RECENT ADVANCES IN CARBON DIOXIDE STIMULATION TECHNOLOGY

Charles M. Fairless and Paul N. Brown, Jr.
Service Fracturing Company

ABSTRACT

The technology associated with the use of carbon dioxide as a component of oilfield stimulation fluids has evolved dramatically since its introduction in the early 1960's. Technology improvements in the mechanical, chemical, and applications areas will be discussed herein.

This paper will be introduced with a brief review of the chemical and physical properties of carbon dioxide which are the basis for the utilization of CO_2 in the stimulation industry.

The introduction will be followed by a discussion of mechanical advances in CO_2 pumping equipment, pressure maintenance devices, heaters, fluid viscosity measurement, flow monitoring instrumentation and safety equipment.

Next, chemical developments such as CO_2-compatible acid, water and alcohol gellants, dispersants, vapor phase stabilizers and crosslinkers will be traced.

Finally, stimulation applications of CO_2 will be described. These applications have multiplied from acid and hydraulic fracturing fluids energized by CO_2 as a minor commingled component for rapid removal of mud, silts, fines, water blocks and emulsions, through miscible hydrocarbon treatments, to dispersions, "foams" and crosslinked alcoholic fracturing fluids where CO_2 is the major component.

INTRODUCTION

Several of the first successful hydrocarbon stimulation treatments utilizing carbon dioxide (CO_2) as a fluid component were performed by Producers Chemical Company in the Texas Panhandle in 1961 and 1962. Carbon dioxide, at 400 scf/bbl, was added to gelled water primarily to speed treatment fluid recovery.[1, 2, 3]

By today's field operations standards, those initial carbonated fluid-based fracture stimulation applications were extremely simple. As with any new technique, primary concerns were for surface safety and ability to place the fluid in the zone of interest.

Today's hydrocarbon stimulation operating standards require substantial prejob engineering with particular emphasis placed on considerations for fluid freezing at the surface, surface and subsurface tubular stresses, "vapor phase" maintenance, "vapor phase" quality, impact on reservoir clays, and fluid lifting during flowback. Additional preplanning considerations are corrosion control, dispersant performance, additive compatabilities, fluid viscosities, proppant addition effects and automated electromechanical control networks.

The driving force for this evolution in technology has been and continues to be the need in the hydrocarbon producing industry for the application of stimulation fluids that possess the unique physical and chemical properties of fluids containing CO_2.

An appropriate beginning to the examination of this driving force is to list the relevant physical and chemical properties of CO_2 (Figure 1) and to follow these through the cycle of a carbonated fluid stimulation treatment (CO_2 frac cycle) (Figures 2 and 3). Under normal field circumstances, CO_2 is brought to an operating location in an over-the-road transport vessel wherein the CO_2 is contained at approximately -10°F and 250 psig. (Point A, Figure 2) Under these conditions, the density of CO_2 is 8.48 ppg. Therefore, an unheated wellbore column of CO_2 has a hydrostatic head similar to that of a column of water. Other CO_2 properties of particular operating significance are the specific heat of the liquid and the latent heat of vaporization (Figure 1). These parameters are utilized to determine the surface temperature of commingled fluids and whether they will remain a liquid at surface treating conditions, to examine subsurface tubular goods' tensile strength limitations versus fluid temperature induced applied forces, and in the estimation of the temperature at which a carbonated fluid must enter the wellbore (at the surface) to develop and maintain CO_2 in the vapor phase behind the perforations throughout a vapor phase dispersion (VPD) stimulation treatment.

After arriving on location, the next significant point of concern in a CO_2 frac cycle is point B of Figure 2, which is the discharge side of high pressure surface pumping equipment. Empirically (Figure 4), CO_2 varies in temperature from -10°F to 30°F over the pressure range of 2000 psig to 8000 psig. From a plot of CO_2 density versus applied pressure at various temperatures (Figure 5), it can be determined that the density of CO_2 varies throughout this typical frac cycle by a maximum of 15 percent. In fact, the variation in the density of CO_2 in a carbonated fracture treatment fluid at the time pumping ceases is seldom greater than 20 percent from the wellhead to near the fracture tip (Figures 3 and 5).

The three most significant chemical properties of CO_2 are its solubility in fluid, its miscibility in fluids and its ability to act as an acid upon solution. Figure 6 illustrates the solubility of CO_2 in water at relevant temperatures.[4, 5] In brines, solubility is approximately 15 percent less than in fresh water.[4, 5] Figure 7 illustrates CO_2 solubility in crude oils.[4, 6] This data illustrates that commingling CO_2 with subsurface fluids under typical stimulation treatment conditions effectively inputs energy to these subsurface fluids internally. This internal energy greatly assists in returning subsurface fluids to the wellbore and subsequently assists in returning these fluids to the surface. Also, one should note that CO_2 dissolved in crude oil substantially reduces the viscosity of the oil (Figure 8).

The pH of carbonated water-based fluids is buffered to between 3 and 4. At this pH, essentially all known reservoir clays are stabilized from swelling[7] and iron precipitation is effectively controlled. Additionally, it has been shown that carbonated methanol can be used to partially dissolve high surface area illite clay hairs and thereby considerably reduce their potential to plug reservoir rock pore throats upon migration.[8]

ADVANCES IN MECHANICAL TECHNOLOGY

Numerous advances have evolved in the process equipment utilized to pump CO_2 since that first carbonated fluid treatment some twenty-five years ago.

Developments in low pressure CO_2 process equipment have relegated the pumping of carbonated stimulation fluids to that of routine and safe. Since CO_2 is delivered to a wellsite as a liquid in a container, the pressure in the container decreases as CO_2 is pumped downhole. This pressure change leads to erratic liquid feed to the pumps which in turn leads to fluid slugging, vapor locking and possibly CO_2 freezing in downstream surface equipment. Two basic systems exist to control wellsite CO_2 vessel vapor pressure. The simplest and most effective of these systems is a patented vapor feedback system[9] (Figure 9). In this system, a small portion of the CO_2 being removed from the delivery container is fed to a low-pressure vaporizer. This vapor is then fed back to the delivery container such that the pressure inside the container remains constant regardless of the liquid level inside the container. The alternate system is to provide an external source of gas such as nitrogen at an appropriate pressure and temperature in an adequate volume plumbed such that the CO_2 container pressure is maintained constant.

The CO_2 is removed from the wellsite container by a low pressure pump which feeds or boosts the high pressure downhole pump. The first of the booster pumps had a capacity rating of 2 BPM at 50 psi differential and required maintenance during and after each use. Due to advances in pump design, some CO_2 booster pumps operate in excess of 100 hours without maintenance and pump up to 24 BPM at 100 psi differential pressure.

The booster pumps are normally coupled to a multi-purpose valving mechanism. These valves are used to vent any CO_2 vapor or solids that may collect in the low pressure equipment and to slowly bring this equipment to operating temperature. They can also be used to make CO_2 available as a fire extinguisher. Originally, these valves were of conventional metallurgy and were hand operated. With current metallurgy, these valves are usually automated and backpressure activated. This minimizes the danger of wellhead pressure leakback into any low pressure equipment.

High pressure equipment advances include improvements in fluid ends, plungers and packing materials which have resulted in pumping CO_2 with conventional high pressure triplex plunger pumps routinely rated to 15,000 psi. These pumps can be operated through below 0°F CO_2 operating temperatures to 150°F conventional liquid pumping temperature cycles up to hundreds of times with minimal metal fatigue and maintenance.

Another significant improvement in high pressure CO_2 equipment technology was made in 1980 by the introduction of patented CO_2 heating.[9] With this capability, the temperature of CO_2 as it enters the wellhead can be controlled. Advantages of this control include minimizing stress placed on downhole tubular goods, eliminating wellhead backpressure requirements to prevent freezing of commingled clean-up fluids, providing the capability for generating a nearly perfect proppant-supporting VPD at the surface under controlled conditions and removing the volume limitations placed on VPD treatments by reservoir temperature.

Remote multiple pump single person controls introduced in 1974 assure a constant ratio of CO_2 to co-fluid from as many as six pumps. This minimizes pad fluid waste and potential formation damage while adjusting CO_2 to co-fluid ratio during job startup. For VPD's, substantially closer control of "foam quality" can be achieved.

Numerous monitoring and control advances have been made since those initial CO_2 stimulations. Since, with only two exceptions amplified later in this paper, CO_2 is used as a component in stimulation fluids, most of these improvements are the result of attempts to improve stimulation fluids in general. Thus, they are generally applicable. The first CO_2 stimulation treatments were pumped using wellsite CO_2 liquid gauges to monitor the amount of CO_2 pumped with little regard to the viscosity of the commingled fluid at the wellhead or downhole. Currently, in-line turbine flow meters monitor CO_2 and commingled fluid rate while vibrating reed viscometers are frequently used to monitor viscosity. These data are transmitted electronically to a data processing unit or a mobile computer housed inside a control van. Here, digital electronics continuously record and display stimulation treatment parameters such as wellhead pressures, bottomhole treating pressure, friction pressure(s), net bottomhole treating pressure, individual fluid component rates, total pumping rate, proppant concentration, surface component fluid temperatures, surface CO_2 temperature and surface and bottomhole commingled fluid temperature. All this data can be formatted and printed during the stimulation treatment to provide for instantaneous continual treatment reporting.

The widespread acceptance and growth of stimulation treatments involving CO_2 has led at least one service company to develop CO_2 specific equipment and to establish a CO_2 department staffed by personnel who work only with CO_2. This department has pumped thousands of CO_2 stimulations with no lost time accidents.[10]

ADVANCES IN CHEMICAL TECHNOLOGY

Improvements in CO_2 associated chemical technology can be conveniently categorized into additives, gellants, dispersants and crosslinkers.

While liquid and vapor phase CO_2 have been used as breakdown fluids for some of the most clay-sensitive formations, cost and temperature change effects have restricted their use. Given these restrictions, few CO_2 breakdown fluid additives such as nonemulsifiers are currently available.

At least one pumping service company has applied a proprietary viscosifier/gelling agent for liquid CO_2.[11,12] Apparent viscosities achieved are reported to be on the order of 10 cp. at the surface.[11] However, the flash point of this viscosifier is extremely low and it is highly flammable and explosive. Also, the addition of proppant to this fluid system requires a highly specialized patented pressurized blender.[13] Thus, gelled liquid CO_2 has not gained widespread acceptance as a stimulation fluid.

The vast majority of carbonated stimulation fluids are commingled multiple phase fluids. The co-fluids are water, aqueous-alcohol, alcohol, hydrochloric acid or hydrocarbon liquids.

CO_2 was originally added to aqueous-based fluids in concentrations of 50 percent or less as an energizer.[1,2,3,4] Here the CO_2 served primarily to achieve rapid return of fluids to the wellbore. Today CO_2 is still frequently dispersed in conventional aqueous-based gelled or crosslinked stimulation fluids as an energizing component.

To stimulate those reservoirs where low reservoir pressure, low permeability and high concentrations of dispersed, water-sensitive clays exist, CO_2 has been used to energize lease crudes and diesel-based treatment fluids that are ungelled or conventionally gelled.

For the most sensitive of the above reservoirs, where it is desirable not only to minimize the water burden placed therein but is also desirable to minimize the liquid burden placed, alcohol is the fluid of choice. Alcohol will vaporize upon release of wellhead pressure at moderate bottomhole temperatures after a stimulation treatment. Thus, alcohol gellants have been developed and CO_2 has been used as an energizing component of alcohol-based fluids.[14] Various combinations of gelled aqueous-alcohol fluids are available to reduce fluid cost and still approach placing a minimum liquid burden on foreign liquid-sensitive formations.

Researchers have noted that unstabilized CO_2 energized fluids functioned as highly complex multiple phase, rheologically undesirable fluids with high leakoff and inadequate proppant support characteristics.[15] Their efforts to increase fluid efficiency led to the development of surfactant dispersing agents to regulate the size of liquid CO_2 droplets in ungelled, conventionally gelled or conventionally crosslinked, commingled energized fluids. These CO_2 energized fluids exhibit rheological, leakoff and proppant support characteristics very similar to the co-fluid.[15]

The next step in the development of CO_2 fluids was based on the recognition that CO_2 droplet size range could be regulated by surfactant dispersants where the concentration of CO_2 in the commingled fluid is greater than 50 percent.[16]

These liquid-liquid dispersions exhibit unique very high fluid efficiencies (very low leakoff coefficients), excellent yield pseudoplastic rheological properties, characterized, economically reasonable friction pressures, and near perfect proppant support. At low temperatures ($\leq$130°F) gelling or gelling and crosslinking the co-fluids enhance desirable performance characteristics. The performance characteristics of these CO_2-based stimulation fluids are significantly improved when compared to co-fluid characteristics.[16, 17, 18]

Economic incentives to drill wells with higher bottomhole temperatures (>200°F) have led to laboratory performance characterization of VPD's of high concentrations of CO_2 in co-fluids.[16, 17] Such VPD's are frequently described by terms generally applied to foams; i.e., a 70% CO_2 vapor phase dispersion is described as a 70 quality foam. These VPD's exhibit unique performance characteristics that are highly desirable for medium (130°F) to high (300°F) temperature stimulation applications. They maintain their viscosity better at high temperature than gelled fluids and are therefore a prime fluid choice for high temperature work.[17] When compared to nitrogen foams, CO_2 VPD's exhibit very similar desirable performance characteristics;[16-21] i.e., excellent proppant support,[17, 22-24] high apparent viscosities,[17] dynamic stabilities at high temperatures that are a strong function of "quality" and dispersant type[17] and a weak function of gelling agent concentration.[17] However, unlike nitrogen foams, the aqueous CO_2 VPD's have a high hydrostatic head. Wellbore CO_2 VPD column density is typically over eight pounds per gallon for a fluid gradient - near that of water! Field application data indicate the crosslinker(s) added to the gellant phase of CO_2 VPD's substantially improve their viscosity retention as a function of temperature.[17, 21] However, controlled laboratory experimental results have not been published at this time to support the field data.

In order for a CO_2 VPD to exist, the CO_2 must be vaporized. From Figures 1, 2 and 3, for CO_2 to exist in the vapor state it must be maintained above its critical pressure of 1071 psi and its critical temperature of 87.8°F. This pressure and temperature must be achieved at the wellsite prior to fluid entering the performations from CO_2 that has arrived on location at approximately -10°F and 250 psig. Wellhead pressure will typically exceed CO_2 critical pressure. And there are two means of achieving CO_2 critical temperature. One patented means is to pump the CO_2 into the wellbore at the surface as a liquid and to depend on hydraulic energy input, co-fluid temperature and the subterranean formation to heat the liquid above its critical temperature.[25] With this heating mechanism, there is a maximum volume of fluid that can be pumped into the reservoir without lowering the bottomhole treating fluid temperature below the critical temperature of CO_2. While this maximum volume can be approximately calculated[26, 27] it often limits job size to less than that which is desirable to achieve maximum productivity increase. [28, 29] The second means to achieve CO_2 critical temperature is to heat the CO_2 at the surface. This patented heating[9] can be used to control CO_2 VPD fluid temperature throughout a job. Advantages to this system are the elimination of the maximum applicable volume limitation, minimum temperature-related stresses applied to tubular goods and the ability to change the fluid temperature "on the fly" as well treating conditions dictate.

There have been several hundred applications of aqueous co-fluid CO_2 VPD's to date.[19, 20, 21] Today, stimulation applications of these VPD's can be described as safe, operationally routine and highly successful in terms of typical productivity increase and rate of clean up.

Aqueous co-fluid CO_2 VPD's employ conventional water applicable gellants such as guar, hydroxypropyl-guar, carboxymethyl-hydroxypropyl guar, carboxymethyl cellulose, carboxymethyl-hydroxyethyl celluose or hydroxyethyl cellulose gelling agents as a vapor phase stabilizer. They employ sulfated alkoxylates, alkyl quaternary amines, betaines, ethoxylated linear alcohols or other water foamers as dispersants. And conventional additives such as nonemulsifiers, paraffin dispersants, inhibitors, sequesterants, etc., are added as individual reservoir and flowback conditions dictate.

Hundreds of field application data also demonstrate that proprietary alcohol gellants in combination with proprietary alcohol functional CO_2 dispersants can be utilized to generate CO_2 VPD's that perform similarly to aqueous-based CO_2 VPD's.[14] While these CO_2-based fluids are less expensive than CO_2-energized gelled alcohol fluids, their cost restricts their routine use to those oil or gas reservoirs where dispersed clays, low permeability and/or low internal pressures necessitate placing a minimum liquid burden on the potential pay zone.

More recently, high percentage CO_2 VPD's in hydrocarbons generated downhole by reservoir conditions have been introduced. These systems are formed by dispersing 30% to 95% CO_2 with a liquid anhydrous fluid at the surface. The liquid anhydrous fluid may consist of from 25% to 75% ethylene glycol and from 30% to 75% hydrocarbon such as kerosene, diesel, light crude oils or the like, stabilized by a surfactant.[30]

This type system appears to be extremely expensive and, to date, no field application data is generally available to characterize these fluids with respect to performance.

APPLICATIONS AND SUMMARY

Table 1 is a list of applications of various CO_2-energized and CO_2-based stimulation fluids. Included are results that are representative of those routinely achieved today using these fluids. The large variety of fluid types, formations and corresponding oil and gas production increases vividly illustrates the current very positive state of the art in CO_2 stimulation technology. This is the result of numerous mechanical, electromechanical, data processing and chemical technological advances contributed by thousands of people in all phases of stimulation service and oil company organizations over the twenty-odd years since that first stimulation application of CO_2.

FUTURE ADVANCES

Future developments in CO_2 stimulation technology are based on today's research. Currently there are studies underway to better define various performance characteristics of both CO_2-energized fluids and VPD's. Higher temperature dispersants and stabilizers are being developed. Research into 100% CO_2 viscosifiers is being conducted. On-location computers are being equipped with software that, when coupled with in-line monitoring devices, are able to control co-fluid concentration, viscosity, and pumping rates based on real time bottom-hole measurements to generate pre-engineered fracture geometry.

Since growth in demand for carbonated fluids will parallel attempts to extract hydrocarbons from more hostile tighter, fluid-sensitive reservoirs, I feel that advances in CO_2 stimulation technology will have an even greater impact on the oil and gas industry in the next 25 years than in the past 25 years.

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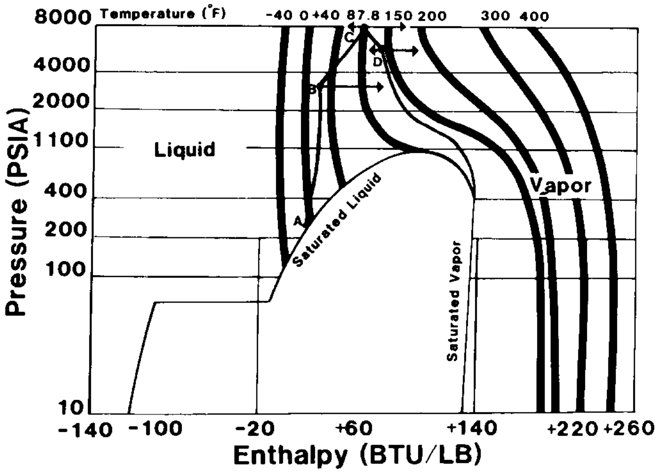
Table 1
CO_2 Stimulation Application Examples

					PRODUCTION HISTORY			
					PRIOR		POST	
CO-FLUID AND CONCENTRATION	CO_2 CONCENTRATION	FORMATION	BHT (F°)	COUNTY, STATE	OIL (BOPD)	GAS (MCFPD)	OIL (BOPD)	GAS (MCFPD)
50%-5% HCL+50 ppt ABE	50%^{a}	Morrow	180	Roberts, Texas	-	40	10	2000
7½% HCL+75#ABF	1250 scf/BBL^{a}	Douglas	160	Roberts, Texas	0	10	65	40
7½% HCL	1500 scf/BBL^{a}	Morrow	190	Lipscomb, Texas	0	30	0	500
50%-5% HCL	50%^{a}	Wolfcamp	135	Glasscock, Texas	0	0	720	50
3% Gelled HCL	1250 scf/bbl	Atoka	170	Lipscomb, Texas	-	-	30	1000
50%-30# Crosslinked 3% HCL	50%^{a}	Morrow	170	Beaver, Oklahoma	-	-	118	40
40# Crosslinked 5% HCL	1000 scf/BBL	Morrow	150	Beaver, Oklahoma	-	200	-	3800
30% 50# Gelled Water	70%^{a}	Canyon Sand	170	Sutton, Texas	N. Avail	N. Avail	N. Avail	N. Avail
30% 40# Gelled Water	70%^{a}	Douglas	140	Hemphill, Texas	-	100	-	4000
40# Crosslinked Gel	1500 scf/BBL	Douglas	140	Hemphill, Texas	NW	NW	-	8000
40# Crosslinked Gel	1250 scf/BBL	Tonkawa	135	Lipscomb, Texas	NW	NW	-	3350
50% - 50# Crosslinked Gel	50%	Greyburg	135	Lea, New Mexico	1	20	30	5000
20% to 35% - 30# Crosslinked Gel	80% to 65%^{a}	Codell-Niobrara	250-240	Weld, Colorado	NW	NW	22	220
30% - 40# Crosslinked Gel	70%^{a}	Granite Wash	175	Roberts, Texas	-	P&A	20	1200
Methanol	3000 scf/BBL	Prue	140	Logan, Oklahoma	N. Avail	N. Avail	N. Avail	N. Avail
5% Gelled Methanol 25% Gelled Water	70%^{a}	Chester (Sand)	170	Beaver, Oklahoma	-	900	50	11000
10% Crosslinked Methanol 20% Crosslinked Water	70%^{a}	Upper Morrow	200	Roberts, Texas	-	20	-	500
25% Crosslinked Methanol	75%^{a}	Morrow	165	Beaver, Oklahoma	NW	NW	-	4000
20% Crosslinked Methanol	80%^{a}	Cleveland	160	Ochiltree, Texas	NW	NW	192	380
20% Crosslinked Methanol	80%^{a}	Red Fork	180	Ellis, Oklahoma	-	100	94	500
20% Crosslinked Methanol	80%^{a}	Cottage Grove	160	Ellis, Oklahoma	NW	NW	25	9700
20% Crosslinked Methanol	80%^{a}	Granite Wash	175	Roberts, Texas	35	50	300	2500
	100%	Pictured Cliffs	90	Rio Arriba, N.M.	-	50	-	900
	100%	Cherokee	180	Custer, Oklahoma	-	500	-	1700

[a] CO_2 heated on surface   N. Avail = Not Available   NW = New Well

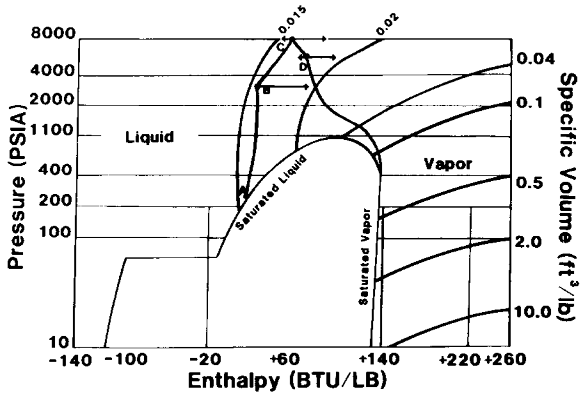
Chemical Symbol		CO_2
Molecular Weight		44.01
Gas, Liquid		Colorless, Odorless
Solid		White
Density:		
Solid	(-110°F)	97.66 Lb./Ft.^{3}
Liquid	(-10°F, 280 PSI)	8.48 PPG
Gas	(60°F, 1)	0.117 Lb./SCF
Air	(68°F, 1)	0.076 Lb./SCF
Specific Heat Liquid (0°F)		0.53 BTU/Lb.° F
	(75°F, 2000 psi)	0.74 BTU/Lb°F
Specific Heat Gas (Cp)		0.199 BTU/Lb.° F
Latent Heat of Vaporization:		
	(0°F, 300 psi)	122 BTU/Lb
	(75°F, 300 psi)	50 BTU/Lb
Critical Temperature		87.8°F
Critical Pressure		1071 PSIA
1 Ton		234.9 Gal.
1 Gal.		76.44 SCF

Figure 1—Properties of carbon dioxide



A = CO_2 in transport or surface storage vessel.
B = CO_2 at the discharge of high pressure downhole pump.
C = CO_2 at perforations.
D = CO_2 at fracture tip after pumping ceases.

Figure 2—CO_2 frac cycle



A = CO_2 in transport or surface storage vessel.
B = CO_2 at the discharge of high pressure downhole pump.
C = CO_2 at perforations.
D = CO_2 at fracture tip after pumping ceases.

Figure 3—CO_2 frac cycle

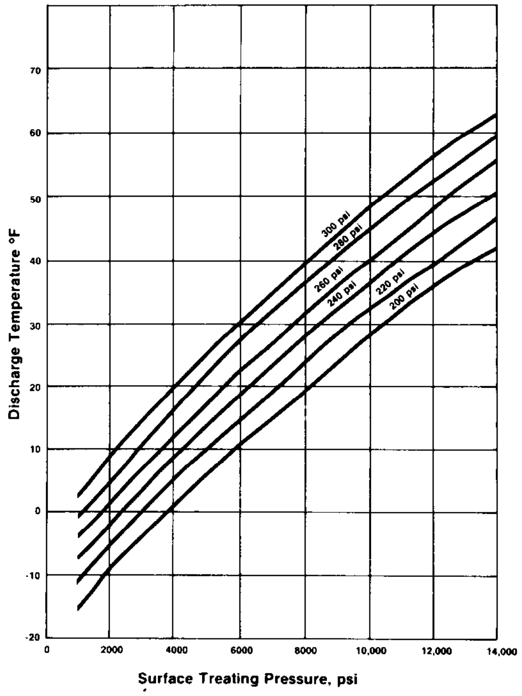


Figure 4—CO_2 discharge temperature

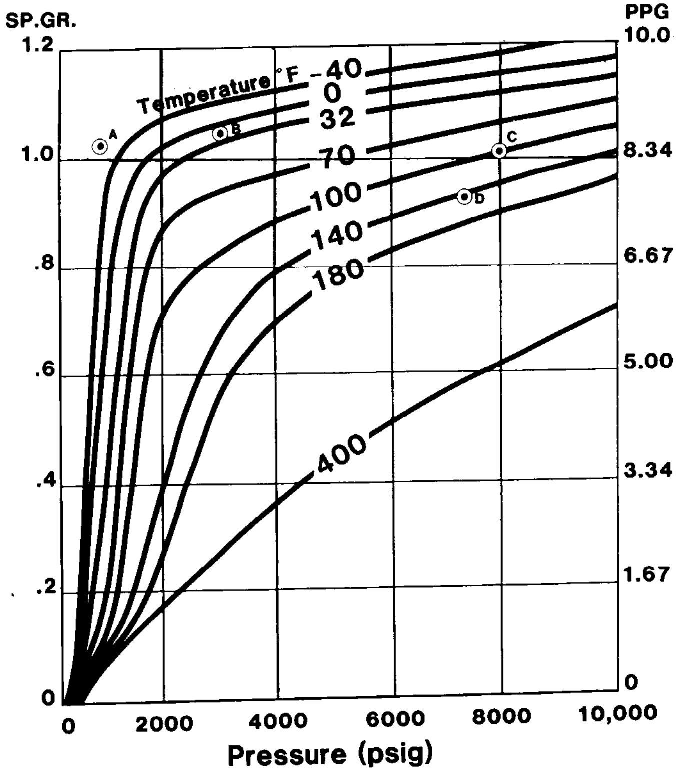


Figure 5—Density of carbon dioxide

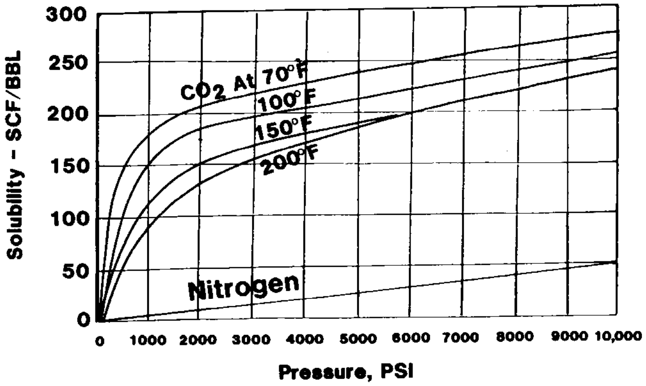


Figure 6—CO_2 solubility in water

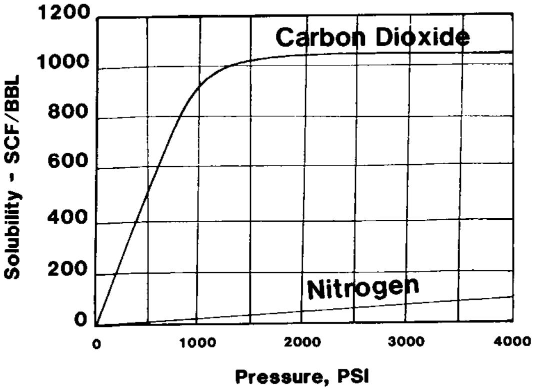


Figure 7—CO_2 solubility in
40° crude 100° F

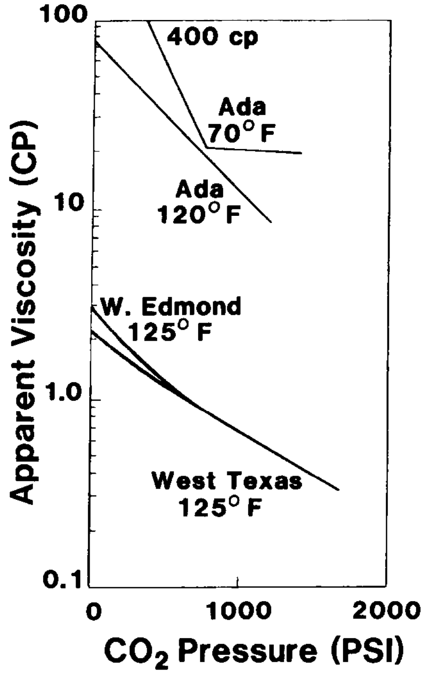


Figure 8—Change in crude oil viscosity with added carbon dioxide

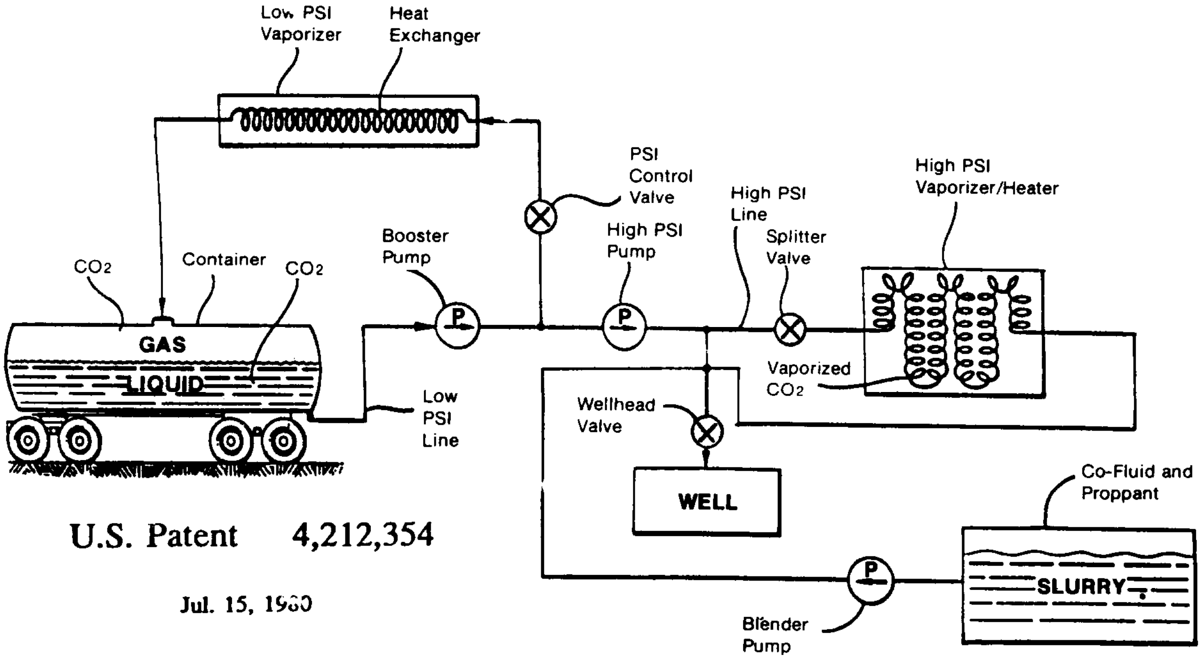


Figure 9
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