CARBON DIOXIDE MINIMUM MISCIBILITY PRESSURE FOR SAUDI ARABIAN CRUDES

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الخلاصـــة :

تم في هذه الدراسة تحديد ضغط الامتزاج الأدنى (ض . أ . أ .) لثاني أكسيد الكربون مع كل من ثلاثة زيوت خام عربية قياسية هي : العربي الخفيف – والعربي المتوسط – والعربي الثقيل ، باستخدام طريقة الأنبوب الرفيع . ولقد افتُرض وقوع الامتزاجية عندما يستخلص أكثر من ٩٠٪ من كمية الزيت الاصلية بعد حقن (١,٢) حجم مسامي من ثاني أكسيد الكربون وبنسبة انتاج غاز / زيت ، تقل عن ٤٠٠٠٠ STB/SCF .

وأظهرت التجارب المُجراة في درجتي حرارة مختلفين أن (ض . أ . أ .) لثاني أكسيد الكربون ازداد من ٢٤٥٠ ر / ب م (رطل / بوصة مربعة) في درجة حرارة ١٧٠°ف (فهرنهايت) إلى ٢٧٦٠ ر / ب م في ١٩٥°ف للزيت العربي الخفيف . ومن ٢٦٧٥ ر / ب م إلى ٣٠٥٠ ر / ب م للزيت العربي المتوسط . ومن الجدير بالذكر أن كثافة ثاني أكسيد الكربون عند (ض . أ . أ .) كانت ٠,٥٠ غم / سم³ للزيت العربي الخفيف في كلا درجتي الحرارة بينما كانت ٠,٥٧ غم / سم³ للزيت العربي المتوسط . أما (ض . أ . أ .) مع الزيت العربي الثقيل فقد حدد بـ ٣١٠٠ ر / ب م في ١٧٠°ف .

ولقد تبين أن ازدياد الوزن الجزيئي لمتقطع (الهبتان – بلس) أثقل في الزيت يسبِّب زيادة (ض . أ . أ .) . كما وجد أن من بين المعادلات الخمسة المستخدمة للتنبؤ بـ (ض . أ . أ .) كانت معادلة (كرنكوست) أقربها للقيم الصحيحة حيث كان الفرق أقل من ٢٥٠ ر / ب م لكلٍّ من الزيت العربي الخفيف والمتوسط .

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INTRODUCTION

Petroleum reservoirs seldom yield more than 40% of their original oil in-place after the primary and waterflooding stages. Carbon dioxide flooding is a successful enhanced oil recovery (EOR) technique whose technical and economic viability has been established in a number of pilot and field-wide projects [1–3].

The high solubility of carbon dioxide in crude oils usually causes significant increases in their volumes and reduction in their viscosities [4] which are the key factors in improving oil recovery. However, under conditions where complete miscibility between CO_2 and a crude oil is achieved, much higher recoveries can be obtained. Of these conditions, a threshold pressure referred to as the CO_2 minimum miscibility pressure (MMP) which is dictated primarily by oil composition and reservoir temperature [5–7] must be met. The CO_2 MMP is therefore an important factor to be considered when the feasibility of a proposed CO_2 flooding project is assessed. Not only should a candidate reservoir be able to withstand an average pressure greater than the CO_2 MMP, but this pressure should be economically attainable in that reservoir.

Saudi Arabian reservoirs, with one quarter of the world's oil reserves, will require EOR at their future stage of development. The economic and technical success of CO_2 flooding of these reservoirs depend on the degree of CO_2 miscibility with Saudi Arabian oils as characterized by the MMP. Although the petroleum literature does present correlations to predict the MMP, their validity has not been assessed for Saudi Arabian oils due to lack of published data on CO_2 MMP for these oils. This study was conducted to generate such data and test those correlations.

Mechanism of CO_2 Crude Oil Miscibility

In a miscible CO_2 injection process, the injected CO_2 is usually not miscible with the reservoir oil at first contact. However, repeated contact by the injected CO_2 with the reservoir oil leads to dynamic miscibility (multiple-contact miscibility) through vaporization and condensation processes. Depending on the operating conditions, mainly temperature and pressure, one of these processes will be the dominant cause of miscibility as dictated by phase equilibria. At high reservoir temperatures and pressures, the gas–oil range hydrocarbons, C_5 through C_{30}, are vaporized into the CO_2 gas phase transitionally miscible with the uncontacted reservoir oil. At low reservoir temperatures and for the same pressure level, CO_2 condensation into the reservoir oil makes the CO_2-rich oil transitionally miscible with the uncontacted reservoir oil. In both cases, breakdown of the miscible front through dispersion is constantly replenished as CO_2 contacts the undisplaced oil. Even though CO_2 miscible displacement could be achieved for a wide spectrum of reservoirs, for some crude oil compositions and reservoir conditions multiple-contact miscibility may not be achieved at all. In these cases, incremental oil recovery can still, nevertheless, be obtained by simple viscosity reduction and swelling of the oil.

DETERMINATION OF MINIMUM MISCIBILITY PRESSURE

1. Experimental Methods

Because of the nature of multiple-contact miscibility, conventional core flooding techniques are impractical due to the great core lengths required. A long, metal tubing packed with sand or glass beads and saturated with the oil is, thus, used to facilitate multiple contact conditions. This slim tube technique has become a standard tool to obtain CO_2 MMP data [8].

The achievement of multiple-contact miscibility is difficult to quantify because slim tube experiments do not directly indicate the achievement of miscibility, but rather exhibit recovery efficiencies characteristic of a miscible displacement [9]. Unfortunately, there are no standard criteria of miscible displacement acceptable to the petroleum industry.

Holm and Josendal [10, 11] defined miscible-type displacements as those that recover more than 80% of oil-in-place at CO_2 breakthrough, and more than 94% when the gas–oil ratio reaches 40 000 SCF/STB. Yellig and Metcalfe [7, 12] defined miscible displacements as those in which recovery at 1.2 pore volumes CO_2 injection is very near the maximum recovery obtained in a series of displacements, and in which transition-zone fluids appear in a capillary sight glass at the end of the slim tube.

Orr *et al.* [8] stated that neither definition is completely satisfactory for comparing results from different laboratories, although both are reasonable for comparing a series of runs performed in the same slim tube at the same displacement rate. Yellig and Metcalfe's definition requires a subjective judgement about transition zone appearance. Holm and Josendal's definition would not necessarily produce the same MMP in different laboratories because oil recovery from a slim tube depends not only on CO_2/oil-phase behavior, but also on displacement rate and the level of dispersion [13], which in turn depends on displacement rate and the particle diameter of the packing material [14].

In this study, the miscible displacement criteria employed are a combination of the definitions of Holm and Yellig, eliminating the subjective judgement of the appearance of the transition zone, and eliminating the need to determine the ultimate recovery which is influenced by the slim tube packing and displacement rate. A gas–oil ratio of 40 000 SCF/STB is taken as the only criterion for the ultimate recovery. Therefore, miscible displacement is achieved when oil recovery at 1.2 pore volumes CO_2 injection is very near the maximum recovery (over 90% original oil in place) attained in a series of displacements, while the gas–oil ratio is close to 40 000 SCF/STB.

2. Empirical Correlations

Several correlations to estimate CO_2 MMP have appeared in the literature. These correlations are useful for screening candidate reservoirs but are not sufficiently accurate for a specific use.

The following are some selected correlations:

1. In 1976, a simple formula was presented by the National Petroleum Council (NPC) based on oil gravity, reservoir temperature, and reservoir depth [15].
2. Cronquist [16] developed a correlation based on an empirical fit of 58 data points predicting the miscibility pressure as a function of reservoir temperature, molecular weight of C_{5+} fraction of the crude and the mole percentage of methane and nitrogen present in the crude. The crude oils tested were ranging from 23.7 to 44° API gravity with reservoir temperatures ranging from 71 to 248°F.
3. Yellig and Metcalfe [12] presented a correlation to estimate minimum miscibility pressure as a function of reservoir temperature only. Their correlation showed that temperature increases MMP by approximately 15 psi $°F^{-1}$ over the range of 95 to 192°F. Their correlation does not account for changes in oil composition.
4. Johnson and Pollin's [17] correlation accounted for oil gravity, molecular weight, reservoir temperature and injected gas composition.
5. In 1982, Holm and Josendal [11] derived a correlation which showed better agreement with MMP data than that of Yellig and Metcalfe. Their correlation was based on temperature and C_{5+} molecular weight.
6. Alston, *et al.* [18] derived a correlation based on their own data on pure CO_2 and live oil systems. Their correlating factors were the reservoir temperature, the molecular weight of the reservoir oil's C_{5+} fraction, the ratio of volatile to intermediate components, and CO_2 purity.
7. Recently, Orr and Silva [19] modified Holm and Josendal's correlation by calculating a weighted composition parameter and determining the corresponding CO_2 density. This density is utilized as the CO_2 density at MMP.

LABORATORY STUDY

1. Crude Oil Samples

Samples of three standard stock tank crude oils were used in this study. These oils, commercially, referred to as Arab Light, Arab Medium, and Arab Heavy, are blends of different Saudi Arabian crudes. Table 1 lists the compositional analysis along with pertinent physical properties of these samples.

Arab Medium and Arab Heavy are mainly produced from sandstone reservoirs while Arab Light is mainly produced from carbonate reservoirs. Saudi Arabian reservoirs have temperatures ranging between 120 and 240°F with the majority falling between 160 and 210°F. The pressures of these reservoirs normally range between 2600 and 3600 psig.

The fact that oil blends are used instead of specific reservoir oils should not diminish the applicability of the results since most Saudi Arabian oils have compatible compositions and properties. Furthermore, this study was intended to establish a range of probable MMP for such oils.

Table 1. Properties of Oil Samples Used in the MMP Tests

Components, Mol%	Arab Light	Arab Medium	Arab Heavy
Carbon Dioxide	0.16	0.06	0.02
Hydrogen Sulfide	0.00	0.00	0.06
Nitrogen	0.00	0.00	0.00
Methane	0.00	0.00	0.00
Ethane	0.00	0.00	0.00
Propane	0.08	0.19	0.12
i-Butane	0.22	0.36	0.14
n-Butane	2.28	2.09	0.60
i-Pentane	1.90	1.80	0.83
n-Pentane	4.00	3.34	1.57
Hexanes	6.26	5.56	3.53
Heptanes Plus	85.10	86.60	93.13
Molecular Weight, C_{7+}	249.00	269.00	298.00
Density, C_{7+}, g cm^{-3}	0.8790	0.8984	0.9136
Specific Gravity, 60°F	0.8679	0.8871	0.9089
Gravity, °API	31.5	28.0	24.2
Viscosity 170°F, cp	2.71	4.43	7.50
Viscosity 210°F, cp	1.99	3.27	4.52

Reservoir oils normally contain quantities of natural gas, mostly methane, in solution. Literature data [7, 10] indicates that the presence of methane in these "live" oils will not alter their CO_2-miscibility characteristics appreciably. CO_2 will merely displace methane from the oil phase creating a small bank of methane-rich gas which moves ahead of the CO_2 front. When most of the methane is removed from the oil, further contact by CO_2 will result in extraction of heavier hydrocarbons. The methane-rich bank will breakthrough immediately before CO_2 and a small decrease in oil recovery will result. Therefore, the MMP obtained in this study using dead (stock tank) oil samples could be slightly lower than those if recombined oils were used.

2. Displacement System

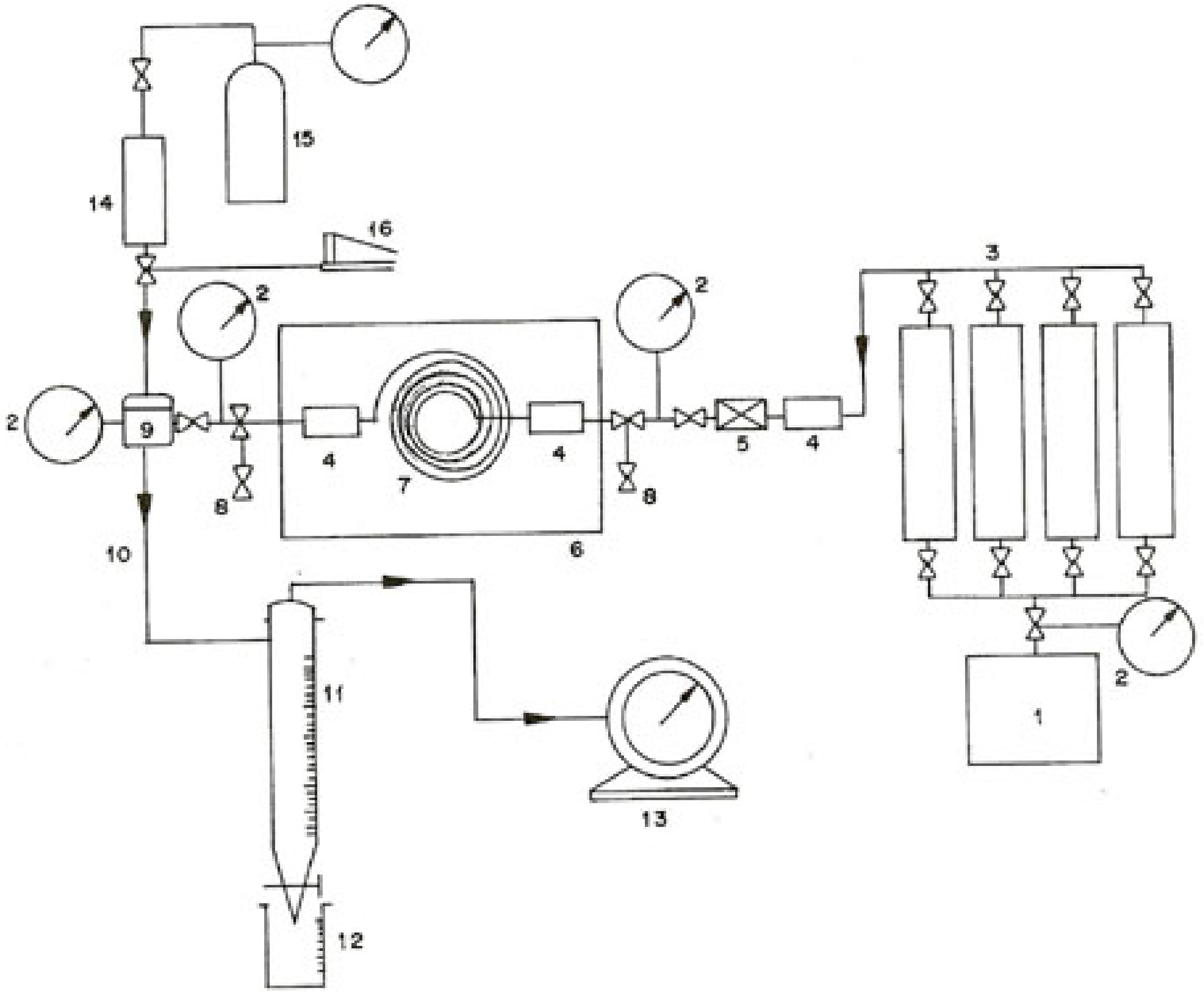
A schematic of the apparatus used in this study is shown in Figure 1. The 42 ft long stainless steel slim tube was packed straight and in the vertical position with glass beads before it was bent into a spiral coil 9.75 inches in diameter. Characteristics of the glass bead pack are listed in Table 2. The slim tube is mounted horizontally inside an air bath with its inlet connected to 3 high-pressure transfer cells containing the three oil samples and a fourth cell containing 99.5% pure CO_2 with less than 20 ppm water content. Oil or CO_2 is pumped out of its cell by mercury injection using a Ruska mercury pump. System pressure is maintained by back-pressure regulator whose setting is controlled by a hand pump and a high-pressure nitrogen supply. Slim-tube oil and gas effluent are separated at one atmospheric pressure and the gas production is metered by a wet-test meter whose water content is pre-saturated with CO_2. All valves, filters, and other fittings used in the apparatus are stainless steel.

3. Test Procedure

A run is preceded by cleaning the slim tube of any residual oil using one and a half pore volumes of benzene and petroleum ether each followed by 3 hours of nitrogen flow for drying. Permeability is measured during nitrogen flow. The tube is then put under vacuum for 24 hours before saturating with oil at the desired run pressure. The air bath temperature is set at the desired run temperature and then allowed enough time to stabilize. The majority of the runs were performed at 170°F with the remaining

Table 2. Characteristics of Slim Tube and Glass Bead Pack

Internal Diameter	: 0.154 in
Length	: 42 ft
Pore Volume	: 4.53 in^3
Permeability	: 11.0 darcies
Packing	: Glass Beads
Porosity	: 42.8%
Diameter Range of Packing	: 100–120 Mesh Size



1. Mercury Pump
2. Gauges
3. High Pressure Cells
4. Stainless Steel Filters
5. Stainless Steel Check Valve
6. Constant Temperature Air Bath
7. Slim Tube Coil
8. Bleeding Lines
9. Back Pressure Regulator
10. 1/8" Transparent Plastic Tube
11. Graduated Glass Separator
12. Graduated Cylinder
13. Wet Test Meter
14. Nitrogen Gas Reservoir
15. High Press. Nitrogen Supply
16. Hand Pump

Figure 1. Diagram of Laboratory Set-Up for Slim-Tube Displacement Tests.

runs performed at 195°F. A run begins by CO_2 injection at a constant rate of 0.25 $cm^3 min^{-1}$ and is continued until a producing GOR of 40 000 SCF/STB is obtained, at which point the oil recovery is termed the ultimate oil recovery. For every oil tested, several runs were performed at increasing pressures until miscibility is achieved as judged by the criteria defined earlier.

RESULTS AND DISCUSSION

1. Displacement Results and MMP

A total of 10 runs were conducted on Arab Light crude oil at 170°F and under pressures ranging from 1500 to 2800 psig. Table 3 lists the recovery data from these runs both at CO_2 breakthrough and at run termination. This data is also plotted in Figure 2. The trends in both curves of Figure 2 show that miscibility is achieved at a pressure of 2450 psig as no significant improvement in either recovery is obtained at higher pressures. It is also noted that transition from immiscible to miscible displacement takes place over a narrow pressure range of approximately 100 psi.

Results for the 9 runs performed on Arab Medium crude oil at 170°F are listed in Table 4 and plotted in Figure 3, while those for the 10 runs on Arab heavy crude at the same temperature are listed in Table 5 and plotted in Figure 4. Results for both oils show similar trends as those for the Arab Light with MMP's of 2675 and 3100 psig, respectively. As expected, the CO_2 MMP increased with the oil

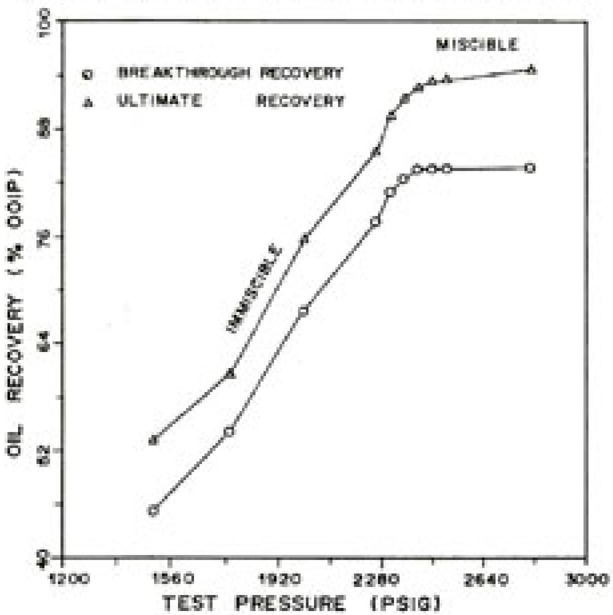


Figure 2. CO_2 MMP Test Results for Arab Light Crude.

Table 3. Arab Light Slim Tube Recovery Results at 170°F

Pressure psig	Recovery Efficiency, %		Displacement Process Type
	Breakthrough	Ultimate	
1500	45.3	53.1	Immiscible
1750	54.2	60.5	Immiscible
2000	67.8	75.6	Immiscible
2250	77.6	85.4	Immiscible
2300	81.1	89.5	Immiscible
2350	82.5	91.4	Near Miscible
2400	83.6	92.7	Near Miscible
2450	83.6	93.4	Miscible
2500	83.6	93.5	Miscible
2800	83.7	94.6	Miscible

*MMP is 2450 psig.

Table 4. Arab Medium Slim Tube Recovery Results at 170°F

Pressure psig	Recovery Efficiency, %		Displacement Process Type
	Breakthrough	Ultimate	
1750	52.2	57.4	Immiscible
2000	64.6	70.5	Immiscible
2250	73.6	80.3	Immiscible
2400	79.8	88.3	Immiscible
2500	82.1	91.2	Immiscible
2600	83.4	93.3	Near Miscible
2700	83.7	93.7	Miscible
2800	83.8	94.7	Miscible
3000	83.8	94.7	Miscible

*MMP is 2675 psig.

Table 5. Arab Heavy Slim Tube Recovery Results at 170°F

Pressure psig	Recovery Efficiency, %		Displacement Process Type
	Breakthrough	Ultimate	
1750	35.6	42.1	Immiscible
2000	50.4	58.2	Immiscible
2250	61.3	71.2	Immiscible
2500	74.0	83.3	Immiscible
2750	79.9	89.8	Immiscible
2900	81.9	91.5	Immiscible
3000	83.4	93.1	Near Miscible
3100	83.8	94.7	Miscible
3200	84.0	94.6	Miscible
3500	84.0	94.7	Miscible

*MMP is 3100 psig.

density since denser oils contain smaller concentrations of the CO_2-extractable fraction needed for miscibility. Similarly, both breakthrough and ultimate recoveries at any pressure in the immiscible displacement regime increase as the oil density decreases as depicted in Figures 5 and 6, respectively. In the miscible displacement regime, however, each recovery is unaffected by the pressure and is virtually equal for all three oils tested. This is once again expected, since in the absence of viscous fingering, which is a characteristic advantage of the slim tube technique, oil recovery in miscible displacement is less affected by oil viscosity or density. Breakthrough and ultimate recoveries in linear and ideal miscible processes, such as solvent injection, are usually very close and near 100%. The fact that some incremental recovery, approximately 10%, is obtained after breakthrough in CO_2 flooding is attributed to continued extraction of residual oil. Also, the oil left in the pack, about 6%, at the end of

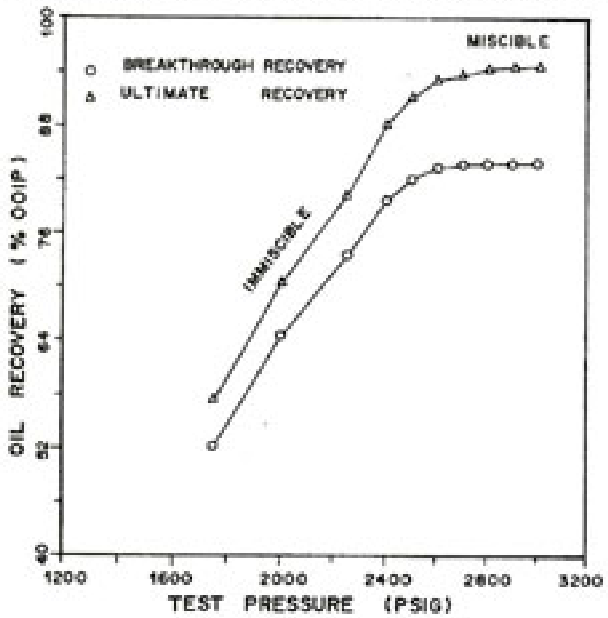


Figure 3. CO_2 MMP Test Results for Arab Medium Crude.

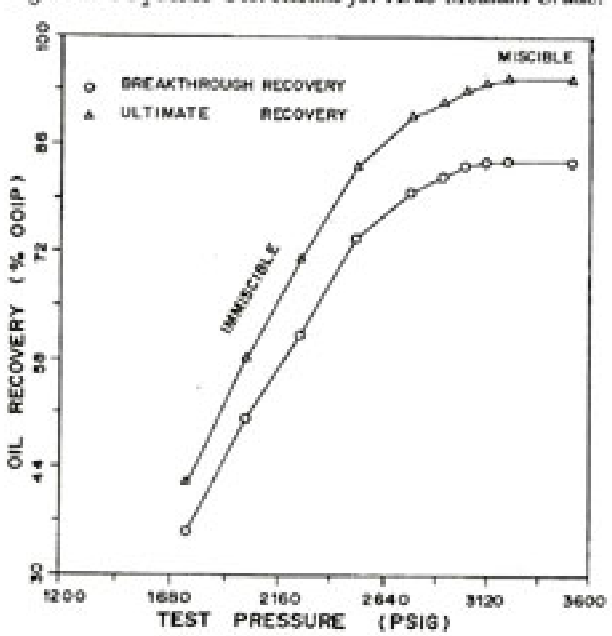


Figure 4. CO_2 MMP Test Results for Arab Heavy Crude.

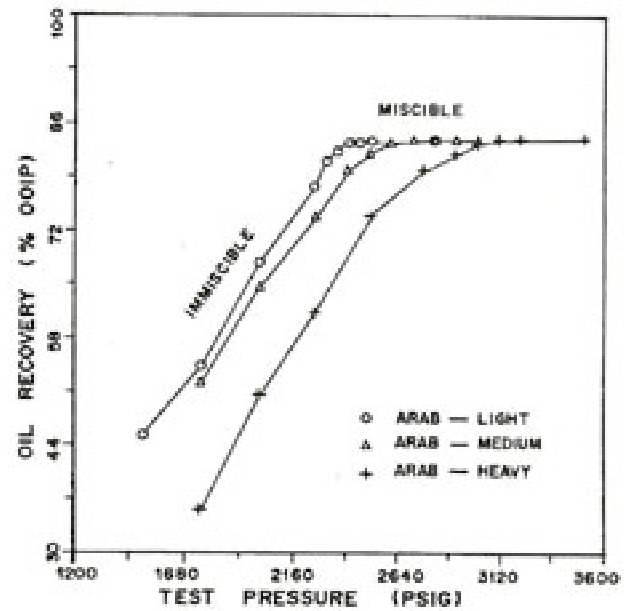


Figure 5. Effect of Pressure on Breakthrough Recovery of the Different Saudi Arabian Crudes.

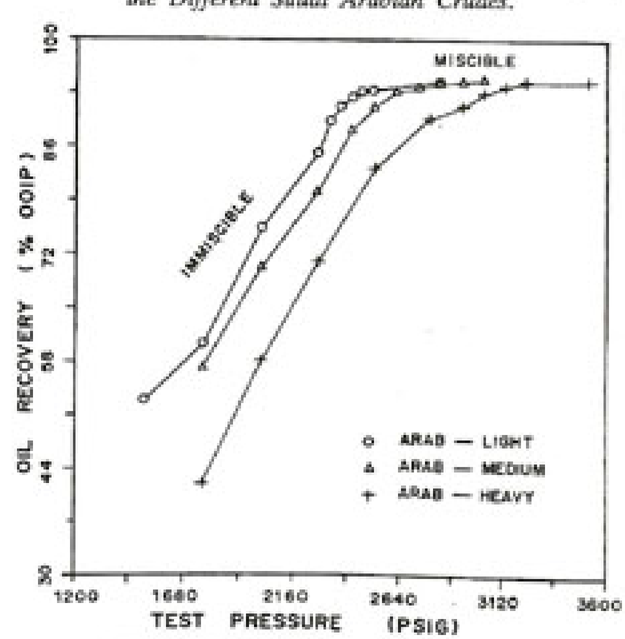


Figure 6. Effect of Pressure on Ultimate Recovery of the Different Saudi Arabian Crudes.

displacement is believed to be immobile heavy residues after extraction of light fraction by CO_2.

Since the composition of an oil is a more relevant factor in miscibility phenomenon than its density, a correlation between the CO_2 MMP for an oil and the molecular weight of its heptanes-plus fraction was sought. As Figure 7 indicates, the MMP for an oil increases at a given temperature as its C_{7+} fraction becomes heavier.

Figure 8 shows the progress of Arab Light oil recovery with CO_2 injection for three different pressures. It is observed that whether the displacement is miscible or immiscible, no significant incremental recovery is achieved beyond 1.2 PV of CO_2 injection. Similar observations were made for Arab Medium and Arab Heavy runs. This justifies our criterion of 1.2 PV injection as a limit in miscibility determination. However, up to 1.3 PV were injected in most runs in order to satisfy the gas–oil ratio criterion of 40 000 SCF/STB.

2. Temperature Effect on MMP

Seven runs were conducted using Arab Light and Arab Medium crudes at 195°F. Those two crudes were selected for temperature effect investigation since they had showed more prospective for CO_2 miscibility. The MMP for Arab Light was found to be 2675 psig, an increase of 12.4 psi °F^{-1}, and the MMP for Arab Medium was 3050 psig, an increase of 15 psi °F^{-1}. These MMP-temperature gradients fall between those concluded by Johnson and Pollen, 10.5 psi °F^{-1}, and Yellig and Metcalfe, 15 psi °F^{-1}. However, it has to be noted here that those investigators assumed their gradients to be applicable to all oils regardless of their properties.

Figure 9 shows the ultimate oil recovery *versus* pressure for the Arab Light crude at the two temperatures tested. It is interesting to note that in

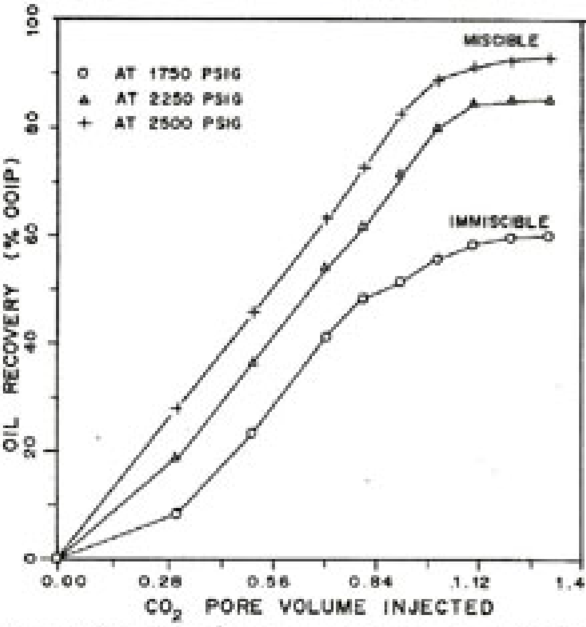


Figure 8. Slim Tube Displacement Data for the Arab Light Crude at 170°F.

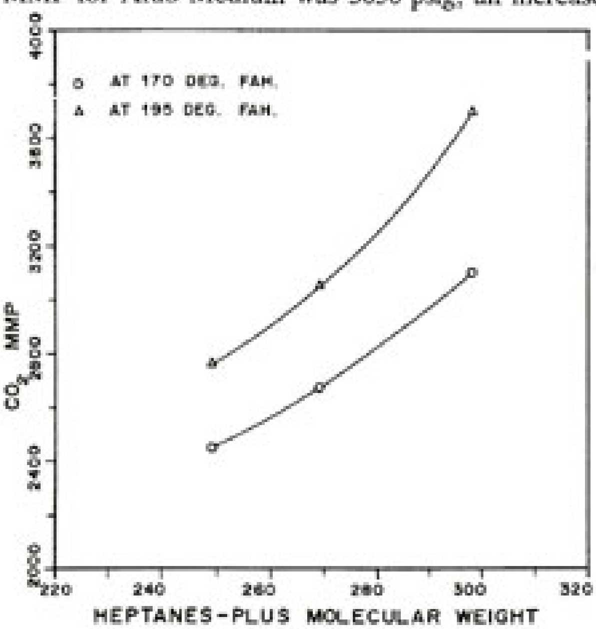


Figure 7. Effect of Oil Heptanes Plus Molecular Weight on MMP.

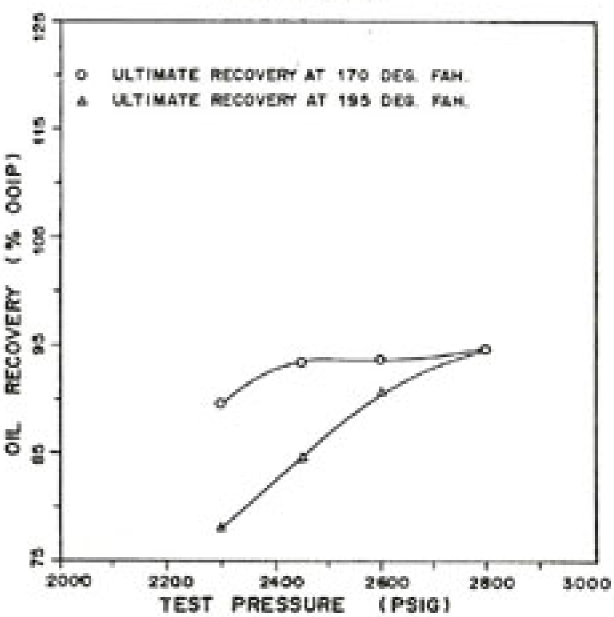


Figure 9. Temperature Effect on CO_2 MMP for Arab Light Crude.

the miscible-displacement regime, *e.g.* 2800 psig, the ultimate oil recovery is independent of temperature while under immiscible pressures, *e.g.* 2300 psig, a higher temperature causes smaller ultimate recovery. This can be explained by the fact that solubility of CO_2 in oil, decreasing with increasing temperatures, influences recovery in immiscible displacement only. A similar observation is made for the Arab Medium runs as shown in Figure 10.

3. CO_2 Density For Miscible Displacement

Comparison of results also shows that for a particular crude the CO_2 density at the MMP is constant for both temperatures. The CO_2 densities for the Arab Light and Arab Medium crudes at the MMP are 0.50 and 0.57 g cm^{-3}, respectively. This fact was also confirmed by other investigators [10, 19]. It is apparent that the ability of the CO_2 phase to extract hydrocarbons from the oil phase improves when both phases have closer densities. This explains the higher CO_2 density required to achieve miscibility with Arab Medium crude. The same principle was used to predict the MMP for Arab Heavy crude at 195°F. Using the CO_2 density of 0.65 gm cm^{-3} computed at 170°F and MMP of 3100 psig, the MMP for Arab Heavy at 195°F was computed to be 3700 psig. This value along with experimentally determined values for Arab Light and Arab Medium at 170°F are also plotted in Figure 11.

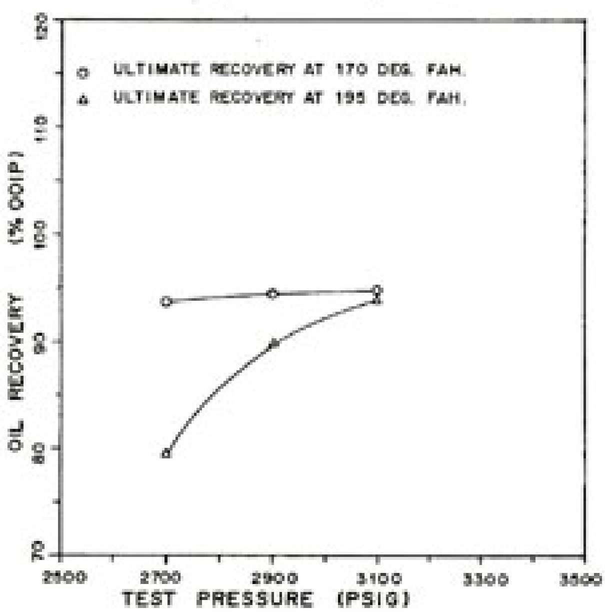


Figure 10. Temperature Effect on CO_2 MMP for Arab Medium Crude.

4. MMP From Correlations

The accuracy of the existing literature correlations discussed earlier was tested against the findings of this study. Table 6 lists the MMP values for the three crudes as predicted by five of these correlations along with the results of this study. Alston *et al.* [18] correlation was excluded because it deals with impure CO_2 streams. It is apparent that every correlation has its own limitations and none can be used with enough confidence when high accuracy is desired. However, Cronquist's correlation consistently produced the least errors. It is interesting to note that Holm and Josendal's, which is based on dead oil samples, did not do as good as Cronquist's. Nevertheless, a correlation that employs our results and any data from similar future investigations should be more suitable for Saudi Arab crudes.

CONCLUSIONS

1. Saudi Arabian crude oils are capable of achieving miscibility with CO_2 at normal reservoir pressures and temperatures.
2. Higher oil density or temperature causes increase in CO_2-MMP for Saudi Arabian crudes. The MMP-temperature gradients varied from 12.4 psi °F for Arab Light to 24 psi °F predicted for Arab Heavy.
3. The CO_2 density at miscible conditions remains apparently constant for a Saudi Arabian crude,

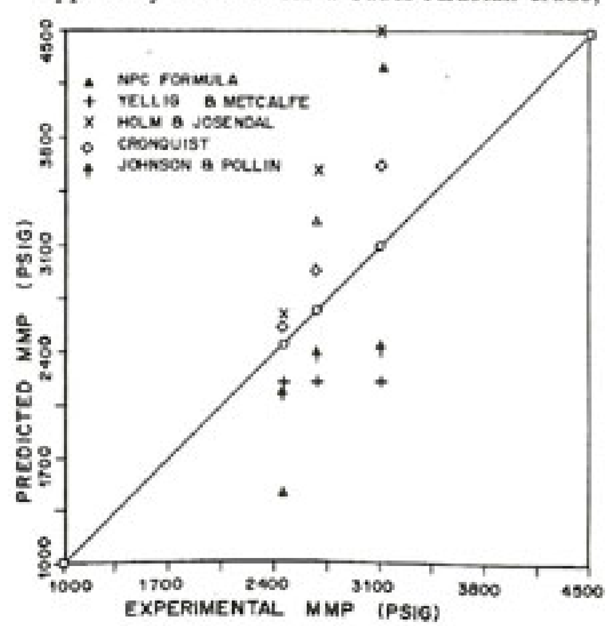


Figure 11. Accuracy of Screening Guides for Predicting CO_2 MMP.

Table 6. Accuracy of Literature Correlations for Predicting CO_2 MMP for Saudi Crudes

Correlation	Predicted MMP ARAB LIGHT		Predicted MMP ARAB MEDIUM		Predicted MMP ARAB HEAVY At 170°F (psig)	Relative Error %	Maximum Error (psig)
	At 170°F (psig)	At 195°F (psig)	At 170°F (psig)	At 195°F (psig)			
This Study	2450	2760	2675	3050	3100	0	0
NPC Formula [15]	1460	1535	3260	3355	4260	9–44	1225
Yellig and Metcalfe [12]	2200	2500	2200	2500	2200	9–29	900
Holm and Josendal [11]	2650	3600	3200	*	*	8–30	840
Cronquist [16]	2565	2937	2873	3300	3628	5–17	528
Johnson and Pollin [17]	2117	2380	2379	2642	2419	11–22	681

*Correlation does not cover this range.

and the ultimate recovery with miscible displacement is independent of temperature.

4. None of the published MMP correlations proved to be satisfactory for Arabian crudes even the one based on dead oil samples. Cronquist's correlation gave the least errors.

5. The slim tube apparatus, test procedure, and miscibility criteria employed in this study were found to be satisfactory with regard to accuracy, reproducibility, and convenience.

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