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**IMPROVEMENT IN OIL RECOVERY USING
COSOLVENTS WITH CO₂ GAS FLOODS**

**By
Clarence Raible**

January 1992

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Bartlesville, Oklahoma**

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U. S. DEPARTMENT OF ENERGY
Bartlesville, Oklahoma**

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U.S. Department of Energy
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IMPROVEMENT IN OIL RECOVERY USING COSOLVENTS WITH CO₂ GAS FLOODS

By Clarence Raible

ABSTRACT

This report presents the results of investigations to improve oil recovery using cosolvents in CO₂ gas floods. Laboratory experiments were conducted to evaluate the application and selection of cosolvents as additives to gas displacement processes. A cosolvent used as a miscible additive changed the properties of the supercritical gas phase. Addition of a cosolvent resulted in increased viscosity and density of the gas mixture, and enhanced extraction of oil compounds into the CO₂ rich phase. Gas phase properties were measured in an equilibrium cell with a capillary viscometer and a high pressure densitometer.

A number of requirements must be considered in the application of a cosolvent. Cosolvent miscibility with CO₂, brine solubility, cosolvent volatility and relative quantity of the cosolvent partitioning into the oil phase were factors that must be considered for the successful application of cosolvents. Coreflood experiments were conducted with selected cosolvents to measure oil recovery efficiency. The results indicate lower molecular weight additives, such as propane, are the most effective cosolvents to increase oil recovery.

INTRODUCTION

Gas flooding processes such as CO₂ displacement have the potential to significantly increase oil production. However, the gas phase is less viscous and has a lower density than the crude oil, which results in by-passed oil and poor sweep efficiency. The recovery efficiency is a product of the displacement efficiency and sweep efficiency. For miscible CO₂ floods, the displacement efficiency is very high. Therefore, the low recovery efficiency is primarily due to poor sweep. For immiscible CO₂ floods, both displacement efficiency and sweep efficiency can be low. The addition of cosolvents has the potential to improve the displacement efficiency and sweep efficiency for immiscible floods. Cosolvents may have an added benefit of reducing the pressure necessary to obtain an economic flood.

The concept of using a cosolvent to increase solvent power of the supercritical gas phase has been noted by a number of investigators. For some studies,¹⁻² the term "entrainer" was used to describe the addition of a second solvent to the supercritical CO₂ phase to enhance extraction of a compound or class of compounds. The addition of a suitable entrainer may improve selectivity and extraction of low volatility compounds into the gas phase.

Previous studies³ at NIPER screened a number of compounds for beneficial properties to increase solubility in the gas phase. Many of these candidate cosolvents had relatively high molecular weights with carbon numbers of C₈ or higher. One potential advantage for using these additives would be the direct solubility of the cosolvent into the gas phase to produce an increase in density and viscosity. The results indicated a few of the compounds were candidate cosolvents. These compounds also improved the extraction of components from the oil phase.

This report summarizes additional studies made to evaluate the application of cosolvents for CO₂ gas displacement. Experiments were conducted to measure improvement in gas phase viscosity and density by the addition of selected cosolvents. In addition, these experiments compared the enhancement of n-hexadecane extraction into the gaseous phase using propane as a cosolvent.

Gas displacement corefloods were conducted with selected cosolvents, and the oil production was compared using these additives. Oil recoveries using different cosolvents provided additional evidence of relative displacement efficiency for crude oil. Other corefloods were conducted to demonstrate partitioning of the cosolvent into the oil phase. The experiments indicated that a higher molecular weight cosolvent was bypassed by the gas flood. The quantity of cosolvent partitioning into the oil phase was another factor that must be considered in the selection of a cosolvent.

PHYSICAL PROPERTIES MEASUREMENTS

Of the compounds studied previously,³⁻⁴ isooctane and 2-ethylhexanol were reported to be candidate cosolvents. Vapor phase measurements indicated that these cosolvents increased the extraction of heavier hydrocarbons into the vapor phase. Isooctane was chosen for further physical property measurements because this compound produced greater enhancement of hydrocarbon extraction into the vapor phase than 2-ethylhexanol. Also for this study, cyclohexanol was selected for physical property measurements as a potential cosolvent because of its high density and viscosity.

According to a paper by Joshi and Prausnitz,⁵ the maximum supercritical extraction of a liquid phase would be obtained with a gas phase solvent near or slightly above the critical temperature. Therefore, for oil displacement by gas in a reservoir, maximum extraction of a crude oil would require a gaseous solvent with a critical temperature near the reservoir temperature. Most reservoirs have temperatures which exceed the CO₂ critical temperature of 31° C. Because the reservoir temperature cannot be changed easily, the only option to maximize the extraction process is to select a suitable gaseous solvent. A mixture of CO₂ and a suitable cosolvent can be used to produce a gaseous mixture with the desired critical temperature for a greater number reservoir applications. Also, a high vapor pressure cosolvent would reduce the amount of

cosolvent that partitions into the liquid or oil phase, and therefore, less of the cosolvent would be bypassed during the flooding process. A volatile cosolvent would improve a sustained cosolvent concentration throughout a gas flood. The most obvious choice for a cosolvent would be a lower molecular weight hydrocarbon such as propane or butane. For these reasons, propane also was selected as a candidate cosolvent for physical properties studies.

Experimental Apparatus

An apparatus constructed previously at NIPER⁴ was used to measure viscosities of gaseous carbon dioxide mixtures. The apparatus shown in figure 1 was housed in a constant temperature oven controlled within $\pm 0.5^\circ$ C of the test temperature. Some of the essential components of the system consisted of a high-pressure windowed cell (100 cm³) used as a mixing and equilibrium chamber. A Ruska magnetically driven pump was used to mix the fluids to achieve fluid equilibrium. Fluid densities were measured using a Mettler-Parr DMA 512/60 high-pressure densitometer. The density system was calibrated with water and vacuum which were used as high and low density standards. The change in instrument response to temperature was measured with vacuum between 25° and 60° C to obtain a system temperature correction. For the instrument's pressure correction, the response was measured with water between 0 and 2,600 psig where the water density was corrected for compressibility. Periodic checks were made for densitometer accuracy with nitrogen and pure CO₂ at the test conditions. Density data for CO₂ and nitrogen were in agreement with the literature⁶⁻⁷ within $\pm 0.2\%$.

Viscosities were measured using a capillary tube viscometer. A 1,266.7-cm-long Monel tube with an 0.13 cm internal diameter was used for gas phase viscosity measurements. Pressure gradients were measured using a Tobar Model 75 differential pressure transmitter calibrated to measure pressures of 0 to 8 in. water column (0 to 0.289 psi). A tandem dual-drive Temco pump was used to provide reciprocating operation of the two floating-piston vessels. The floating-pistons and coupled pump system were used to achieve steady-state gas flow through the capillary tube of the test fluids. The identical pump pistons were driven through a transmission that permitted selection of laminar flow rates of the test fluids.

Experimental Procedure

The physical properties of cosolvent blends and gas phase extraction of liquid hydrocarbons were measured with the apparatus shown in figure 1. Volume of the equilibrium system were measured by the Boyle's law pressure-volume relationship. Gaseous blends of propane were prepared by connecting a cylinder containing a predetermined weight of propane in the equilibrium system as shown in figure 1. The remaining equilibrium system was evacuated and filled with

FIGURE 1. - Schematic diagram of carbon dioxide and cosolvent equilibrium cell and capillary viscometer for high pressure gas phase measurements.

CO₂ using an air-actuated pump capable of boosting CO₂ to the desired test pressure. Propane was then mixed with CO₂ by opening valves to the propane cylinder. Blend composition was computed from the molar volume of CO₂ and weight of propane. Samples of the gas mixture also were analyzed by gas chromatography as a cross check of the mixture composition.

Liquid samples were introduced into the system by filling a floating piston vessel with the appropriate liquid. A measured volume of the liquid was then injected into the equilibrium system by means of a syringe pump. Equilibrium between the cosolvent gas mixture and the liquid phase was achieved by fluid circulation with a magnetically operated high pressure pump. To achieve equilibrium with fluids in the floating piston vessels, fluids in these vessels were filled and withdrawn periodically using the dual piston pump. Fluid equilibrium at the desired test pressure was determined by monitoring the densitometer for a constant density reading. A series of differential pressure measurements were made across the capillary tube at different flow rates. Gas flow rates were determined by the pump injection rate which ranged from 32 to 512 cm³/hr. The measurement of absolute viscosities was based on application of Poiseuille's law for flow of Newtonian fluids through a capillary tube⁸ using the differential pressures and mass flow rates.

To test the experimental accuracy of the capillary viscometer, measurements were made for CO₂ between a pressure of 1,600 and 2,500 psia. The results agreed with literature data⁶ to within $\pm 5\%$.

Experimental Results of Physical Properties Measurements

Cosolvents used for this study were propane, cyclohexanol, and isooctane. Table 1 shows the density and viscosity of isooctane mixtures at miscible conditions of 60° C and 2,200 psia. The data in figure 2 are presented on the basis of weight because this is a more descriptive measure of the actual quantity or mass of each compound present in the binary mixture. As the concentration of isooctane increased, mixture density increased until the fluid density leveled at about 30 wt % with a density of 0.725 g/cm³. A density of 0.68 g/cm³ was measured for liquid isooctane at 60° C and 2,200 psia. Also, as shown in figure 2, mixture viscosity increased with higher isooctane concentration. At 40 wt % of isooctane, the viscosity of the mixture measured 0.11 cP, an 140% increase in viscosity. A curve fit of the viscosity data was used to project and estimate the apparent viscosity at a 100% concentration of isooctane. This projection indicated a viscosity of about 0.34 cP for pure isooctane. This is a value which is close to the viscosity of liquid isooctane at 60° C (see table 2). A viscosity of 0.4 cP was measured for isooctane at 2,200 psia and 60° C.

Viscosity and density data for cosolvent mixtures of 2-ethylhexanol from a previous study³ were plotted in figure 3. These results also indicated a leveling of mixture density at a blend concentration of about 25 wt %. The level density of 0.86 g/cm³ was also slightly above the

TABLE 1 - Physical properties of CO₂ + isooctane mixtures at 60° C and 2,200 psig

Isooctane		Mixture Density g/cm ³	Density Increase %	Mixture Viscosity cP	Viscosity Increase %
Mole fraction	Wt. fraction				
0.0000	0.0000	0.6012	--	0.0464	--
0.0382	0.0934	0.6686	11.2	0.0532	14.7
0.0771	0.1781	0.6984	16.2	0.0665	43.4
0.1009	0.2257	0.7086	17.9	0.0727	56.7
0.1249	0.2703	0.7168	19.2	0.0825	77.9
0.1500	0.3142	0.7222	20.1	0.9020	94.5
0.1750	0.3551	0.7234	20.3	0.0991	113.7
0.2001	0.3937	0.7246	20.5	0.1078	132.4
0.2251	0.4299	0.7228	20.2	--	--

FIGURE 2.- Viscosity and density of isooctane and CO₂ mixtures at 60° C and 2,200 psig.

TABLE 2.- Viscosity and physical properties of cosolvents extrapolated from the literature⁹⁻¹⁰

Compound	Viscosity (cP) (at specified temperature)			Density (20°C) g/cm ³	MW g/mol
	20° C	40° C	60° C		
Isooctane	0.50	0.41	0.34	0.6919	114.23
2-Ethylhexanol	9.8	4.4	--	0.8332	130.23
Cyclohexanol	68.0	23.5	--	0.9624	100.16

FIGURE 3.- Viscosity and density of 2-ethylhexanol and CO₂ mixtures at 40° C and 2,000 psig. Data was taken from reference 3.

measured liquid density of 0.833 at 20° C. A curve fit of the viscosity data gave a projected viscosity of 3.4 cP at a 100% concentration of 2-ethylhexanol. These values are also reasonably close to the density (0.835 g/cm³) and the viscosity (5.3 cP) measured for 2-ethylhexanol at a temperature of 40° C and 2,200 psi.

Inspection of the data shown in figures 2 and 3, reveal that critical gas phase mixtures of 2-ethylhexanol had a much greater increase in viscosity and higher density than isooctane mixtures. Comparison of the fluid mixtures reveals that the more dense and viscous liquid had a higher viscosity in the miscible gas phase. The data suggests that to obtain the maximum effect for increasing the gas phase viscosity, it would be desirable to use a highly viscous fluid.

On the basis of higher density and viscosity, cyclohexanol was selected as a candidate cosolvent (see table 2). The results of gas phase mixtures of cyclohexanol are listed in table 3. At 2,450 psi and 40.8° C, a maximum concentration of 3.3-mol % (7.3 wt %) was measured in the gas phase saturated with cyclohexanol. The solubility of this compound was limited even at these conditions of relatively low temperature and high pressure. At the conditions of gas phase saturation, the gas phase density was 6.5% higher and viscosity increased 32% above pure CO₂ at these conditions. However, because of the limited solubility in the CO₂-rich phase, cyclohexanol was not considered a cosolvent candidate for reservoir applications. Cosolvent miscibility is a factor which must be considered in selection of candidate cosolvents.

TABLE 3. - Viscosity and density of CO₂ + cyclohexanol mixtures at 40.8° C and 2,450 psia

Cyclohexanol		Mixture Density g/cm ³	Density increase %	Mixture Viscosity cP	Viscosity Increase %
Mole fraction	Wt. fraction				
0.000	0.000	0.7987	0.0	723.3	0.0
0.030	0.065	0.8455	5.8	870.1	22.0
0.033	0.073	0.8509	6.5	939.3	31.7

Additional experiments were performed to measure the physical properties of propane as a cosolvent. As shown in figure 4, a 30-mol % propane blend had a higher viscosity than pure CO₂ at a temperature of 60° C. The relative viscosity changed with pressure from approximately 30% at 1,600 psia down to about 11% at 2,500 psia. Relative density of the blend also changed with pressure. As shown in figure 5, the density of the blend was about 20% greater than CO₂ at 1,600 psi and the relative density decreased with higher pressure where the density at 2,500 psi was lower than CO₂ density by about 12%. This relative decrease in viscosity and density with pressure was probably related to a difference in compressibility of CO₂ and propane. With increasing pressure, the more compressible CO₂ had a greater change in density and viscosity.

FIGURE 4. - Viscosity of a 30-mol % blend of propane and CO₂ measured at 60° C.

FIGURE 6 - Viscosity of n-hexadecane extraction with CO₂ at 60° C.

FIGURE 7. - Density of n-hexadecane extraction with CO₂ at 60° C.

FIGURE 8. - Viscosity of n-hexadecane extraction with 30-mol % propane/CO₂.

FIGURE 9. - Density of n-hexadecane extraction with 30-mol % propane/CO₂.

cosolvent mixtures. At 50° C and 2,000 psig, extraction of n-hexadecane was made with CO₂ with a 5 volume % isooctane blend, and with a 5 volume % 2-ethylhexanol blend. Gas phase viscosity of each extracted mixture was measured and compared with pure CO₂ viscosity at these conditions. The viscosity of the mixtures (CO₂, isooctane, and 2-ethylhexanol) increased by 10, 24, and 47% respectively. Also, the extracted mixtures were analyzed for the vapor phase concentration of n-hexadecane. The gas phase mixture concentrations of n-hexadecane were 2.2, 6.2, and 4.4-mol % respectively. The addition of isooctane increased n-hexadecane extraction by nearly 190%. The cosolvent 2-ethylhexanol increased the n-hexadecane extraction by about 100%. These results indicate that the increase in gas phase viscosity was in large measure due to the cosolvent additive in the gas phase and to a lesser extent extraction of n-hexadecane. The more dense and viscous 2-ethylhexanol contributed to a substantially higher viscosity even though more n hexadecane was present in the vapor state with the isooctane cosolvent.

The experimental results of a 30-mol % propane mixture also indicated a higher viscosity due to the presence of propane in the gas phase. Gas phase extraction of n-hexadecane using a propane cosolvent mixture indicated only a minor increase in density and viscosity. Most of the change in physical properties was due to the properties of the cosolvent blend.

Other experimental results⁴ using an isooctane mixture (8-mol %) to extract a crude oil (22.7° API gravity) were reported at the experimental conditions of 50° C and 2,200 psig. A 32% increase in viscosity was measured when compared to the viscosity of pure CO₂. By comparison, the viscosity of a 7.7-mol % blend of isooctane (table 2) was 43% higher when compared with pure CO₂ at the experimental conditions of 60° C and 2,200 psia. Therefore, much of viscosity increase also can be attributed to the presence of cosolvent isooctane in the vapor phase and not the extracted hydrocarbons. Again, extracted hydrocarbons appeared to have less effect on increasing vapor phase viscosity than the solubility of the cosolvent.

Summary

Cosolvents must have an appreciable solubility in carbon dioxide in order to effectively improve properties of the gas phase. Physical property studies suggest that the vapor phase solubility of the cosolvent is more important for improvement of gas phase viscosity than enhanced extraction of heavier hydrocarbons from a liquid or oil phase. Also, there appeared to be a relationship between the cosolvent liquid phase properties and the critical phase properties of density and viscosities. However, for extraction studies, the actual contribution of each of these factors for improvement in gas phase viscosity was complicated by the quantity of cosolvent that partitions into the oil phase. Cosolvent partitioning into the oil phase is a factor that must be considered for gas flood applications in a reservoir. No attempt was made in these physical

property studies to evaluate the effect of cosolvent loss due to partitioning into the oil phase. This factor will be considered in a later section of this report.

GAS COREFLOOD EXPERIMENTS USING COSOLVENTS

Gas coreflood experiments were conducted to investigate the following: (1) comparison of oil displacement efficiency using propane and isooctane as cosolvents in CO₂ floods, (2) the potential for using cosolvents to improve oil recovery in cyclic floods and (3) the possibility of a chromatographic effect or bypassing the secondary solvent during the gas flood.

Experimental Apparatus

Coreflood experiments were conducted using a 57-cm-long core with a diameter of 5.08 cm. Prior to core insertion into a Buna-N sleeve, the core was wrapped with several layers of aluminum foil. The aluminum wrapping was used to minimize CO₂ permeation through the rubber sleeve into the overburden fluid. Water used as the overburden fluid was maintained at approximately 1,500 psi above the test pressure for displacement experiments. A Ruska displacement pump was used to inject oil into floating-piston transfer cylinders containing CO₂ and test blends. A dome-loaded back pressure regulator was used to control the core outlet pressure at the desired test pressure. The produced fluids were flash separated at atmospheric pressure with the oil and brine measured in a volumetric trap and the gas measured with a wet test meter.

CO₂ Coreflood Experiments Comparing Propane and Isooctane as Cosolvents

The cosolvents selected for coreflood tests were propane and isooctane. These experiments were conducted to provide information on the effectiveness in oil recovery using cosolvents with a relatively high and low molecular weights. Isooctane was used for one set of experiments because previous screening studies indicated this cosolvent to be one of the more effective additives for hydrocarbon extraction and improvement in viscosity of the gaseous phase.

Other corefloods were conducted using propane as a cosolvent additive at the same test conditions. Propane was selected for these experiments because it could be used as a mixed solvent with the desired critical temperature. Depending on the composition, a mixture of propane and CO₂ could provide an optimum solvent with a critical temperature about the same as the coreflood temperature. It is estimated that a solvent mixture of approximately a 70/30 blend of propane/CO₂ would have the desired critical temperature at these experimental conditions. A small slug of this mixture displaced by a gas drive should provide an effective solvent which would be miscible with the oil in place. As discussed by Haynes and Alston,¹² small slugs of a light hydrocarbon will lower the reservoir pressure necessary to achieve miscibility.

Experimental Test Conditions

A number of corefloods were performed to test the recovery efficiency of using small slugs of gas phase additives. The two Berea cores used in these experiments had a porosity of 19 and 18% with pore volumes of 216 and 208 cm³, respectively. The Delaware-Childers crude oil used in these experiments had a 33.6° API gravity. Prior to gas injection, the brine saturated cores were flooded with crude oil and then followed by 1.25 PV of brine to obtain cores with watered-out saturation of crude oil. The test temperature was 150° F (65.5° C) and a gas injection pressure of 1,600 psi. At these conditions CO₂ was not miscible with the crude oil. The tests were terminated when the oil production dropped to 0.1 ml for 0.05 PV of injected CO₂ which was usually 1.0 to 1.2 PV of injected CO₂.

Each of the cosolvents were injected initially at the beginning of the coreflood. One test used a 0.2 PV of 20-mol % (11.0 mL) isooctane blend and the second test used a 10.7-mL slug of liquid isooctane. The isooctane was injected using a floating-piston transfer cylinder containing the cosolvent mixture. The liquid isooctane slug was injected by connecting a tube containing a measured weight of isooctane in series with the CO₂ injection source.

Although it was estimated that a 70/30 blend of propane and CO₂ would be the most effective mixture for oil recovery, the propane was injected as a pure slug for the following reasons. Only a small slug of propane was used (about 0.08 PV) and the CO₂ displacement would rapidly dilute the propane by diffusion and CO₂ penetration of the propane slug by gas fingering. For the highest recovery efficiency, sustaining the desired slug mixture for as long as possible would create a maximum oil bank. It is believed this can be accomplished by injection of a propane slug and allowing dilution by the large excess of CO₂ used for flood displacement.

Results of Corefloods

The results using isooctane and no cosolvent are compared in table 4. Since a portion of the injected isooctane was produced and measured with the recovered oil, the injected isooctane was included as a part of the oil-in-place as a basis for measuring oil recovery. There was a small increase in oil recovery (4%) for the experiment using the liquid isooctane slug. Because of coreflood inaccuracies, it is not known if this small increase indicates higher recovery using the liquid injection. As shown in table 4, there was an average of 9.35% higher oil recovery using the isooctane cosolvent.

A comparison of the quantity of isooctane and propane used for these tests are shown in tables 4 and 5. Based on cosolvent weights, the amount of cosolvent used for each coreflood was approximately the same, i.e. the weight of cosolvent was about one tenth of the weight of oil-in-

TABLE 4. - Comparison of oil recovery for CO₂ displacement with and without isooctane at 1,600 psi and 150° F (65.5° C).

Test Condition	Gas iC ₈ Mixture	Liquid iC ₈	----- No iC ₈ -----	
Quantity of iC ₈ , g	7.61	7.40	none	none
Wt. iC ₈ /Wt. oil-in-place	0.122	0.100	--	--
Oil-in-place, OIP, mL	72.9	86.3	84.8	79.7
S _{of} , % (OIP)	--	--	55.6	53.3
S _{of} , % (OIP + iC ₈)	47.5	42.7	--	--

TABLE 5. - Comparison of oil recovery for CO₂ displacement with and without propane at 1,600 psi and 150° F (65.5° C).

Test Condition	Propane Slug			No Propane	
Quantity of C ₃ , g	7.88	8.3	8.3	--	--
Wt. C ₃ /Wt. oil-in-place	0.093	0.103	0.101	--	--
Oil-In Place, mL	98.0	94.7	96.1	87.3	90.7
S _{of} , % (OIP)	37	40	41	59	62

place. The results using propane as a cosolvent are shown in table 5. These tests produced an average of 21% higher oil recovery than comparative tests without propane. This was approximately double the increase obtained with isooctane.

Discussion of Oil Recovery Comparing Isooctane and Propane as Cosolvents

These tests indicate propane is a more effective cosolvent than isooctane at these conditions. Other candidate cosolvents with the desired critical temperature are rather limited at these experimental conditions. At higher reservoir temperatures a few other cosolvents become cosolvent candidates, such as isobutane and butane. Isooctane with a higher critical temperature and lower volatility is not considered a viable cosolvent at these conditions. Another factor for a higher MW hydrocarbon, such as isooctane, is the quantity that partitions into the oil phase. If a large portion of the cosolvent partitions into the oil, the amount of cosolvent in the vapor phase is reduced and less cosolvent is available to alter properties of the gas phase. In addition, a greater quantity of the cosolvent will be bypassed as the gas flood progresses through the reservoir. A demonstration of this possibility was the objective of the next set of coreflood experiments.

Demonstration of Cosolvent Bypassing

The concept of this work is to add small quantities of a cosolvent to increase solubility and extraction of compounds from oils into the gas phase, thereby increasing the gas phase viscosity and density to reduce the gas mobility. It would be advantageous to use a relatively high molecular weight cosolvent which would significantly increase the viscosity and enhance hydrocarbon extraction into the gas phase. However, high concentrations of these cosolvents in the gas phase may not be possible because of high molecular weight cosolvents will partition into the oil. In addition, cosolvents with a high solubility in the oil may be bypassed as gas displacement progresses through the reservoir. These experiments were conducted to demonstrate the possibility of a "chromatographic" effect or bypassing of the secondary cosolvent, especially for higher molecular weight compounds.

Experimental Test Conditions

For these corefloods, a mixture of normal paraffins was used as the oil phase and isooctane was used as the secondary cosolvent. Isooctane was chosen because previous work⁴ had indicated isooctane with a reasonably high molecular weight to be a potential cosolvent candidate.

A Berea core 5.08-cm diameter and 57-cm-long was used for CO₂ displacement experiments. The core had a pore volume of 258 cm³, a porosity of 21.9%, and a brine permeability of 700 mD. A test temperature of 150° F (65.5° C) was used with a gas injection pressure of 1,600 psi. Two synthetic oils were prepared from pure normal paraffins. Each oil composition was chosen to facilitate analysis by gas chromatography of isooctane and produced oil. For the first coreflood, the synthetic oil composition (by weight) was 5% octane, 10% dodecane, 60% hexadecane, and 25% octadecane. Prior to gas displacement, the core was flooded with approximately 300 mL of the synthetic oil and then flooded with brine to obtain a watered-out core with a synthetic oil saturation of 79.7 mL (31% S_{or}).

Approximately 0.1 HCPV of isooctane (5.7 g) was injected before CO₂ injection. Produced fluids were flash separated and liquid samples were collected in traps chilled with salt and ice to approximately -20° C. The reason for using low temperature traps was to insure collection of all produced hydrocarbons and prevent any hydrocarbons from escaping with CO₂ production. Periodic samples were collected as the displacement test progressed. The CO₂ flood was terminated after approximately 1.2 PV of CO₂ was injected. At this point, oil production decreased to less than 0.1 mL for 0.05 PV of injected CO₂ and production was largely gas.

A second coreflood, at the same test conditions, was conducted with a normal paraffin oil which had a lower average molecular weight. The oil composition (by weight) was 10% hexane, 15% octane, 50% decane, and 25% dodecane. A relatively large slug of isooctane (15.45 g) was injected at the beginning of CO₂ displacement (0.29 HCPV)

Experimental Results

Some of the analysis results of the produced oil are listed in table 6. Of the OOIP, approximately 55% was produced by the CO₂ displacement process. As shown in figure 10, a higher fraction of the lighter oil components was produced with proportionately less of the heavier compounds. The lighter molecular weight compounds were more miscible with the gas phase and therefore, were more readily produced with CO₂ displacement. However, of the injected isooctane cosolvent, only 30% was measured in the produced oil. Consequently, some of the isooctane partitioned into the oil phase which was bypassed with residual oil remaining in the core after gas displacement.

For the second coreflood (figure 11), 71% of the OOIP was produced after one PV of CO₂ injection. No appreciable difference was measured in production rate of each oil component. Isooctane production was delayed but increased rapidly as a greater amount of oil was produced from the core. After 0.9 PV of CO₂ injection, the percentage of produced isooctane compared with the amount injected was approximately equal to the percentage of oil recovery. Because of near miscible conditions of the lighter oil and larger quantity of injected isooctane, more oil was produced with the second flood. In addition, because less oil remained in the core, a larger portion of the isooctane was produced.

These experiments were conducted to demonstrate that a higher molecular weight cosolvent will partition into the oil remaining in the reservoir during the CO₂ displacement process. A large fraction of the cosolvent was bypassed even though the coreflood was limited in length (2 ft). In a reservoir, this will result in bypassing of the secondary cosolvent as the gas flood progresses through the reservoir. These corefloods indicate that higher molecular weight compounds are not viable candidates as cosolvents which largely partition into the oil phase at these conditions.

TABLE 6. - Quantity of hydrocarbons in produced oil from CO₂ displacement coreflood

Hydrocarbon compound	Oil composition, %	Quantity in core, g	Quantity produced, g	Production recovery, %	Boiling point, °C
Oil mixture					
nC ₈	5.0	3.0	2.1	70	126
nC ₁₂	10.0	6.1	3.8	62	216
nC ₁₆	60.0	36.5	19.3	53	287
nC ₁₈	25.0	15.2	8.2	54	316
Total	100.0	60.8	33.4	55	--
Cosolvent					
iC ₈	--	5.7	1.7	30	100

FIGURE 10.- The cumulative weight of each hydrocarbon produced compared with weight of hydrocarbon originally present in the core. The isooctane curve is based on the cumulative weight of isooctane produced compared with the injected weight of 5.7 g.

FIGURE 11.- The cumulative weight of each hydrocarbon produced compared with the hydrocarbon weight in the core at the start of the coreflood. The isooctane curve is based on the cumulative weight of isooctane produced compared with the weight injected (15.45 g)

Cyclic CO₂ Displacement With Propane as a Cosolvent

For this year, another objective was the application and evaluation of cosolvent additives to increase production of huff 'n puff gas floods. Previously, corefloods were used to demonstrate that small slugs of propane effectively increased oil recovery for continuous CO₂ displacement floods. These experiments were conducted as cyclic floods to determine if propane as an additive cosolvent would increase recovery of a light gravity crude oil.

Experimental Test Conditions

For cyclic CO₂ displacement experiments, a Berea core was used with a 5.08-cm-diameter and 57-cm length. The pore volume and porosity were 208 cm³ and 18% and the core had a brine permeability of 12 mD. Delaware-Childers crude oil used in these experiments had a 33.6° API gravity. Prior to gas flooding experiments, the brine saturated core was flooded with crude oil and brine to obtain a core with a watered-out oil saturation. The test temperature and gas injection pressure were the same as used in previous tests, i.e., 150° F and 1,600 psi.

All cyclic corefloods were performed according to the following sequence. The slug size of gas injection was designed so that only brine was displaced at the core outlet. Previous experience had established that oil production started after approximately 40 mL of brine production and for these tests, gas injection was terminated after 40 mL of brine production. After completion of gas injection, the core was shut-in and allowed to soak for a period of 20 hours. All flows were then reversed to simulate cyclic production. The produced brine was injected at a flow rate of 0.5 mL/min. and a pressure of 1,600 psi to simulate water invasion. After completion of brine injection, the core pressure at the gas injection inlet was gradually reduced to atmospheric pressure stepwise in approximately 50 psi increments. At each pressure, fluid production was allowed to cease and the quantity of fluids was measured to simulate the puff portion of the cyclic flood. Produced fluids were flash separated to measure the quantity of oil, brine, and gas.

Experimental Results of Cyclic Corefloods With Propane as a Cosolvent

The results of cyclic tests with injection of CO₂ and blends of CO₂/propane are shown in table 7. Comparison of these results indicated propane as a cosolvent does not increase oil production. The highest concentration propane blend (17.3-mol % propane) produced significantly lower oil recovery for both the brine injection and blowdown steps of the production cycle.

The reason for lower oil production may be due in part to the limitations of the cyclic coreflood apparatus. It is believed that the cosolvent propane caused greater mobilization and banking of the oil-in-place during the gas injection step. Therefore, the oil was removed from the

TABLE 7. - Comparison of cyclic corefloods with injection of CO₂ and blends of CO₂/propane

Test condition	CO ₂ injection duplicate tests		CO ₂ /propane blend injection	
	First run	Second run	10.6-mol % propane	17.3-mol % propane
Oil-in-place, mL	100.0	101.2	92.4	102.0
Produced oil/OIP by brine injection, %	16.2	18.3	17.9	13.7
Produced oil/OIP by blowdown, %	<u>11.3</u>	<u>10.0</u>	<u>6.7</u>	<u>6.0</u>
Total produced oil/OIP, %	27.5	28.3	24.6	19.7

gas injection end of the core and less oil was available to be produced during the production cycle. The same conditions may exist to some extent in a reservoir although radial flow conditions and formation heterogeneities also would be present in a reservoir. The production phase would be less influenced by the linear flow patterns found in a laboratory coreflood. However, on the basis of these laboratory tests, there is no evidence that the use of propane as a cosolvent will increase production of cyclic gas floods.

DISCUSSION

The results of this study indicate there are a number of constraints that must be considered in the selection of a cosolvent to be used in conjunction with CO₂ gas displacement. Past studies have inferred some of these constraints. However, the selection of potentially viable cosolvent candidates, if any, becomes greatly simplified by stating some of the basic physical requirements of the cosolvent. Also, reservoir conditions will determine if the application of a cosolvent will substantially increase oil recovery efficiency. To some extent, reservoir conditions also will influence the selection of a cosolvent.

First, the reservoir conditions for gas flooding conditions must be considered to determine if application of a cosolvent would significantly improve oil recovery. Reservoirs will not be candidates for cosolvent application if reservoir conditions are sufficient to achieve CO₂ miscibility with the crude oil. The gas phase at miscible conditions will be saturated with crude oil components and the addition of a cosolvent probably will have a marginal effect on gas phase properties. Therefore, injection of small quantities of a secondary cosolvent probably would not substantially improve oil recovery in reservoirs which are miscible with CO₂.

There are a number of constraints for the selection of a cosolvent. One prerequisite is the solubility of the cosolvent in the gas phase. The cosolvent must be miscible with the gas phase at the reservoir conditions. A compound with limited gas phase solubility will partition into the liquid phase (oil or brine) and will not be present in the vapor phase to enhance the gas flood process. Specific examples of potential cosolvents, such as cyclohexanol and decanol, are not viable secondary solvents because of limited gas phase solubility.

Also, all cosolvents will partition between the carbon dioxide vapor phase and the crude oil liquid phase. If most of a cosolvent partitions into the crude oil, lower concentrations of the cosolvent will be present in the vapor state to improve gas phase properties. Low vapor phase concentration of the secondary solvent would reduce the "entrainer" effect for enhancing extraction of oil components. Also, cosolvents that largely partition into the oil phase will be bypassed during a gas flood. Two examples of compounds that largely partition into the oil phase are the cosolvents isooctane and 2-ethylhexanol. Although these compounds meet the criteria for miscibility, they will not meet the condition for limited partitioning into the oil phase. Coreflood experiments demonstrated that isooctane was bypassed in a synthetic oil phase. It follows that 2-ethylhexanol with a higher molecular weight and higher boiling point would largely partition in the oil phase and be bypassed with a gas flood. Only at very high reservoir temperatures would a high molecular weight compound such as isooctane be sufficiently volatile. High temperature conditions would normally be associated with high pressure and deep reservoirs. Conditions which are not amenable to gas flood applications because of increased costs.

Another requirement for a cosolvent candidate is limited solubility in brine. Compounds which are soluble in brine will be ineffective for a gas flooding process. Polar compounds such as lower molecular weight alcohols are examples of brine solubility.

There are other desirable properties for cosolvents which are not constraints for cosolvent application. It would be advantageous for a cosolvent to be a compound which is highly viscous with a high density to improve the gas phase properties. However, the more dense and viscous compounds are often polar liquids such as alcohols or glycols. Often these compounds are not miscible with CO₂ or to some extent they are soluble in brine. In addition, even if it was possible to use a polar cosolvent in the supercritical gas phase, polar compounds have less solubility for saturated hydrocarbons or paraffins contained in crude oils. Therefore, a polar cosolvent would be less effective for the gas phase extraction of crude oil components.

One final constraint must be considered in the potential application of cosolvents to gas displacement processes. The cost of the cosolvent must be inexpensive in order for the process to be cost effective in oil recovery. In view of the economic constraints, the only potential cosolvents are low cost hydrocarbons which probably are liquified petroleum gases, such as propane and butane.

CONCLUSIONS

In conclusion, there are a number of constraints and requirements that must be considered in the selection of a cosolvent for gas flooding. The results of this study indicate that there only a limited number of compounds that are potential cosolvent additives. Coreflood tests indicated that higher molecular weight cosolvents such as isooctane would be bypassed by a gas displacement flood and these compounds would not be effective in sustaining improved oil recovery throughout a gas flood.

Coreflood tests indicated that propane had a higher oil recovery efficiency than isooctane as a cosolvent additive. There are a number of possible reasons propane was a superior cosolvent. It is believed the primary reason was the addition of propane was more effective in achieving miscibility during the coreflood. Also, the more volatile propane was more effective in sustaining miscible conditions throughout the flood. Experimental tests indicated that the gas phase mixture of propane produced a small increase in gas phase viscosity and this contributed mobility control and an increase in oil recovery.

The addition of a cosolvent in gas flooding may influence other recovery mechanisms that were not considered as a part of this study. It is not known what effect a secondary solvent would have on oil swelling, gas/oil interfacial tension, and oil viscosity. However, a secondary solvent would be expected to change the oil properties of a gas displacement. The effect of cosolvents on the properties of the oil phase is a potential area for further research.

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