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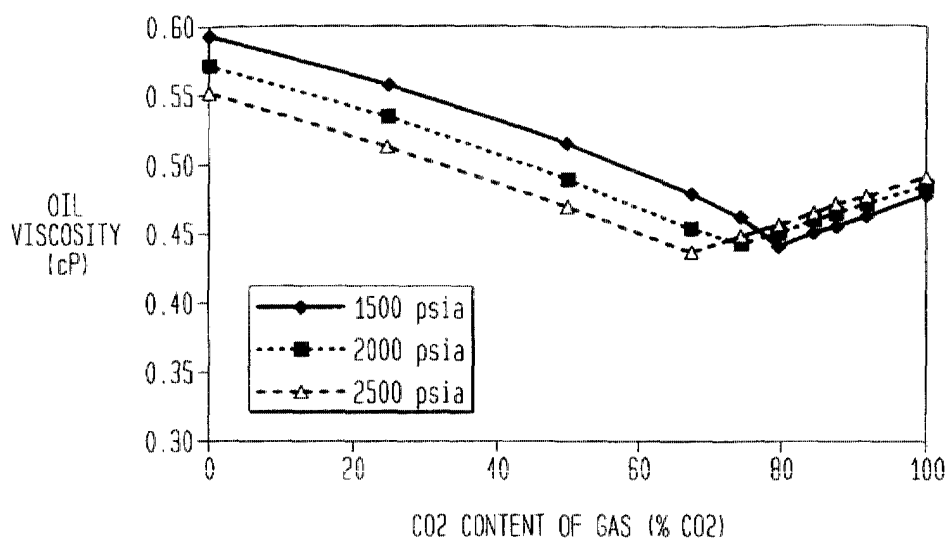
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(54) Enhanced oil recovery method using CO₂ injection

(57) A method for enhancing the recovery of oil from underground formations is disclosed. A gas mixture which contains greater than 50% by volume carbon dioxide, the remainder typically being an inert gas, is in-

jected in the underground formation to lower the oil viscosity and surface tension and increase the oil swelling. Preferably, the gas mixture contains greater than 60% by volume carbon dioxide with a gas mixture containing greater than 70% by volume carbon dioxide preferred.

FIG. 1



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Description

[0001] The present invention provides for a method for enhancing the recovery of oil from underground formations. More particularly, the present invention provides for injecting into the oil in the underground formation a gas mixture which contains at least 50% by volume carbon dioxide and the remainder nitrogen or other inert gas.

[0002] Oil or gas and any water which is contained in the porous rock surrounding the oil or gas in a reservoir or formation are typically under pressure due to the weight of the material above them. As such, they will move to an area of lower pressure and higher elevation such as the well head. After some pressure has been released, the oil may still flow to the surface but it does so more slowly. This movement can be helped along by a mechanical pump such as the grasshopper pumps one often sees. These processes are typically referred to as primary oil recovery. Typically, less than 50% of the oil in the oil formation is recovered by primary techniques. Recovery can be increased by pursuing enhanced oil recovery (EOR) methods. Typically, these methods are divided into two groups: secondary and tertiary.

[0003] Secondary EOR generally refers to pumping a fluid, either liquid or gas, into the ground to build back pressure that was dissipated during primary recovery. The most common of these methods is to inject water and is simply called a waterflood.

[0004] The tertiary recovery schemes typically use chemical interactions or heat to either reduce the oil viscosity so the oil flows more freely or to change the properties of the interface between the oil and the surrounding rock pores so that the oil can flow out of the small pores in the rock and enter larger channels where the oil can be swept by a driving fluid or move by pressure gradient to a production well. The oil may also be swelled so that a portion of the oil emerges from small pores into the channels or larger pores in the rock. Typical of these processes are steam injection, miscible fluid injection and surfactant injection.

[0005] Thermal techniques employing steam can be utilized in a well to well scheme or also in a single-well technique which is known as the huff and puff method. In this method, steam is injected via a well in a quantity sufficient to heat the subterranean hydrocarbon-bearing formation in the vicinity of the well. The well is then shut in for a soaking period after which it is placed on production. After production has declined, the huff and puff method may again be employed on the same well to again stimulate production.

[0006] The use of carbon dioxide and its injection into oil reservoirs is known for well to well and single well production enhancement. The carbon dioxide dissolves in the oil easily and causes the oil to swell and reduces the viscosity and surface tension of the oil which in turn leads to additional oil recovery. The carbon dioxide may also be employed with steam such that the steam and carbon dioxide are injected either simultaneously or sequentially, often followed by a soak period, followed by a further injection of carbon dioxide or other fluids.

[0007] US-A-2 623 596 describes enhanced recovery using gases in an injection well with oil recovery from a separate production well. Enhanced recovery using CO₂ and N₂ mixtures is discussed with data presented showing oil recovery increasing monotonically as CO₂% in the gas mixture is increased. However, the data presented does not demonstrate results when between 85% CO₂ and 100% CO₂, is employed.

[0008] US-A-3 295 601 teaches that a slug of gas consisting of carbon dioxide and hydrocarbon gases, preferably of two to four carbon atoms, or nitrogen, air, hydrogen sulfide, flue gases and similar gases in a gas mixture, when injected in a well, establishes a transition zone. This transition zone is then driven through the injection well by a driving fluid which will produce oil from the stratum and reduce viscous fingering. The preferred slug of gas consists of 50% carbon dioxide and a substantial concentration of C₂ to C₄ hydrocarbon gases such as 10 to 50% by volume. It appears that the remainder of the gases in this gas mixture are selected from the group consisting of nitrogen, air, hydrogen sulfide and flue gases and similar gases would make up the balance in the preferred composition of carbon dioxide and C₂ to C₄ hydrocarbon gas.

[0009] US-A-5 725 054 teaches a method for recovering oil from a subterranean formation by injecting into said well a gas mixture which comprises carbon dioxide and a gas selected from the group consisting of methane, nitrogen and mixtures thereof. The gas mixture comprises about 5 to about 50% by volume of carbon dioxide. As noted in the examples, the highest percentages were 50% by volume carbon dioxide.

[0010] The present inventors have discovered that the use of carbon dioxide in percentages greater than 50%, up to 99%, along with nitrogen or another gas, preferably an inert gas as the remainder of the gas mixture will enhance oil production.

[0011] The present invention provides a method for enhancing the recovery of oil from an underground formation comprising injecting into the oil a gas mixture comprising at least 50% by volume of carbon dioxide. In addition, the present invention provides a method for lowering the viscosity and surface tension as well as increasing the volume or swelling of the oil in an underground formation comprising injecting into the oil a gas mixture comprising at least 50% by volume carbon dioxide.

[0012] The gas mixture preferably includes an inert gas. The inert gas is preferably nitrogen. Other inert gases such as helium and argon may also be employed. The present invention also comprises a method for enhancing the recovery of oil from an underground formation comprising injecting into the oil a gas mixture which comprises carbon dioxide

and nitrogen. The carbon dioxide is present in the gas mixture in an amount of at least 50% by volume. The introduction of a combination of carbon dioxide and nitrogen gas to the formation provides an unexpected advantage of lower oil viscosity and surface tension than the introduction of carbon dioxide or nitrogen alone. This will also provide greater oil swelling than the use of carbon dioxide or nitrogen alone. The use of nitrogen adds an economic advantage to the mixture as there is lower cost than that for pure carbon dioxide consumption.

[0013] For purposes of the present invention, oil is defined as being a hydrocarbon which comprises paraffin, aromatic or naphthene constituents or mixtures thereof.

[0014] The mixture of the carbon dioxide and nitrogen will be injected into the formation containing the oil at a pressure of 100 pounds per square inch to 20,000 pounds per square inch depending upon the depth of the oil reservoir. This injection method allows for use of a WAG (water alternating gas) well-to-well process whereby an injection of gas is followed by a waterflood to drive the oil and enhance production at the well head. This injection method will also work in a huff and puff process. In the huff and puff process, the mixture would be injected into the formation. The formation would then be sealed allowing a soak period of determinate length of time, followed by an improved oil recovery or production period.

[0015] The mixtures of carbon dioxide and nitrogen may be created by any means. Preferably, a carbon dioxide-rich stream and a nitrogen-rich stream are combined or a hydrocarbon is combusted using air or oxygen-enriched air to produce the carbon dioxide. Other inert gases, when combined with carbon dioxide in an optimum ratio, are believed to minimize oil viscosity and surface tension while increasing swelling.

[0016] One means for producing the carbon dioxide-rich gas stream involves the use of a power plant or co-generation plant at or near the well site. Oxygen-enriched air and hydrocarbon are combusted to generate power and carbon dioxide-rich gas. The power is used to operate an air separation plant which provides the oxygen for the oxygen enrichment of the power or co-generation plant. Additional nitrogen and/or steam produced may also be used to enhance oil recovery by placing these materials in an injection well either individually or in combination with the carbon dioxide-rich gas stream. The combination of heat and carbon dioxide can further improve recovery and little carbon dioxide would be lost to the aqueous phase as a result.

[0017] Another means for producing the carbon dioxide is by injection of pure oxygen, oxygen-enriched air or air downhole. For wells that are sufficiently deep enough, the temperature will be sufficient to sustain combustion and produce carbon dioxide. For example, a 8000 foot deep well may have a temperature of 300°F which is hot enough to produce the carbon dioxide necessary for the enhanced oil recovery.

[0018] In a preferred embodiment of the present invention, a carbon dioxide-nitrogen mixture with carbon dioxide present greater than 50% by volume is injected into the formation at or near the production well by optimizing the composition of the gas mixture. Due to the varied rates in the uptake of carbon dioxide and nitrogen, a near optimum composition can be maintained in the formation at that injection location. A second mixture of carbon dioxide and nitrogen would then be injected through injection well(s) located at a distance from the production well. The composition of this gas mixture would be such that the viscosity and surface tension of the oil is higher than that of the oil near or at the production well but still reduced in comparison to the untreated oil. Gas may be fed continuously to the injection well(s) or the well(s) can be shut for a period of at least a day to facilitate the uptake of the gas by the oil.

[0019] Oil is driven to the production well and fingering or bypass of the gas though the oil is minimized as a result. In this preferred embodiment, more than one remote injection point may be employed such that the viscosity and surface tension of the oil at the remote injection point becomes higher with each injection point further away from the well head injection point by optimizing the content of the carbon dioxide and nitrogen gas mixture. Accordingly, the nitrogen content of the gas mixture will increase as one injects the mixture further from the production well. This gradient will result in a raising of carbon dioxide content above the 50% by volume as one injects at points getting sequentially closer to the production well. In this embodiment, a later possibly intermittent use of carbon dioxide flood, nitrogen flood or water flood to drive the oil to the production well would further improve yields.

[0020] A preferred composition for use in the methods of the present invention is that of at least 50% by volume carbon dioxide, the remainder being nitrogen or other inert gas including helium, argon or steam. In a more preferred embodiment, greater than 60% carbon dioxide by volume with the remainder being one or more inert gases would comprise the gaseous mixture. In the most preferred embodiment, greater than 75% by volume of the gas mixture would be carbon dioxide and the remainder being inert gases.

[0021] In an additional embodiment, hydrocarbons can be added to the above described compositions. These hydrocarbons, such as methane, ethane and propane can come from traditional sources but may also come from the associated gas produced during oil production. The hydrocarbons can be separated from oil and reinjected into the ground or may be separated from oil and reinjected into the ground after burning a portion of the hydrocarbon in air, oxygen or oxygen enriched air.

[0022] The method according to the invention will now be described by way of example with reference to the accompanying drawings in which Figure 1 is a graphical representation of the effect of carbon dioxide content of gas on paraffin oil viscosity.

[0023] Figure 2 is a graphical representation of carbon dioxide content of gas on naphthene oil viscosity.

[0024] Figure 3 is a graphical representation of carbon dioxide content of gas on aromatic oil viscosity.

[0025] Figure 4 is a graphical representation of carbon dioxide content of gas on paraffin oil surface tension.

[0026] Figure 5 is a graphical representation of carbon dioxide content of gas on naphthene oil surface tension.

[0027] Figure 6 is a graphical representation of carbon dioxide content of gas on aromatic oil surface tension.

[0028] Figure 7 is a graphical representation of carbon dioxide content of gas on paraffin oil viscosity at various temperatures.

[0029] Figure 8 is a graphical representation of carbon dioxide content of gas on paraffin oil surface tension at various temperatures.

[0030] Figure 9 is a graphical representation of carbon dioxide content of gas on paraffin oil volume at various temperatures.

[0031] Three model oils were studied to explore the potential of mixtures of carbon dioxide and nitrogen for enhanced oil recovery. A simulation was developed based on the Peng-Robinson equation of state for vapor-liquid equilibrium, the Twu model for liquid phase viscosity and a modified form of the Brock and Bird equation for surface tension. The three oils employed in this study were of paraffin, naphthene and aromatic types. A gas mixture of carbon dioxide and nitrogen with a usage rate of 1 mole per mole of oil was presumed and a small quantity of water was added to the mixture since typically carbon dioxide flooding operations follow water flood procedures or are conducted as in the WAG method alternatively with waterflood. The quantity of water was based on 20% saturation for a typical oil. Pressures in the range of 1,500 psia to 2,500 psia and temperatures in the range of 75°F to 200°F were studied.

[0032] As shown in Figures 1, 2 and 3, and Tables 1, 2 and 3, the relationship of a paraffin, naphthene and aromatic oil viscosity at 75°F to the percentage of carbon dioxide in the oil recovery gas mixture is demonstrated. It can be seen that greater than 50% carbon dioxide in the gas mixture is advantageous in lowering the oil viscosity relative to the use of 100% carbon dioxide.

Table 1:

Effect of CO ₂ Content of Gas on Paraffin Oil Viscosity at Various Pressures and 75 F			
CO ₂ content of gas (%)	Oil viscosity at 1500 psia (cP)	Oil viscosity at 2000 psia (cP)	Oil viscosity at 2500 psia (cP)
0	0.592	0.571	0.552
25	0.557	0.534	0.513
50	0.515	0.49	0.468
68	0.478	0.453	0.437
75	0.462	0.443	0.449
80	0.45	0.451	0.457
85	0.451	0.46	0.466
88	0.456	0.465	0.472
92	0.464	0.472	0.479
100	0.478	0.487	0.493

Table 2:

Effect of CO ₂ Content of Gas on Naphthene Oil Viscosity at Various Pressures and 75 F			
CO ₂ content of gas (%)	Oil viscosity at 1500 psia (cP)	Oil viscosity at 2000 psia (cP)	Oil viscosity at 2500 psia (cP)
0	1.93	1.87	1.82
25	1.69	1.62	1.57
50	1.44	1.38	1.32
68	1.26	1.19	1.14
75	1.18	1.12	1.07

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Table 2: (continued)

Effect of CO₂ Content of Gas on Naphthene Oil Viscosity at Various Pressures and 75 F			
CO ₂ content of gas (%)	Oil viscosity at 1500 psia (cP)	Oil viscosity at 2000 psia (cP)	Oil viscosity at 2500 psia (cP)
80	1.12	1.06	1.02
85	1.06	1.01	0.997
88	1.02	0.993	1.01
92	0.986	1.01	1.02
100	1.02	1.04	1.05

Table 3:

Effect of CO₂ Content of Gas on Aromatic Oil Viscosity at Various Pressures and 75 F			
CO ₂ content of gas (%)	Oil viscosity at 1500 psia (cP)	Oil viscosity at 2000 psia (cP)	Oil viscosity at 2500 psia (cP)
0	0.827	0.811	0.797
25	0.7566	0.738	0.722
50	0.679	0.658	0.642
68	0.615	0.595	0.578
75	0.587	0.567	0.552
80	0.566	0.547	0.532
85	0.544	0.526	0.512
88	0.529	0.512	0.519
92	0.51	0.52	0.527
100	0.527	0.537	0.544

[0033] Figures 4, 5 and 6 and Tables 4, 5 and 6 show the relationship of a paraffin, naphthene and aromatic oil surface tension at 75°F to the percentage carbon dioxide and the oil recovery gas mixture for three different pressures. As can be seen in Figures 4, 5 and 6, greater than 60% carbon dioxide in the gas mixture is advantageous in reducing surface tension in comparison to the use of pure carbon dioxide.

Table 4:

Effect of CO₂ Content of Gas on Paraffin Oil Surface Tension at Various Pressures and 75 F			
CO ₂ content of gas (%)	Oil surface tension at 1500 psia (dyne/cm)	Oil surface tension at 2000 psia (dyne/cm)	Oil surface tension at 2500 psia (dyne/cm)
0	19.22	18.39	17.65
25	17.1	16.19	15.41
50	14.93	13.99	13.21
68	13.27	12.35	11.8
75	12.59	11.86	11.86
80	12.09	11.91	11.9
85	11.96	11.95	11.95
88	11.98	11.98	11.98
92	12.02	12.02	12.02

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Table 4: (continued)

Effect of CO₂ Content of Gas on Paraffin Oil Surface Tension at Various Pressures and 75 F			
CO ₂ content of gas (%)	Oil surface tension at 1500 psia (dyne/cm)	Oil surface tension at 2000 psia (dyne/cm)	Oil surface tension at 2500 psia (dyne/cm)
100	12.09	12.1	12.1

Table 5:

Effect of CO₂ Content of Gas on Naphthene Oil Surface Tension at Various Pressures and 75 F			
CO ₂ content of gas (%)	Oil surface tension at 1500 psia (dyne/cm)	Oil surface tension at 2000 psia (dyne/cm)	Oil surface tension at 2500 psia (dyne/cm)
0	29.21	28.56	27.96
25	26.14	25.3	24.59
50	22.93	21.97	21.23
68	20.4	19.44	18.73
75	19.34	18.42	17.72
80	18.53	17.64	16.97
85	17.69	16.85	16.59
88	17.16	16.61	16.62
92	16.65	16.66	16.66
100	16.72	16.73	16.73

Table 6:

Effect of CO₂ Content of Gas on Aromatic Oil Surface Tension at Various Pressures and 75 F			
CO ₂ content of gas (%)	Oil surface tension at 1500 psia (dyne/cm)	Oil surface tension at 2000 psia (dyne/cm)	Oil surface tension at 2500 psia (dyne/cm)
0	29.84	29.29	28.79
25	26.71	25.96	25.33
50	23.41	22.53	21.87
68	20.81	19.94	19.28
75	19.73	18.87	18.25
80	18.92	18.08	17.48
85	18.06	17.28	16.72
88	17.52	16.77	16.76
92	16.8	16.8	16.8
100	16.86	16.86	16.86

[0034] Figures 7 and 8 and Tables 7 and 8 show the relationship of a paraffin oil viscosity and surface tension at various temperatures to the percentage carbon dioxide and the oil recovery gas mixture. As demonstrated in the earlier examples, greater than 50% carbon dioxide in the gas mixture is advantageous in comparison to the use of pure carbon dioxide. Oil viscosity is greatly reduced at around 70 to 80% carbon dioxide while surface tension remains approximately constant at the higher carbon dioxide concentrations.

Table 7:

Effect of CO₂ Content of Gas on Paraffin Oil Viscosity at Various Temperatures and 2000 psia					
CO ₂ content of gas (%)	Oil viscosity at 75 F (cP)	Oil viscosity at 100 F (cP)	Oil viscosity at 125 F (cP)	Oil viscosity at 150 F (cP)	Oil viscosity at 200 F (cP)
0	0.571	0.486	0.419	0.365	0.282
50	0.49	0.429	0.375	0.329	0.257
75	0.443	0.387	0.341	0.301	0.235
80	0.451	0.394	0.342	0.298	0.229
85	0.46	0.402	0.348	0.304	0.23
88	0.465	0.407	0.352	0.307	0.233
92	0.472	0.413	0.358	0.312	0.237
100	0.487	0.426	0.369	0.321	0.244

Table 8:

Effect of CO₂ Content of Gas on Paraffin Oil Surface Tension at Various Temperatures and 2000 psia					
CO ₂ content of gas (%)	Oil surface tension at 75 F (dyne/cm)	Oil surface tension at 100 F (dyne/cm)	Oil surface tension at 125 F (dyne/cm)	Oil surface tension at 150 F (dyne/cm)	Oil surface tension at 200 F (dyne/cm)
0	18.39	17.3	16.21	15.13	13
50	13.99	12.91	12.29	11.63	10.26
75	11.86	10.53	10.06	9.582	8.574
80	11.91	10.52	9.887	9.265	8.167
85	11.95	10.52	9.888	9.266	8.044
88	11.98	10.52	9.887	9.266	8.046
92	12.02	10.52	9.888	9.266	8.044
100	12.1	10.52	9.887	9.265	8.045

[0035] Figure 9 and Table 9 show the relationship of a paraffin oil relative volume at various temperatures as to the percentage carbon dioxide in the oil recovery gas mixture. The relative volume is taken in comparison to a standard oil volume. Roughly 70% to 99% carbon dioxide in the gas mixture is advantageous in comparison to the use of pure carbon dioxide to maximize swelling in this case. As swelling of the oil increases, the oil will exit small pores within the subterranean formation and can be swept or driven to the production well by use of the various flood techniques.

Table 9:

Effect of CO₂ Content of Gas on Paraffin Oil Relative Volume at Various Temperatures and 2000 psia*					
CO ₂ content of gas (%)	Oil relative volume at 75 F	Oil relative volume at 100 F	Oil relative volume at 125 F	Oil relative volume at 150 F	Oil relative volume at 200 F
0	1.036	1.053	1.071	1.090	1.131
50	1.118	1.135	1.154	1.176	1.235
75	1.193	1.222	1.244	1.27	1.353
80	1.188	1.217	1.249	1.287	1.392
85	1.183	1.211	1.243	1.280	1.398

*Relative volume is in comparison to a standard oil volume

Table 9: (continued)

Effect of CO₂ Content of Gas on Paraffin Oil Relative Volume at Various Temperatures and 2000 psia*					
CO ₂ content of gas (%)	Oil relative volume at 75 F	Oil relative volume at 100 F	Oil relative volume at 125 F	Oil relative volume at 150 F	Oil relative volume at 200 F
88	1.179	1.207	1.239	1.276	1.391
92	1.175	1.203	1.234	1.271	1.383
100	1.167	1.194	1.224	1.261	1.366

*Relative volume is in comparison to a standard oil volume

Claims

1. A method for enhancing the recovery of oil from an underground formation comprising injecting into said oil a gas mixture comprising at least 50% by volume carbon dioxide.
2. A method according to claim 1, wherein the remainder of said gas mixture additionally includes one or more of the following: at least one inert gas; at least one hydrocarbon; steam; and air.
3. A method according to claim 2, wherein the inert gas is one or more of the following: nitrogen, helium, and argon.
4. A method according to any one of the preceding claims, wherein said gas mixture is injected into said oil at the well head.
5. A method according to claim 4, wherein said gas mixture is injected into a single production well head.
6. A method according to claim 5, wherein said injection is cyclical.
7. A method according to any one of the preceding claims, wherein said gas mixture is injected into an injection well other than a production well head.
8. A method according to claim 7, wherein said gas mixture is injected in an alternating pattern with a driving fluid.
9. A method according to claim 8, wherein said driving fluid is selected from the group consisting of steam, water, nitrogen, carbon dioxide and air.
10. A method according to any one of the preceding claims, wherein said gas mixture is injected into said oil at a pressure ranging from about 100 psi to about 20,000 psi.
11. A method according to any one of the preceding claims, wherein after injection of said gas mixture said underground formation is sealed for at least one day.
12. A method according to claim 11, wherein said sealed underground formation is opened and a flood of a material selected from the group consisting of carbon dioxide, nitrogen, water or brine is driven through said injection point.
13. A method according to claim 12, wherein said gas mixture is injected into said underground formation in at least two distinct injection points wherein the volume percentage of nitrogen in said mixture is higher at said second injection point than said first injection point and said first injection point is closer to said at least one production well than said second injection point.
14. A method according to any one of the preceding claims, wherein said gas mixture further reduces the viscosity and the surface tension of said oil in said underground formation.
15. A method according to any one of the preceding claims, wherein the gas mixture contains at least 70% by volume of carbon dioxide.

FIG. 1

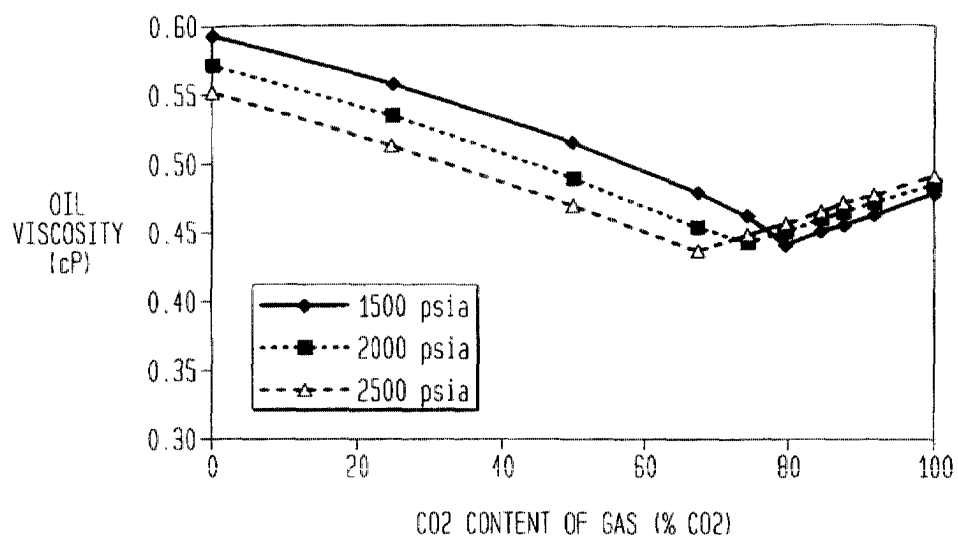


FIG. 2

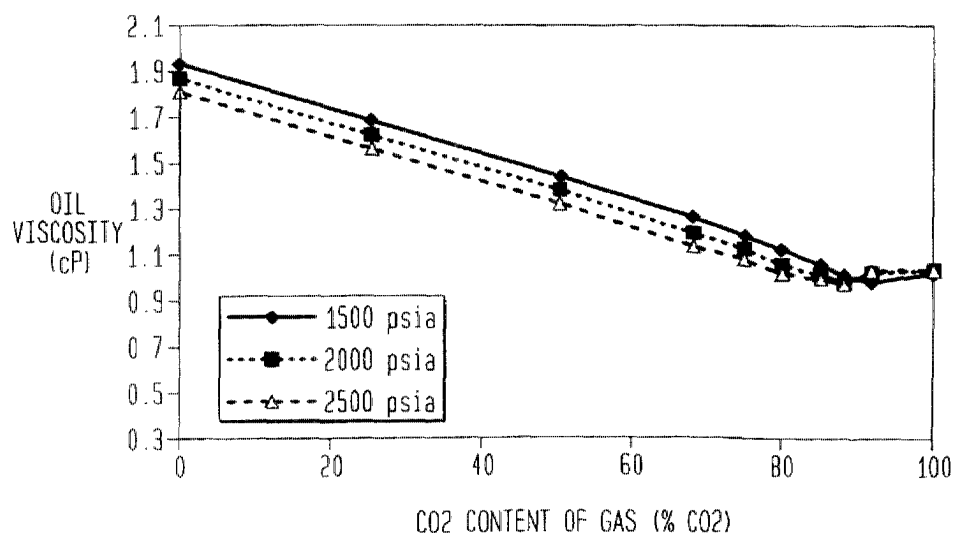


FIG. 3

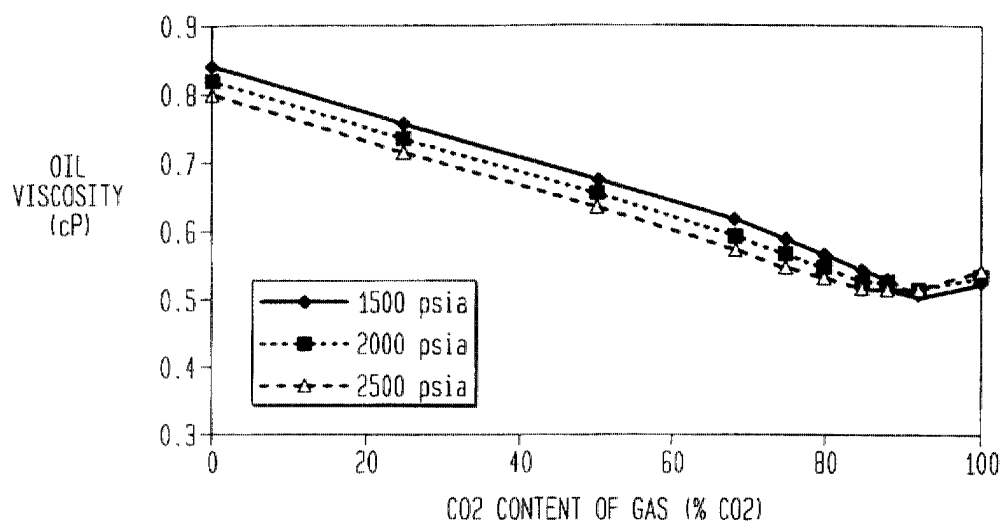


FIG. 4

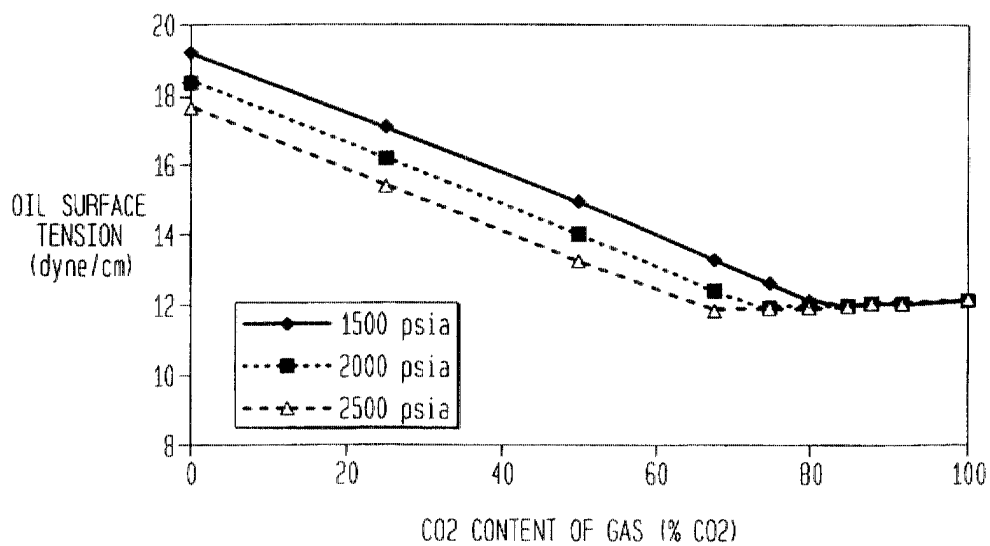


FIG. 5

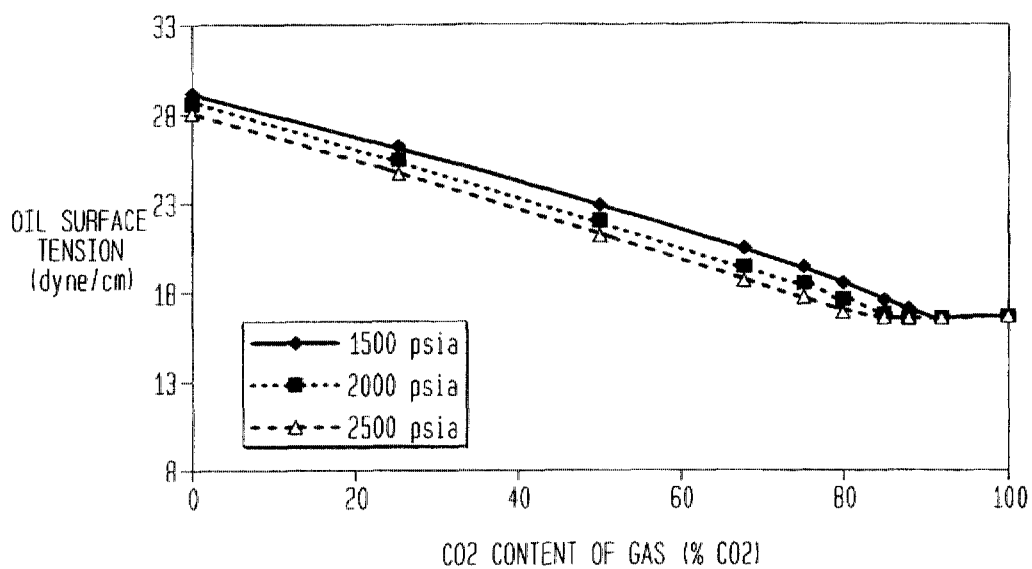


FIG. 6

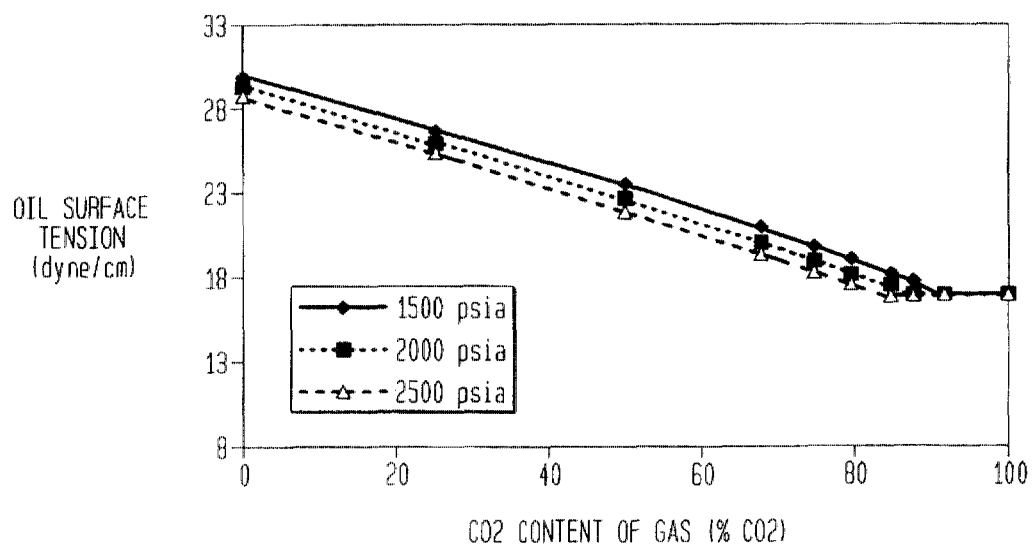


FIG. 7

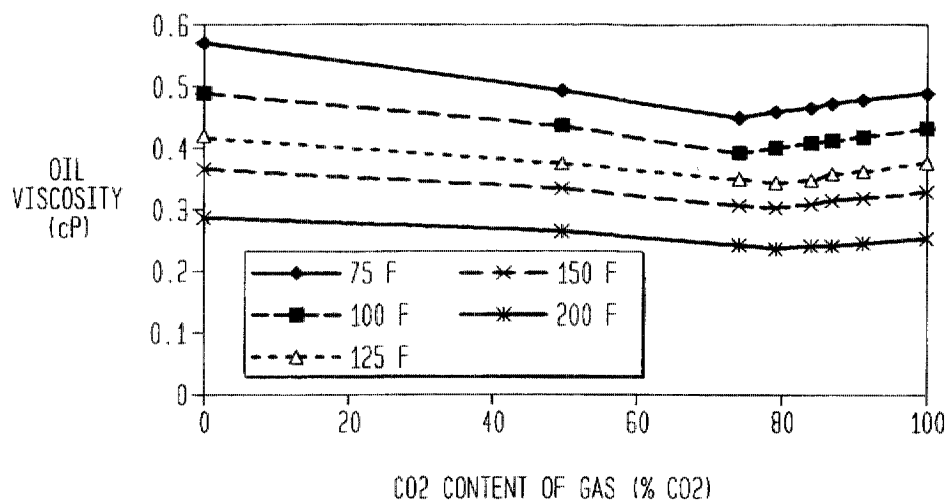


FIG. 8

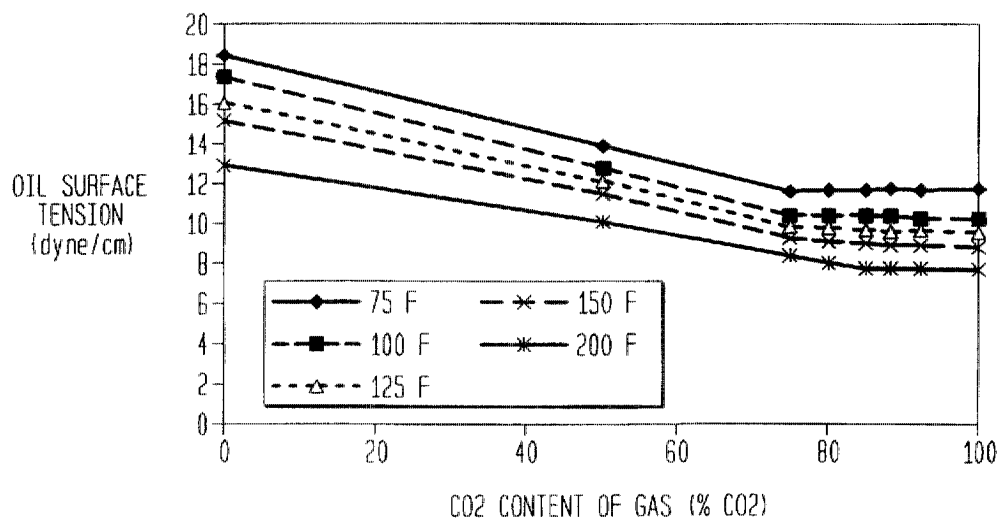


FIG. 9

