or for the CO₂ to mix well with the oil. CO₂ in the liquid state mixes or dissolves quite well into the oil. Therefore, at temperatures above the critical temperature of CO₂ it becomes a gas. As pressure is increased, the molecules are pressed closer together. Although, CO₂ above its critical temperature can never become a liquid, the increase pressure suppresses or reduces much of the kinetic forces of the gas. Therefore, "miscibility pressure" is reached when much of the kinetic forces are reduced and CO₂ approaches the properties of a liquid. The results in Table 8 for temperatures 100° and 130°F might indicate that the kinetic forces of the CO₂ molecules are being reduced and they are approaching a condition that is similar to a liquid state due to increased pressure. Therefore, the oil yields could increase. This might be emphasized in the discussion of oil yields with changing temperature which is part of the next section. Figure 6 presents the results of Table 8 as plots of oil recoveries against pressure.

A second part of this study presents the results of oil recoveries as a function of temperature. These results are presented in Table 9 as averages of two or more tests. A graphic representation of these results is also presented in Figure 7. A general overall view in Table 9 and Figure 7 shows that oil recoveries are greater below the critical temperature of CO₂ (liquid state) and usually decrease when the temperature is raised above the critical (gaseous) state). The only deviation from this is at 100°F with a pressure of 1000 psi. At that pressure the oil yield at 86° and 100°F are about the same. At most pressures oil recoveries peak at 86°F. It is interesting to note that at temperatures of 75° and 86°F, there is an increase in oil recovery with increase of pressure. Although these increases are small, this condition does not hold true for tests at 100°F. At a temperature of 130°F, the increase is again evident.

TABLE 9

Oil Recovery by CO₂ Flooding as a Function of Temperature

Temperature °F	Oil Recovery (Percent PV)				
	1000 psi	1155 psi	1300 psi	1500 psi	1800 psi
75	47.8	48.3	49.5	51.3	50.1
86	58.1	49.6	48.3	51.2	50.5
100	46.9	47.2	46.4	47.2	48.1
130	40.5	43.8	45.2	47.6	46.4

FIGURE 6 - OIL RECOVERY BY CO₂ FLOODING AS A
FUNCTION OF PRESSURE

FIGURE 7 - OIL RECOVERY BY CO₂ FLOODING AS A FUNCTION OF TEMPERATURE

Figures 8 and 9 represent the oil production histories from CO₂ displacement through Berea sandstone cores. They are typical of the tests made and they also include the blow downs from the tests. As can be seen that regardless of temperature or pressure, all the oil to be produced by displacement will be produced by less than 0.5 pore volume. Also, "blow down" or pressure lowering to atmospheric will produce from 20 to 30 percent more oil.

The Effect of CO₂ Slug Injection Size

Table 10 lists the results of the tests made for this report. Column 3 of Table 10 shows the amount of brine that was used for displacement following the introduction of the CO₂ slug. This appears to be an important factor in total oil recovery (ΔS_o). Previous tests showed that the use of displacement fluid of greater than 1 pore volume gave lower ΔS_o values because it inhibited "blow down" which can provide a substantial increase in total oil recovery. The results in Table 10 show that displacement fluid of less than 1 pore volume (although "blow down" yields were high) gave smaller oil displacement values and thus smaller total oil recoveries. Comparing test B-34-12 (Table 2, which used 0.4 pore volume of displacement fluid) with B-34-14 (using 1 pore volume of displacement fluid) corresponding total oil recoveries were 38.5 and 44.6 percent pore volume. Using results from all tests for 20 percent PV CO₂ slug, the average oil recovery yield for 0.4 PV displacement fluids was 38.7 percent PV and that for 1 PV displacement fluid was 45.6 percent PV. Thus, the use of 1 pore volume of displacement fluid (brine) appears to give the larger total oil recovery.

The tests in Table 10 are listed according to the time they were made and not according to the CO₂ slug size but can be compared to Table 11 which lists the tests according to increasing CO₂ slug size. This shows an increasing trend of oil recovery with CO₂ slug size. When comparing this with the ratio of barrels of oil produced per ton of CO₂ used (second to last column, Table 10), an opposite trend is shown. Test B-34-21, using 3.7 percent PV CO₂ slug, gave a total oil yield of 40 percent PV and Test B-34-22, using 40.8 percent PV CO₂ slug, gave a total oil yield of 51.5 percent PV. Their corresponding ratios of barrels of oil per ton of CO₂ were 86.0 and 10.1 barrels. Therefore, this ratio does not indicate by itself optimum CO₂ slug size. Many other values must be considered; this report will evaluate only a few.

Table 11 lists only the tests that are of importance to this report (oil recovery with increasing CO₂ slug size). All tests were made using 1 pore volume of displacement fluid (2 percent brine). Where it was possible, duplicate tests were made. The two important sets of results in Table 11 are Total Oil Recovery (ΔS_o) and Residual Oil. These show an increasing oil recovery with increasing CO₂ slug size and a decreasing residual oil. This change is shown in Figure 10-A. This plot shows all tests and no attempt has been made to correct any of the values. The curve tends to show a large change when the CO₂ slug size is increased from ~3.0 percent PV up to 15.0 percent PV. Whereas the change in slope above 15.0 percent PV up to 41.0 percent PV is much smaller and almost becomes linear. A possible explanation for this is that two types of actions are taking place in recovering the oil. In the lower range, the CO₂ dissolves in the oil and causes the oil to swell and increase in volume. This increase in oil volume is overcome by the displacement of the oil from the core. This, of course, is followed by displacement of the oil by water-flooding. In the upper range of the curve (15 to 41 percent PV CO₂ slug size),

FIGURE 8 - OIL PRODUCTION HISTORY OF CO₂ DISPLACEMENT

FIGURE 9 - OIL PRODUCTION HISTORY OF CO₂ DISPLACEMENT

TABLE 10

Oil Recovery Results from Core Tests by CO₂ Injection

Run No.	Type of Flood	Displaced ^(a) Fluid (PV)	Percent of Pore Volume				GBT ^(b) CO ₂	Charge CO ₂	Grams Charge CO ₂	Ratio ^(c)	
			So	Displaced Δ So	Blow Down Δ So	Total Δ So				(bbl) Ton	Oil CO ₂
B-34-8	CO ₂ /Brine	1.0	69.2	20.0	8.5	28.5	96.0	2.8	1.1	78.2	
B-34-9	CO ₂ /Brine	1.0	70.4	17.7	16.1	33.8	98.0	5.6	2.1	48.7	
B-34-10	CO ₂ /Brine	1.0	71.1	33.5	13.4	46.9	27.7	19.9	7.9	17.5	
B-34-11	CO ₂ /Brine	1.0	73.1	22.3	13.1	35.4	66.9	9.6	3.7	28.2	
B-34-12	CO ₂ /Brine	0.4	73.1	19.2	19.2	38.5	26.9	22.6	8.3	13.8	
B-34-13	CO ₂ /Brine	1.0	72.1	21.5	13.5	35.0	39.6	9.7	3.5	29.2	
B-34-14	CO ₂ /Brine	1.0	69.2	34.6	10.0	44.6	31.5	22.9	8.1	16.4	
B-34-16	CO ₂ /Brine	1.0	69.2	40.4	6.9	47.3	27.7	31.9	11.9	11.8	
B-34-17	CO ₂ /Brine	1.0	73.1	32.7	13.4	46.1	32.3	15.6	5.6	24.2	
B-34-18	CO ₂ /Brine	1.0	70.2	33.9	11.5	45.4	34.2	15.7	5.7	23.5	
B-34-19	CO ₂ /Brine	1.0	70.2	29.6	13.5	43.1	86.9	6.5	2.4	53.2	
B-34-20	CO ₂ /Brine	1.0	70.2	30.0	13.5	43.5	64.6	9.2	3.4	37.6	
B-34-21	CO ₂ /Brine	1.0	72.1	28.5	11.5	40.0	99.9	3.7	1.4	86.0	
B-34-22	CO ₂ /Brine	1.0	71.1	46.1	5.4	51.5	28.5	40.8	15.1	10.1	
B-10-23	CO ₂ /Brine	1.0	69.8	33.8	12.9	46.7	28.3	22.3	7.9	16.1	
B-10-27	CO ₂ /Brine	1.0	69.2	34.6	9.6	44.2	31.7	23.0	8.0	15.0	
B-10-24	CO ₂ /Brine	0.4	70.8	19.6	14.2	33.8	25.8	21.6	7.3	12.7	
B-10-25	CO ₂ /Brine	0.4	70.8	29.6	14.2	43.8	34.6	22.9	7.7	15.5	
B-10-28	CO ₂ /Brine	1.0	72.9	35.0	14.2	49.2	27.5	22.9	8.2	16.3	
							6.2				
							6.2				
							6.2				
							4.3				

(a) The brine was made from 2 percent NaCl in distilled and demineralized water.

(b) Gas breakthrough of CO₂.

(c) Ratio of barrels of oil for each ton of CO₂.

(d) Equal slugs of CO₂ were alternated with brine.

TABLE 11

Results of Oil Recoveries from Core Tests Using CO₂ Injection

Run No.	Displaced Fluid	Charge CO ₂	So	Percent of Pore Volume				Percent Oil In-Place	
				Displaced Δ So	Blow Down Δ So	Total Δ So	Residual Oil	Total Δ So	Residual Oil
B-34-8	1.0	2.8	69.2	20.0	8.5	28.5	40.7	41.1	58.9
B-34-21	1.0	3.7	72.1	28.5	11.5	40.0	32.1	55.5	44.5
B-34-9	1.0	5.6	70.4	17.7	16.1	33.8	36.6	48.1	51.9
B-34-19	1.0	6.5	70.2	29.6	13.5	43.1	27.1	61.4	38.6
B-34-11	1.0	9.6	73.1	22.3	13.1	35.4	37.7	48.4	51.6
B-34-13	1.0	9.7	72.1	21.5	13.5	35.0	37.1	48.6	51.4
B-34-20	1.0	9.2	70.2	30.0	13.5	43.5	26.7	61.9	38.1
B-34-17	1.0	15.6	73.1	32.7	13.4	46.1	26.9	63.1	36.9
B-34-18	1.0	15.7	70.2	33.8	11.6	45.4	24.8	64.6	35.4
B-34-10	1.0	19.9	71.1	33.5	13.4	46.9	24.2	65.9	34.1
B-34-14	1.0	22.9	69.2	34.6	10.0	44.6	24.6	64.4	35.6
B-34-16	1.0	31.9	69.2	40.4	6.9	47.3	21.9	68.3	31.7
B-34-22	1.0	40.8	71.1	46.1	5.4	51.5	19.6	72.4	27.6

it would appear that the oil has reached the CO_2 saturation point and excess CO_2 remains behind the moving oil bank. The excess CO_2 probably exerts a chromatographic effect and acts as a carrier of the oil, left behind, through the porous medium. This would tend to give the upper portion of the curve a linear effect. On this basis, increasing the CO_2 slug size above 41 percent PV would continue to give small increases in oil recovery, but the increase probably would not warrant the increased cost of larger CO_2 slug sizes.

An attempt was made to correct the results in Table 11 adjusting the ΔS_o values to a common S_o value. The initial oil saturation values varied with the different tests and this could affect the recovered oil values; raising or lowering them. Therefore, a proportional percent of the varied oil saturation values was applied to the oil recovered values using 69.2 percent PV as a base S_o . These values are listed in Table 12. Also, duplicate tests were averaged in an attempt to eliminate errors of changing core characteristics. Also, listed in Table 12 are the average residual oil and CO_2 slug size values. The results were plotted in Figure 10-B (ΔS_o versus CO_2 slug). A comparison of Figure 10-A with Figure 10-B shows that the corrected average values has not changed the general shape of the curve but has brought the points more in line with the curve. Therefore, it appears that the conclusions made for Figure 10-A still hold for Figure 10-B.

Comparing oil recovery (ΔS_o) of duplicate tests (listed in Table 12) with test numbers (B-34), it is seen that most of the earlier tests gave low results and the later tests gave higher results. This could indicate that the continuous cleaning and resaturation of the core can change the core characteristics. If the assumption is made that the core surface is of the water-wetting type, then the continuous cleaning of that surface with isopropanol could change it to an oil-wetted surface. This change could increase oil saturations and oil recoveries and, therefore, alter the conclusions that would be made on the basis of a series of results.

Therefore, in an attempt to eliminate errors, a number of the earlier tests were taken out and the later tests were used to plot oil recovery versus CO_2 slug size. These results are listed in Table 13 and plotted in Figure 11. As can be seen in Figure 11, the same general curve is obtained as was obtained in Figures 10-A and 10-B. This tends to show that correction of the results for errors, averaging the tests, or eliminations of possible faulty tests do not change the general trend of the curve. Also, in Table 13 and Figure 11 are the corrected results for residual oil. The results for percent of original oil-in-place in Table 13 were also plotted and they resulted in the same general curves as those found in Figure 11.

Unlike chemical flooding, waterflooding, and surfactant flooding, the liquid CO_2 process has two stages for oil recovery: 1) oil recovered by displacement, and 2) oil recovered by "blow down" (pressure lowering to atmospheric). Therefore, it becomes important to analyze the results and conditions under which oil is recovered in these two stages. The actual mechanisms that take place in these two stages is not known. In the first stage (oil recovered by displacement), it is believed that the liquid CO_2 dissolves into the oil and this causes an increase in volume by swelling. It also lowers the viscosity to provide for a more mobile oil. This increase in the volume of the oil is relieved by the formation of an oil bank which displaces the oil ahead of it. In the second

FIGURE 10 - OIL RECOVERY BY CO₂ SLUG SIZE
(A) INITIAL OIL SATURATION UNCORRECTED, (B) CORRECTED

TABLE 12

Results of Oil Recovery with Constant Oil Saturations

Run No.	So	Δ So	Average	Residual Oil	Average	CO ₂ Slug	Average	B'ow Down ^(a) Pressure	Average
B-34-8	69.2	28.5	33.4	40.7	35.8	2.8	3.3	110	179
B-34-21	69.2	38.4		30.8		3.7		248	
B-34-9	69.2	33.2	37.9	36.0	31.4	5.6	6.1	220	280
B-34-19	69.2	42.5		26.7		6.5		340	
B-34-11	69.2	33.5	36.7	35.7	32.5	9.6	9.5	418	434
B-34-13	69.2	33.6		35.6		9.7		440	
B-34-20	69.2	42.9		26.3		9.2		443	
B-34-17	69.2	43.6	44.2	25.6	25.0	15.6	15.7	465	527
B-34-18	69.2	44.7		24.5		15.7		585	
B-34-10	69.2	45.6	45.1	23.6	24.1	19.9	21.4	565	673
B-34-14	69.2	44.6		24.6		22.9		780	
B-34-16	69.2	47.3	47.3	21.9	21.9	31.9	31.9	780	780
B-34-22	69.2	50.1	50.1	19.1	19.1	40.8	40.8	810	810

stage (oil recovered by "blow down" or pressure lowering), the dissolved liquid CO_2 becomes a gas, when the pressure is lowered below the critical pressure, and causes additional expansion of the oil. The expanding CO_2 gas seeks an escape route and in doing so, it acts as a carrier for the oil. Therefore, additional oil is recovered.

The results of these two stages (displaced oil and "blow down" oil) are listed in Table 13 and plotted in Figure 12. Total oil recovery has also been plotted in Figure 12 to show the combined effect of the displaced oil and the "blow down" oil. The curve for displaced oil appears to be linear. As the CO_2 slug size increases, the recovered oil increases in a proportional amount. It is very likely that the curve will level off at some point above 50 percent PV CO_2 slug. When comparing this curve with that of the total oil recovery curve shown above, it can be seen that there tends to be a leveling off. This leveling off is shown with the bottom curve of Figure 12, the "blow down" oil.

The curve for the "blow down" oil appears to reach at maximum at 12 percent PV CO_2 slug. Any increase above that in the CO_2 slug size shows a decrease in oil recovery, which probably comes close to zero at a point in the high CO_2 concentrations.

It is felt that the maximum oil recovery point in the "blow down" is important because it could show the point of maximum liquid CO_2 saturation of the oil or the maximum expansion of the oil at and behind the "oil bank" and, therefore, displaces more oil. This probably a chromatographic effect, which has been discussed above. This maximum point of 12 percent PV CO_2 slug corresponds with the change in slope point of the total oil recovery curve above. Therefore, the increase in displaced oil, about 10 percent PV CO_2 slug, leaves less oil that can be recovered by the "blow down". This could mean that complete recovery of all the oil in a reservoir is not possible with liquid CO_2 .

One of the important factors of oil recovery from "blow down" is the pressure at which maximum oil is recovered. For this reason, the pressure was lowered in steps for all tests and amounts of oil recovered at each pressure was recorded. The pressures, at which maximum oil was recovered, were averaged for duplicate tests and this data is listed in Table 12. These results have been plotted against CO_2 slug size and are shown in Figure 13. As can be seen, the pressure is dependent on the CO_2 slug size and increases as CO_2 increases.

In an effort to determine the water distribution throughout the experimental Berea core, it was removed from its holder for analysis. The core was cut into three equal sections; inlet, middle and outlet. Each section was subjected to a Dean-Starr type of analysis, using n-heptane as the azeotropic solvent. The results showed that the water distributions throughout the three sections were uniform with 49 percent of the pore volume in each section containing water. The residual oil from the last test made on that core was 20 percent PV. The test had been made with a 40.8 percent PV CO_2 slug. These results showed that 31 percent PV of the CO_2 slug remained in the core. Therefore, it can probably be assumed that liquid CO_2 injection gives a uniform sweep of the core, or it may be possible that this uniformity is brought about as a result of the "blow down" step.

FIGURE 11 - RECOVERED AND RESIDUAL OIL Vs CO₂ SLUG SIZE
(CORRECTED AND AVERAGED)

TABLE 13

Corrected Results Due to Changes in Core Characteristics

Run No. B-34-	21	19	20	18	10	16	22
<u>% PV</u>							
CO ₂ Slug	3.7	6.5	9.2	15.7	21.4	31.9	40.8
So	69.2						69.2
Displaced Oil	27.3	29.2	29.6	32.2	33.6	40.4	44.9
Blow Down Oil	11.1	13.3	13.3	12.0	11.5	6.9	5.2
Total Δ So	38.4	42.5	42.9	44.2	45.1	47.3	50.1
Residual Oil	30.8	26.7	26.3	25.0	24.1	21.9	19.1
<u>Oil-in-Place (%)</u>							
Total Δ So	55.5	61.5	62.0	63.9	65.2	68.3	72.3
Residual Oil	44.5	38.5	38.0	36.1	34.8	31.7	27.7

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FIGURE 12 - DISPLACED AND BLOWDOWN OIL Vs CO₂ SLUG SIZE

FIGURE 13 - "BLOWDOWN" PRESSURE FOR MAXIMUM OIL RECOVERY

The optimum CO₂ slug size for maximum oil recovery cannot be determined without comparing the costs of CO₂ operation, but the results of this report can provide a basis for this determination. If we consider the 40.8 percent PV CO₂ slug test with an oil recovery yield of 51.5 percent PV, we find that ten barrels of oil can be produced for each ton of CO₂. Assuming \$46 for a ton of CO₂ (9) (lowest price which does not include shipping and all other costs of operation), the 10 barrels obtained can provide a revenue from \$116 to \$150 with an average of \$137, according to projected prices (9). If the optimum CO₂ slug size is considered the point of maximum increase of oil (in the 12 to 15 percent PV range to give an oil recovery of 45.8 percent PV), then this would provide about 24 barrels of oil per ton of CO₂. This would give a revenue from \$279 to \$360 with an average of \$330. It would appear that the additional 4.7 percent PV of oil recovered using 40.8 percent PV CO₂ slug could not provide sufficient revenue to warrant the additional costs involved. These prices do not reflect the actual cost of CO₂ or the revenue obtained from the oil produced because prices have since increased. But, they do show a ratio between cost and revenue and predicts that more profit can be obtained by using the 12 to 15 percent CO₂ slug.

CONCLUSIONS

The Effect of Temperature

1. Using 15 percent PV CO₂ slugs at 100°F, secondary tests recovered about 9 percent more oil than the tertiary tests. When the CO₂ slug size was more than doubled, secondary tests recovered about 11 percent more than the tertiary test.
2. In tertiary tests at 100°F, increasing the CO₂ slug size from 15 percent to almost 50 percent PV did not noticeably increase oil recovery. Therefore, at 100°F, CO₂ slug size does not appear to be a critical condition.
3. In contrast, tertiary tests at 75°F with increasing CO₂ slug size from 10 percent to 20 percent PV did show a small but definite increase in oil recovery of about 5.5 percent.
4. The popular belief of increasing the temperature from 75°F (CO₂ as a liquid) to 100°F (CO₂ as a gas) so as to provide more and better contact of the CO₂ with the oil was found not to be true in this study. In tertiary tests at 75° and 100°F, using 15 percent PV CO₂ slugs, there was no increase in oil recovery -- the recoveries were the same. This was also true in secondary tests made at 75° and 100°F. Although better contact of CO₂ and oil may come about at 100°F, it is also true that the CO₂ (as a gas) in oil does not remain in solution, but tends to escape with an increase in temperature. Therefore, increase in oil recovery must come about from increase of the solubility of CO₂ in oil.
5. Decreasing the flow rate to one-half to provide more residence time for the CO₂ to make contact and to dissolve into the oil, made significant increases in oil recovery. Tests made at 100°F and decreasing the flow rate from 20 ml/hr to 10 ml/hr increased the oil yield by about

4.5 percent. Tests at 75°F, under the same conditions, gave an oil yield increase of over 5 percent.

6. In secondary and tertiary tests, the use of a pre-injected heavy oil slug to form an oil front and to slow down the flow of CO₂ did not increase oil recovery -- the yields were the same with and without the heavy oil slug.
7. The use of pre-injected nitrogen or a mixture of nitrogen and carbon dioxide did not increase oil recovery but gave a small decrease which was not significant.
8. At 100°F, the combined waterflood and CO₂ flood of tertiary tests recovered almost 10 percent more oil as did the CO₂ flood of secondary tests. This is to be expected, but it is probably not economical to pre-water flood. Also, many reservoirs have very tight formations and waterflooding is not feasible.
9. Secondary tests made at 75°, 86°, 100°, and 130°F showed that oil yields increased with an optimum at 86°F and then decreased with increasing temperatures above 86°F. This was found to be true with the same pore volume CO₂ slug (about 15 percent) and also with an increasing pore volume CO₂ slug (up to 69 percent). Increasing the temperature appeared to not only inhibit the oil recovered by displacement but gave a corresponding decrease in oil recovered by blow down. It is important to consider the role of the "blow down" when determining a set of conditions for oil recovery. Blow down yields can be as high as 26 percent of the oil-in-place as found for a temperature of 86°F and as low as 10 percent for a temperature of 130°F.

The Effect of Pressure

1. At temperatures of 75° and 86°F, or below the critical temperature of CO₂, changing the pressure had no significant effect on oil recovery in the range of 860 to 1800 psi. This is to be expected because CO₂ is in the liquid state under these conditions.
2. At a temperature of 130°F, oil yields show a small increase with increasing pressure. It is possible that a miscibility pressure may be reached above 1800 psi. As the pressure increases, the kinetic forces of the gas molecules decrease and, therefore, more CO₂ molecules remain in solutions to recover more oil. The density of the CO₂ also increases. Theoretically, solubility of the CO₂ in the oil and oil in the CO₂ can increase with increasing pressure until CO₂ gas has similar properties as those of the CO₂ liquid. Therefore, at a temperature of 130°F, increasing the pressure above 1800 psi could recover more oil.
3. Varying the temperature for a particular pressure, in most tests, gave maximum oil yield at 86°F. And at all pressures, oil yields decreased with higher temperatures.

The Effect of CO₂ Slug Injection Size

1. It has been shown that the use of liquid CO₂ as a secondary oil recovery method can produce a substantial amount of oil which is much larger than that obtained by waterflooding. A 40.8 percent PV CO₂ slug recovered 51.5 percent PV of oil while waterflooding recovered only 34.6 percent PV of oil. The oil recovered by liquid CO₂ was equivalent to 72.4 percent of the original oil-in-place and left a residual oil of 28.6 percent. Although pre-waterflooding as a secondary recovery method followed by liquid CO₂ flooding as a tertiary recovery method yielded the same 51.5 percent PV of oil, waterflooding cannot be used in many oil reservoirs because of their low permeabilities.
2. It has been shown that as the CO₂ slug size is increased (2.8 to 40.8 percent PV), there is a proportional increase in oil recovery (28.5 to 51.5 percent PV). Increasing the liquid CO₂ slug size from 2.8 to 12.0 percent PV gave a sharp increase in oil recovery. But an increase from 12.0 to 40.8 percent PV gave smaller increases in oil recovery. Above 32.0 percent PV, the curve indicated a tendency to level off, therefore, a maximum oil recovery would probably be reached somewhere about 50 percent PV.
3. The change in slope of the curve, by the increase of liquid CO₂ slug size in the two ranges of 2.8 to 12.0 percent PV and 12.0 to 40.8 percent PV, indicated that at least two different mechanisms of oil recovery took place. The first, in the range of 2.8 to 12.0 percent PV, probably was the dissolving of the CO₂ into the oil and thus the expansion of the oil volume. This followed by the formation of an oil bank and the displacement of the oil by the movement of the oil bank. The second mechanism, which seems to occur in the 12 to 40.8 percent PV CO₂ range, appears to be caused by the excessive amount of CO₂ which follows behind the moving oil bank. The excess CO₂ appears to sweep the oil left behind by dissolving the oil into the CO₂, thus providing a chromatographic effect.
4. The above conclusion is complemented by the curve obtained when oil recovery obtained from the "blow down" stage is plotted against CO₂ slug size. This "blow down" curve shows the same two ranges where there is a sharp increase in oil recovery in the 2.8 to 12 percent PV CO₂ slug size range, but a gradual decrease in oil recovery in the 12 to 40.8 percent PV range. A maximum "blow down" oil recovery is reached at about 12 percent PV CO₂ slug size which could mean that maximum oil bank formation and oil saturation has been reached. In the range from 12 to 40.8 percent PV, the gradual decrease in oil recovery indicates that there is less oil remaining for "blow down" because more oil has been displaced before "blow down." At about 32 percent PV, the curve tends to start leveling off and will probably reach a point of no change somewhere about 50 percent PV CO₂ slug size. The curve obtained by plotting the oil recovered by displacement against CO₂ slug size shows increasing oil recovery with increasing CO₂ slug size. This supports the conclusion for the decreasing oil recovery from "blow down" in the range of 12 to 40.8 percent PV CO₂ slug size.
5. Oil recovered from the "blow down" can be very important and can yield as much as 13.5 percent PV additional oil to be displaced oil. To make full use of the "blow down" stage, pressure decreases should be controlled in

steps because the oil recovered is dependent on the pressure and the concentration of oil and CO₂. Therefore, the pressure or pressures at which maximum oil is obtained should be known. As the CO₂ concentration decreases, the pressure increases for maximum oil recovery in the CO₂ slug size range of 12 to 40.8 percent PV.

6. The use of liquid CO₂ flooding appears to give a uniform sweep of the porous medium. At the end of the tests, the core was analyzed for concentrations of water at inlet, middle, and outlet sections. Water was found to be uniform throughout. From this, it can probably be assumed that the oil concentration and the CO₂ concentration are also uniform throughout. Of the 40.8 percent PV CO₂ slug that was injected for the last test, 31 percent PV remained in the core. The uniform spread throughout the core may be brought about by the "blow down" at the end of the test.
7. Although one test was made using alternate slugs of CO₂ and brine for a total CO₂ slug of 23 percent PV, the oil recovery was only a little more than using a single slug of 23 percent PV. This does not show the value of using alternate slugs as opposed to single slugs of CO₂ and, therefore, a study should be made.
8. The use of a 15 percent PV CO₂ slug appears to give maximum oil in terms of barrels per ton of CO₂. It provides 24 barrels of oil at an average revenue of \$330 as compared to \$137 for 10 barrels of oil when using a 40.8 percent PV CO₂ slug.

General

Although the temperature of a petroleum reservoir is fixed and cannot be changed without incurring high costs, the results of this report can help to determine the amount of oil that can be recovered by CO₂ injection at that particular reservoir temperature. It also provides some understanding of the mechanism of oil recovery in relationship to the reservoir pressure. These results of reservoir temperature also help to predict the optimum CO₂ slug injection size for maximum oil recovery.

Reservoir pressure can be changed within limits and the results of this report show that small changes in pressure can maximize oil recovery. Reservoirs with pressures below 900 psi would recover less oil with CO₂ injection. If possible, the pressure should be increased to 900 psi or above to maximize oil recovery. At reservoir temperatures of over 100°F, the higher the pressure the greater the oil recovery.

The CO₂ slug injection size is one of the conditions that can be changed regardless of the petroleum reservoir. Its only limitations are the costs. This report presents the optimum slug size as being in a range between 12 and 15 percent PV. Larger amounts would increase oil recovery, but the costs would be much too high for the revenue received.

REFERENCES

1. Comberiati, J. R., C. D. Locke and K. I. Kamath, Improved Method for Enhanced Oil Recovery, U. S. Patent No. 4, 224, 992, September 30, 1980.
2. Stalkup, F. I., Carbon Dioxide Miscible Flooding; Past, Present, and Outlook for the Future, J. Pet. Tech., August 1978, pp. 1102-1112.
3. Beeson, D. M., and G. D. Ortloff, Laboratory Investigation of the Water-Driven Carbon Dioxide Process for Oil Recovery, Trans., AIME, 1959, v. 216, pp. 225-231.
4. Holm, L. W., Carbon Dioxide Solvent Flooding for Increased Oil Recovery, Trans., AIME, 1959, v. 216, pp. 225-231.
5. Rathmell, J. J., F. I. Stalkup, and R. C. Hassinger, A Laboratory Investigation of Miscible Displacement by Carbon Dioxide, Paper SPE 3483 presented at SPE-AIME 46th Annual Fall Meeting, New Orleans, October 3-6, 1981.
6. Holm, L. W., and V. A. Josendal, Mechanisms of Oil Displacement by Carbon Dioxide, J. Pet. Tech., December 1974, pp. 1427-1436.
7. Huang, T. S. E., and J. H. Tracht, The Displacement of Residual Oil by Carbon Dioxide, Paper SPE 4735 presented at the SPE-AIME Improved Oil Recovery Symposium, Tulsa, April 22-24, 1974.
8. Warner, H. R., An Evaluation of Miscible CO₂ Flooding in Waterflooded Sandstone Reservoirs, J. Pet. Tech., October 1977, pp. 1339-1347.
9. Chemical and Engineering News, Key Chemicals -- Carbon Dioxide, January 26, 1978, p. 13.

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