Phase Relations of Miscible Displacement in Oil Recovery

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Miscible displacement as an oil recovery process has received wide interest in the literature recently. Essentially three basic processes have been proposed for attaining miscible displacement in our oil reservoirs: high pressure gas, enriched gas, and miscible slug processes.

The present paper relates and compares the phase relations and mass transfer mechanisms of these various basic miscible displacement processes. It also discusses the effects of the various operating variables, such as pressure, temperature, injected gas composition, etc., on the applicability of the process and considers the pertinent conditions that restrict the application of each process. It is to be recognized that at times a miscible displacement may be attempted but not attained, or unforeseen conditions may destroy miscibility once it has been attained. The authors discuss the results of such conditions. The mechanisms of the miscible displacement processes are explained in a conceptual analysis based on the triangular phase diagram. Although the multicomponent reservoir fluid system cannot be represented rigorously from a thermodynamics standpoint by these diagrams, they are useful for cenceptual analysis. Their limitations are presented by the authors along with data supporting the concepts developed.

The imagination of the crude oil production industry has been captured by the various processes for oil recovery by miscible displacement. The fact that miscible displacement can result in 100% oil recovery in the volume of the reservoir swept has not been responsible for the interest. This has been known for many years. It is the fact that processes have been conceived to allow economic attainment of miscible displacement. Reservoir engineers have long realized that capillary forces cause the retention of residual oil behind a flood front. These oil retaining capillary forces are a result of the boundary or interfacial tension between the in-place oil and the displacing fluid. Thus if the interface between displaced and displacing phases were removed, the capillary forces would be removed also. Complete oil recovery in the swept area would then be realized. Miscible displacement accomplishes this end.

It is the purpose of this paper to examine the phase relations of the various techniques that have been proposed for attaining miscible displacements. Success in developing and maintaining the proper conditions for miscibility in the reservoir depends upon an understanding of these phase relations. Selection of the best process and engineering of it for a specific reservoir must rely upon this understanding of the processes and how they are related through phase relations.

A further purpose of this paper is the discussion of the application and limitations of the triangular phase diagram for picturing miscible displacement processes. This diagram, though an over-simplified picture of a complex system, has proved helpful in concept formation. It may also be used semi-quantitatively.

One can group the various miscible displacement processes into two natural divisions: those processes in which miscibility already exists between the displaced and displacing fluids and those in which the injected fluid is not miscible with the oil, but by some process in the reservoir it develops the required miscible displacement. The propane or miscible slug process (*1, 2*) is an example of the former. Propane as a liquid is already miscible with the reservoir oil. The high pressure gas process (*3, 4, 5, 6*) and the enriched gas drive (*7, 8*) are members of the second class of processes. In these latter processes the gas injected is not miscible with the reservoir oil, but when it is brought into intimate contact with the oil in the reservoir pores, a miscible displacement will be developed. As a basis for comparing and discussing these processes, one can use the triangular phase diagram.

REPRESENTATION OF PHASE RELATIONS ON A TRIANGULAR DIAGRAM

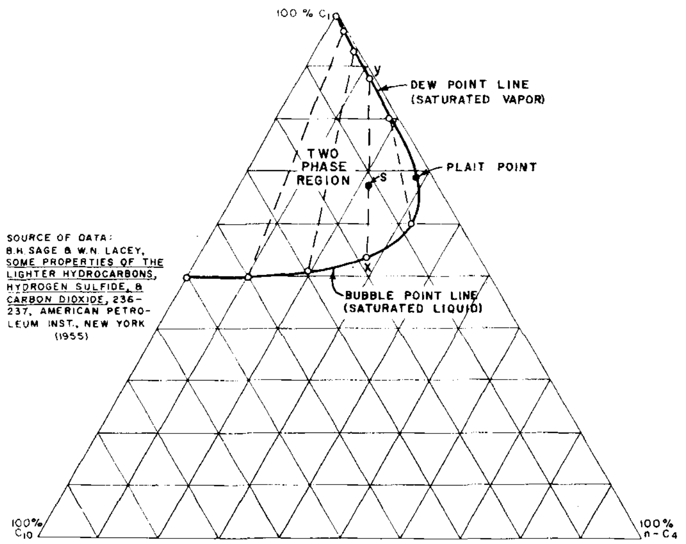
A triangular diagram was first proposed by J. Willard Gibbs (9) to present phase relations of a three pure-component system. Since then it has been used extensively for liquid-liquid, liquid-solid, and more recently for gas-liquid systems (*10, 11*).

Figure 1 shows the phase diagram for the ternary system methane, *n*-butane, and decane at 160°F. and 2,500 lb./sq. in. abs. (*11*). The phase boundary curve on the diagram separates the single-phase and two-phase regions. At the pressure and temperature given any system of the three components whose composition is inside this curve will form two phases. Any system outside of this curve will be in a single phase at equilibrium.

The lower part of the curve is a bubble-point line and gives the liquid-phase composition of any two-phase system. The upper part of the curve is a dew-point line and gives the gas-phase composition of the two-phase system. The lines that connect gas- and liquid-phase compositions that are in equilibrium with each other are called *tie lines.* Any system composition along a tie line will break into two phases with compositions given by the ends of that tie line. The bubble- and dew-point lines meet at the plait point where the liquid and gas phases become identical.

In Figure 1 it is noted that the plait point does not coincide with the point of maximum bulge of the phase boundary curve, nor are the tie lines parallel to each other or the C_1 to C_{10} side of the diagram. The plait point can be on, above, or below the point of maximum bulge depending upon the components of the system.

With this diagram one needs only to know the composition of the system of the three components to define their phase relationship at the given pressure and temperature. For example if the system composition is located at point *s* (Figure 1) in the two-phase region, then the composition of the gas phase is *y*, while the composition of the liquid phase in equilibrium with this gas is point *x*. If one applies the phase rule to a ternary system of two phases in equilibrium, for a given pressure and temperature the number of additional independent variables that must be set to define the system is one. For example if the concentration of only one



SOURCE OF DATA:
B.H. SAGE & W.N. LACEY, SOME PROPERTIES OF THE LIGHTER HYDROCARBONS, HYDROGEN SULFIDE, & CARBON DIOXIDE, 236-237, AMERICAN PETROLEUM INST., NEW YORK (1955)

Fig. 1. Phase relations for methane-*n*-butane-decane system at 160°F. and 2,500 lb./sq.in.abs. (mole %).

of the components in either phase is set, the system is defined. In the single-phase region the concentrations of two of the components must be set to define the system.

TRIANGULAR DIAGRAM APPROXIMATION OF THE PHASE RELATIONS OF SYSTEMS WITH MORE THAN THREE COMPONENTS

The hydrocarbon fluids found in oil and gas reservoirs contain hundreds of components (*12*). It is immediately apparent from the phase rule that the concentration of hundreds of components must be set to rigorously define such a system. This would be practically impossible to obtain. An approximation method has been devised (*13*) to handle these systems. Three groups of components are used to define the composition of the system. These groups are the very volatile components such as nitrogen and methane, the components of intermediate volatility such as ethane through hexane in the paraffin series, and the components heavier than hexane. A phase diagram based on such a composition measure fails to define rigorously the phase relations of a complex system in several ways: the distribution of the individual components within each group is not given, this is basic to the method; because the components within a group have different volatilities, they are not distributed in that group the same way in the gas and liquid phases; and the position of the phase boundary curve on the triangular coordinates and the slope of the tie lines depend on the over-all composition which cannot be given simply by a C_1, C_2 to C_6, and C_{7+} split since the composition of either of the multicomponent groups can vary. The latter two deviations from the behavior of the three pure-component system can best be demonstrated by example. The phase relations of a typical complex fluid system are shown in Figure 2. (These data were determined experimentally.) The gas phase at *y* is in equilibrium with the liquid phase at *x*. A more detailed breakdown of the composition of these phases is given in the table below:

Components		Gas phase at *y*, (mole %)		Liquid phase at *x*, (mole %)		Distribution of intermediate components in intermediate group, (mole %)	
Individual	groups					Gas phase	Liquid phase
C_1	C_1		74.55		53.16		
C_2	C_2—C_6	22.25	9.15	25.84	9.06	41.1	35.0
C_3			6.48		7.66	29.1	29.6
C_4			3.31		4.23	14.9	16.3
C_5			1.84		2.48	8.3	9.6
C_6			1.47		2.41	6.6	9.5
C_{7+}	C_{7+}		3.20		21.00		
			100.00		100.00	100.00	100.00
Molecular weight of C_{7+}			151		217		

Note the differences in distribution of the individual components in the intermediate group between the gas and liquid phases. Since the ethane is the most volatile individual component, one would expect it to tend to concentrate in the gas phase. The preceding table shows that it does just that. Also, as expected, the hexane tends to concentrate in the liquid phase. The differences in C_2 to C_6 composition shown above are relatively small because these equilibrium phases are not far from the plait point in composition. At the plait point the gas and liquid phases become identical.

The difference in internal composition of a group between liquid and gas phases is more pronounced for the heptane plus group. This is reflected by the molecular weight. The molecular weight shown in the preceding table for the heptane plus components in the gas phase is about that of decane; it is about that of penta-decane in the liquid phase.

Figure 3 shows how the slopes of the tie lines differ depending on the over-all composition which in turn was set by the process used to reach equilibrium. The dashed tie lines were obtained from a multiple batch-contact study in the following manner: 1. A reservoir fluid L_1 was combined with a gas G_1 to give a mixture M_1. This mixture, upon reaching equilibrium, separated into the gas phase G_2 and liquid phase L_2. 2. L_2 and G_1 were combined to form mix M_2 which separated into G_3 and L_3, etc. The one dotted tie line was obtained for a sample produced at one stage during the multiple contact process occurring when gas G_1 was injected into a porous medium containing liquid L_1. The system had the same C_1, C_2 to C_6, C_{7+} composition as could be obtained by the previous batch gas-liquid mixing. However the compositions of the C_2 to C_6 and C_{7+} groups were internally different and the tie-line slope was changed. This shift of the tie-line slope is extremely important to two of the miscible displacement processes as will be discussed later. At this stage of the discussion it is sufficient to state the reasons why the tie-line slope differs. One is that the batch-contact sequence did not follow the sequence occurring in the porous medium. When gas G_1 contacts reservoir fluid L_1, equilibrium is attained, and the gas now has composition G_2. Because of its higher viscosity the oil phase L_2 is less mobile than the gas phase G_2. This gas then moves forward in the porous medium to contact more L_1. Note that this is quite different from the batch-contact experiment where the original gas was contacted and brought to equilibrium with oils of successively changed composition. Also in the porous medium the actual mixing is a continuous rather than a batch process.

MISCIBLE DISPLACEMENT PROCESSES

In view of the approximations involved in representing the phase relations of complex systems on a triangular diagram, the authors shall first discuss the processes in terms of the analogue system methane-*n*-butane-decane. Then it will be shown that this diagram, though approximate, is very useful in evaluating the complex fluid found in practice.

Injection Gas Miscible in All Proportions with Reservoir Fluid

One way to achieve a miscible displacement in the reservoir is to inject a gas that is miscible in all proportions with the reservoir fluid (*14, 15*). The phase relations involved are shown in Figure 4 for the analogue system. This figure shows that at a pressure of 3,250 lb./sq. in. abs. or higher all mixtures of gas G_1 and liquid L_1 are completely miscible and form a single phase. Another way to show the pressure requirements is the pressure composition relationship (commonly called a *P-X diagram*) of the mixtures of G_1 and L_1 which lie along the line L_1G_1, Figure 4. This is shown in Figure 5 as the upper curve. This curve relates the bubble-point pressure and composition and dew-point pressure and composition. It separates the single-phase region and two-phase region. This also shows that if the pressure is maintained above 3,250 lb./sq. in. abs., all mixtures of gas G_1 and liquid L_1 are a single phase. This pressure is generally referred to as the *cricondenbar,* the maximum pressure at which condensation can occur.

In nearly all actual reservoir systems the cricondenbar is above the pressure which the reservoir rock can withstand without fracturing. Typically, the cricondenbar is above 6,000 lb./sq. in. abs. for these cases. The *P-X* diagram for a typical reservoir fluid and injection gas is shown in Figure 6, upper curve. Even when the reservoir rock will withstand the cricondenbar, in most cases economics eliminates this process because the same result can be achieved by another process with the same injection gas at a much lower pressure.

HIGH PRESSURE GAS PROCESS (MISCIBILITY ATTAINED BELOW THE CRICONDENBAR)

One way to reduce the cricondenbar is to use a gas that is richer in intermediates. Again referring to the analogue system, Figure 5, one finds that a gas G_2 (85% C_1 to 15% C_4) is miscible in all proportions with liquid L_1 at a pressure above 2,750 lb./sq. in. abs. The use of a richer gas G_3 (78.5% C_1, 21.5% C_4) reduces the cricondenbar further to 2,500 lb./sq. in. abs. In a like manner a lower cricondenbar results when a richer gas is combined with the typical reservoir fluid (Figure 6, lower curve). One could inject these rich gases and achieve the desired results, but again this expensive approach is not necessary.

The rich gas is not necessary because a lean gas is enriched when it contacts the reservoir fluid. This is shown for the analogue system in Figure 7a. Suppose the lean gas G_1 (100% C_1) is mixed with liquid L_1 at 2,500 lb./sq. in. abs. with a resulting mixture M_1. Since this is in the two-phase region, it separates into a gas phase G_2 (83% C_1, 16% C_4, 1% C_{10}) and a liquid phase L_2. If the enriched gas G_2 is mixed with the liquid L_1 to form mixture M_2, again two phases are formed. The gas phase G_3 (77.7% C_1, 21.0% C_4, 1.3% C_{10}) from this second contact is even richer than that from the first contact. In the limit the gas phase is enriched until it is completely miscible with the liquid L_1. If L_1 is on a line tangent to the phase boundary curve through the plait point, the gas will become enriched to the plait-point composition, G_4 (68.6% C_1, 28.4% C_4, 3.0% C_{10}).

In the reservoir in which a reservoir fluid L_1 is to be recovered by injection of gas G_1, the same gas enriching process will occur. The injected gas comes into contact with the reservoir fluid and is enriched as equilibrium is approached. This enriched gas is less viscous than the reservoir fluid and is not yet miscible with it. It will therefore move forward more rapidly than the reservoir fluid just contacted and will come in contact with fresh reservoir fluid. Now a further gas enriching takes place. This enriching process continues until the leading edge of the injected gas phase attains the composition of the plait point.

The relative position of the fluids formed in the high pressure gas process in a porous medium is shown schematically in Figure 7b. The fluids represented here are from the batch-contact description of the process given above. In an actual case the gas composition varies continuously along the line through G_1, G_2, G_3, and G_4 (Figure 7*a*). Note that the rich gases formed from the multiple contacts with L_1 lie in between the injected gas G_1 and reservoir liquid L_1 in what is termed a "transition zone." The fluid at the leading edge of this zone is completely miscible with the reservoir liquid, whereas the fluid at the trailing edge of this zone is completely miscible with the injected gas. All contiguous fluids in the zone are also completely miscible.

It is evident from Figure 7*a* that this enrichment to the plait point will occur only if the liquid L_1 lies on a line which is tangent to the plait point. It is also evident that the lean gas G_1 will be enriched to the point of miscibility

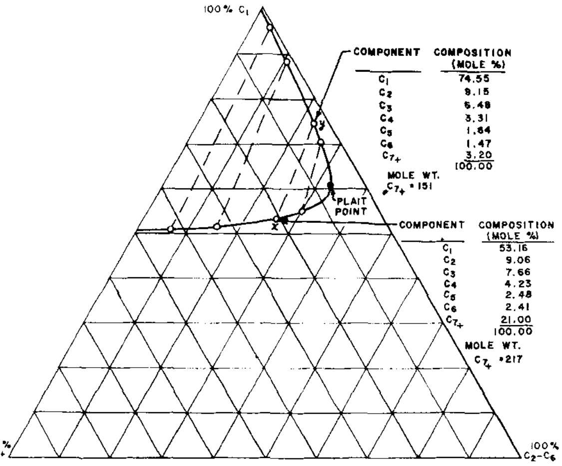


Fig. 2. Phase relations of the University Block 31 Field Reservoir fluid at 140°F. and 4,000 lb./sq.in.abs. (mole %).

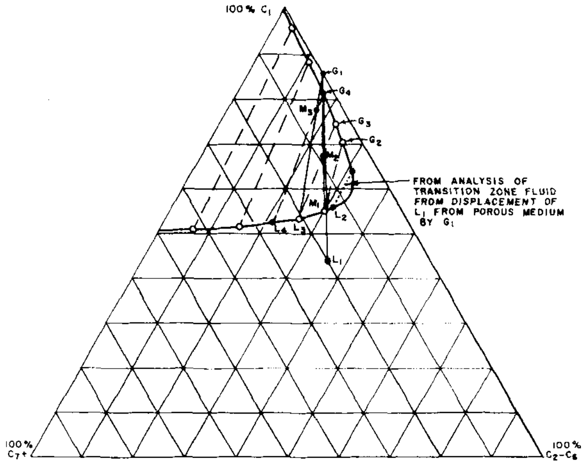


Fig. 3. Comparison of tie line slopes-batch contact vs. data from a displacement (exemplified by University Block 31 data, P = 4,000 lb./sq.in.abs., T = 140°F.).

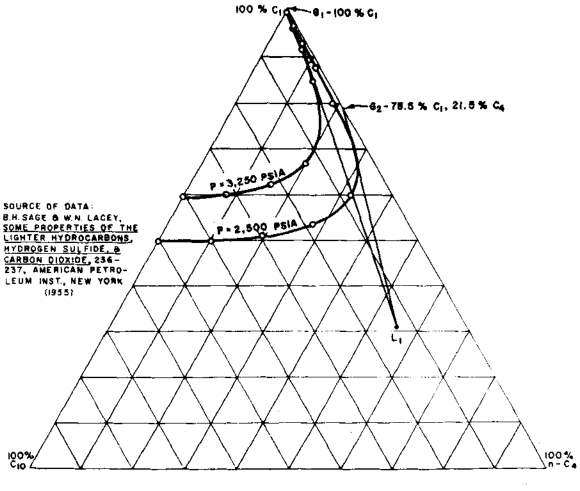


Fig. 4. Required butane in injected gas for miscibility with reservoir fluid (operation above the cricondenbar) $T = 160°F$. (mole %).

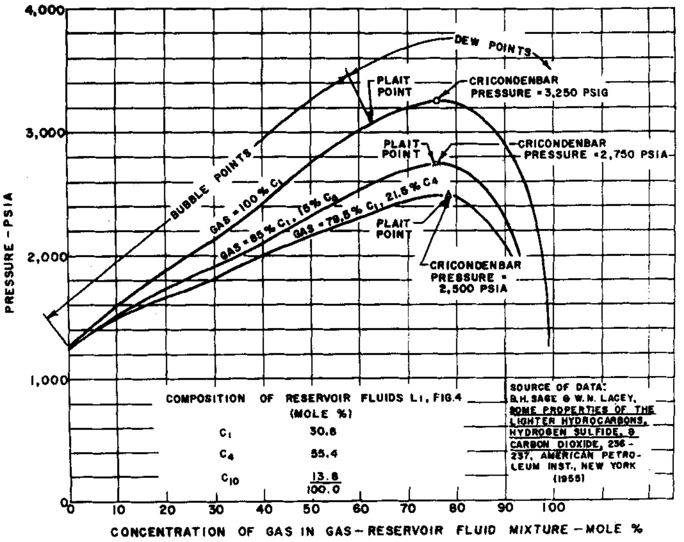


Fig. 5. Effect of gas composition on the cricondenbar of the gas (C_1 to n-C_4), decane system at 160°F.

with any liquid lying to the right of this tangent line. Of course any liquid lying to the right of the second line shown in Figure 8 is miscible with gas G_1 without any enrichment. It also follows that the gas G_1 cannot become enriched enough to become miscible with any liquid lying to the left of the line tangent to the plait point. This is clearly seen if one notes what happens if the liquid L_a, Figure 7*a*, is contacted in the way described above with gas G_1. The gas cannot enrich itself beyond G_a since it is in equilibrium with the saturated liquid lying on the connecting line, a portion of which is a tie line, between G_a and L_a. At this point it is still immiscible with the liquid L_a.

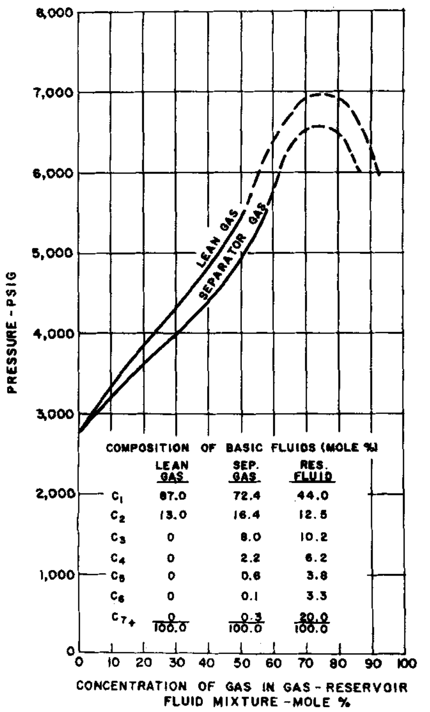
From this discussion one sees that the triangular diagram can be divided into three regions (Figure 8). If one knows the composition of the liquid to be displaced and the composition of the displacing gas and the operating pressure and temperature, one can easily determine the kind of displacement mechanism to expect, immiscible or miscible, by such a diagram. Any oil in the region susceptible to miscible displacement by the high pressure gas process will be undersaturated.

Earlier it was pointed out that the slope of the tie lines near the plait point is important to two of the miscible displacement processes. The high pressure gas process is one of them as the discussion above shows. One should re-examine the phase relations of the reservoir fluid system (*16*) presented earlier to find out how important the tie-line slope was in evaluating this system for the high pressure gas process. Figure 9 shows the tangent line through the plait point based on the batch-contact data. In accordance with these data the injected gas cannot become enriched enough to be miscible with the reservoir fluid at 4,000 lb./sq. in. abs. On the other hand the line based on compositions of fluids actually displaced from porous media clearly shows that a miscible displacement should be possible at a pressure below 4,000 lb./sq. in. abs. Figure 10 indicates that a miscible displacement should ocur at a pressure as low as 3,500 lb./sq. in. abs. A series of tests in laboratory porous media in which the reservoir fluid was displaced by the lean gas at different pressures confirmed this (Figure 11). These data show a sharp increase in recovery as the pressure is increased to 3,500 lb./sq. in. abs. Beyond this pressure little further improvement occurred as is expected when miscible displacement occurs. The excellent agreement in this case of the miscibility pressure from the phase relations on the triangular diagram with that from the porous media test data is unusual, since the phase diagram is really only an approximation. The phase-relations data of the complex reservoir fluid systems are usually not this quantitative but generally predict the miscibility pressure within 200 to 300 lb./sq. in. of that from the porous-media tests.

A miscible displacement should recover 100% of the reservoir liquid. The fact that this was not quite reached in the miscible displacement runs (pressure $\geqq$ 3,500 lb./sq. in. abs.) is attributable to the fact that the gas must travel some distance through the porous medium before miscibility is achieved. Some of the reservoir liquid at the injection end of the system is unrecoverable. This is the oil that has been denuded of the intermediates by the injected gas in the process of enriching this gas. It has the composition L_R shown on Figure 10 for the 3,500 lb./sq. in. abs. displacement.

The amount of reservoir oil used up in enriching the gas and left as unrecoverable residual is a very small per cent in the reservoir application of the process. The length of porous medium through which the gas must travel before miscibility is reached should be a constant for a given porous medium if this length were solely a function of the phase relations. The experimental data from high pressure gas displacements in porous media of three different lengths indicate that the path length required to establish miscibility is not a constant but depends to some degree on the over-all length of the porous medium. This is shown by the data of Figure 12 which shows that the residual oil content of the porous media, expressed as a percentage of the total pore volume, decreased as the length of the porous media was increased, but did not decrease to the extent predicted by the constant path-length assumption. Despite this lower change with length the experimental data when extrapolated indicate that the residual oil from the application of the high pressure gas process to a typical reservoir (1,000 ft. in length) will be relatively small (about 3% of the pore volume).

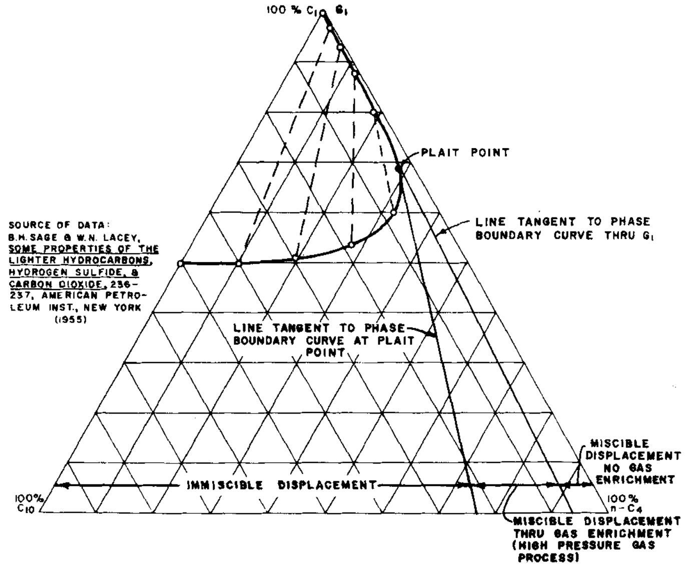
Because porous media are not perfectly uniform the injection gas will advance unevenly or finger into the oil-saturated portion of a porous medium. This causes part of the reservoir oil to be bypassed by the leading gas with which it is completely miscible and come in contact with a transition fluid with which it is not completely miscible (that is L_1 is bypassed by G_4 and is contacted by G_3, Figure 7*a*). However when this happens the high pressure gas process mechanism causes the transition fluid to become enriched until it is completely miscible with the bypassed oil. Thus the high pressure gas process mechanism re-establishes



COMPOSITION OF BASIC FLUIDS (MOLE %)

	LEAN GAS	SEP. GAS	RES. FLUID
C_1	87.0	72.4	44.0
C_2	13.0	16.4	12.5
C_3	0	8.0	10.2
C_4	0	2.2	6.2
C_5	0	0.6	3.8
C_6	0	0.1	3.3
C_{7+}	0	0.3	20.0
	100.0	100.0	100.0

Fig. 6. Effect of gas composition on the cricondenbar of the gas, University Block 31 Reservoir fluid system at 140°F.



SOURCE OF DATA: B.H. SAGE & W.N. LACEY, SOME PROPERTIES OF THE LIGHTER HYDROCARBONS, HYDROGEN SULFIDE, & CARBON DIOXIDE, 236-237, AMERICAN PETROLEUM INST., NEW YORK (1955)

Fig. 8. Phase relations on triangular diagram predict composition of reservoir fluid necessary for miscible displacement by high pressure gas process (exemplified by analogue data, $P = 2{,}500$ lb./sq.in.abs., $T = 160$°F., mole %).

miscibility when it is lost through gas fingering.

CONDENSING GAS-DRIVE PROCESS (ENRICHED GAS DRIVE)

Many reservoir liquids are low in concentration of the intermediate components. In these cases the development of miscibility by the high pressure gas process generally requires pressures above the maximum pressure the reservoir rock can withstand. One way to overcome this difficulty is to enrich the reservoir fluid with intermediates. When a rich gas displaces such a reservoir fluid, intermediates condense out of the gas into the reservoir liquid, creating a band of enriched liquid. Under the proper conditions the reservoir fluid is converted into a liquid that is miscible with the rich gas. This is the condensing gas drive process (7).

The above condensation mechanism can be demonstrated by use of a triangular diagram (Figure 13*a*). The injection gas G_1 mixes with the reservoir fluid L_1 to give a mixture M_1. In the attainment of equilibrium there has been a mass transfer of intermediate components from the gas to the liquid, and a liquid phase L_2 is formed which is richer in intermediates than the reservoir fluid. Next this enriched liquid is combined with a new batch of the injection gas. Further enrichment of the liquid phase ocurs. This process of liquid-phase enrichment can be continued until composition L_4 is reached, the plait-point composition. This material is miscible with the injection gas.

In a porous medium under proper conditions the above process will take place, but in a continuous rather than batch type of mechanism. The injected enriched gas will come into contact with the reservoir fluid, and intermediates will be transferred from the gas to the liquid. The gas has a lower viscosity and moves on out into the reservoir leaving the oil to be contacted by a fresh batch of enriched injected gas. This process continues until a band of oil has been enriched until it is completely miscible with the injection gas. When this is attained all of the oil is pushed out of the porous system by the injection gas. The gas that is stripped of its intermediates by the oil moves on ahead of the enriched oil and contacts the reservoir oil L_1. The volume of this gas is small in comparison with the volume of the reser-

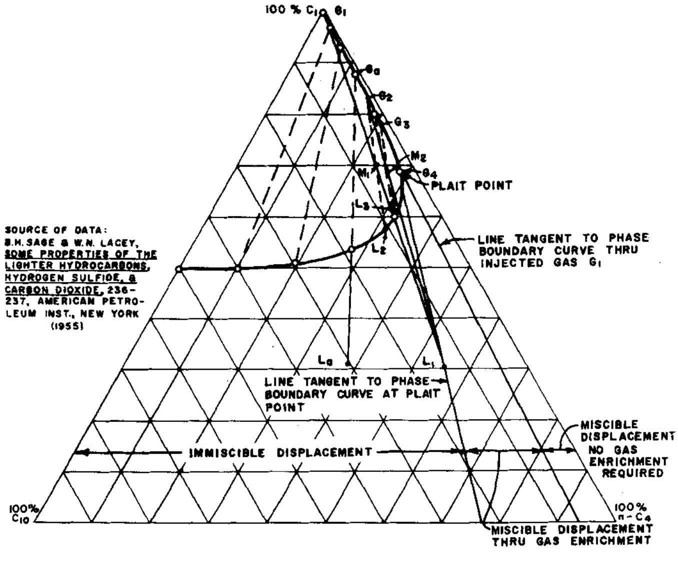


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Fig. 7*a*. High pressure gas process mechanism demonstrated on triangular phase diagram of analogue system ($P = 2{,}500$ lb./sq.in.abs., $T = 160$°F., mole %).

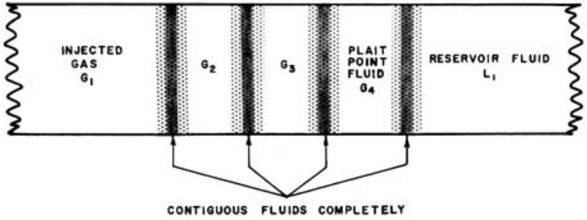


Fig. 7*b*. Relative positions of the fluids of the high pressure gas process in a porous medium.

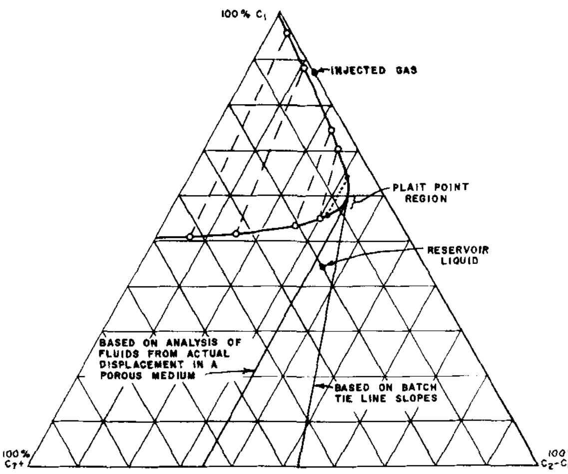


Fig. 9. Importance of slope of tie lines at the plait point in determining whether miscibility by high pressure gas process is possible (exemplified by University Block 31 data, P = 4,000 lb./sq.in.abs., T = 140°F., mole %).

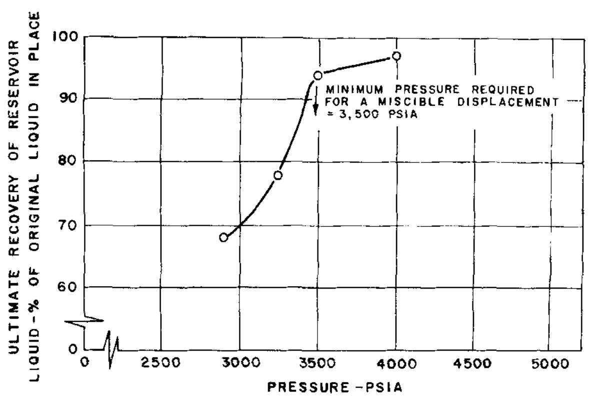


Fig. 11. Miscibility pressure determined from laboratory run *pressure-recovery curve, 123-ft. laboratoy core (lean gas* displacing University Block 31 Reservoir fluid).

voir oil it contacts. It is either dissolved completely by the oil or remains a free gas phase which occupies a small part of the pore space in the oil region. The relative position of the fluids in the condensing gas-drive process in a porous medium is shown schematically in Figure 13b; only the fluids that are important in the miscible displacement are shown (the stripped gas is omitted). The fluids from the batch-contact description of the process of Figure 13*a* are represented here. In the actual process enriched liquid composition varies continuously from L_1 to L_4.

In order to determine under what conditions this mechanism operates the triangular diagram is divided in a manner shown in Figure 14. The intersection of the tangent line through the plait point with the C_1 to C_4 side of the diagram shows the leanest gas that will generate miscibility with any reservoir liquid lying to the left of this line. The intersection of the line tangent to the phase boundary curve through the reservoir fluid with the C_1 to C_4 side shows the richest gas that can be used for this process. This gas, and all richer gases, are already miscible with L_1; thus no transfer of intermediates is necessary.

This process differs from the high pressure gas process in that the reservoir fluid is enriched through mass transfer from the rich injected gas. In the high pressure gas process the reservoir fluid is stripped of some of its intermediates and heptanes and heavier components by the injected gas. This process, like the high pressure gas process, generates a miscible displacement at pressures much below the cricondenbar. The cricondenbar for gas G_a and liquid L_1 (Figure 14) is 3,200 lb./sq. in. abs., whereas a miscible displacement occurs at 2,500 lb./sq. in. abs. by the condensing gas-drive mechanism.

The rich gas in a condensing gas-drive operation will typically contain about 50 mole % intermediates (mostly propane and butane) (*17*). Economics will generally prohibit the continuous injection of rich gas. After injection of sufficient rich gas to develop the miscible transition zone and sufficient rich gas to displace this gas miscibly, one can inject a less costly lean gas. Since the lean gas is miscible with this slug of rich gas, the rich gas is completely displaced by the lean gas and stays ahead of it to miscibly displace the enriched reservoir oil. At the present time the size of the rich gas slug necessary to ensure miscibility throughout the displacement is not well defined. The authors believe that the slug quantity required will generally be less than 20% of the rock pore volume.

MISCIBLE SLUG PROCESS

The high pressure gas process and the condensing gas-drive process both create a transition fluid which at its leading edge is miscible with the reservoir oil and at its trailing edge is miscible with the injection gas. A miscible displacement will also result if a fluid with these same miscibility properties is injected rather than generated in place. This is the miscible slug process. Its main advantage over the

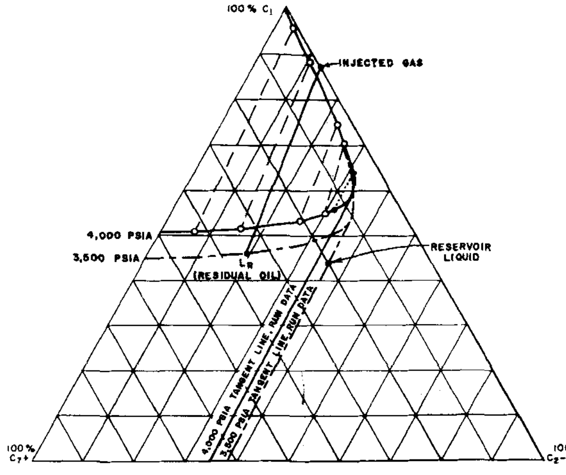


Fig. 10. Phase relations of complex systems on a triangular diagram help in determining miscibility pressure for high pressure gas process (exemplified by University Block 31 data, T = 140°F., mole %).

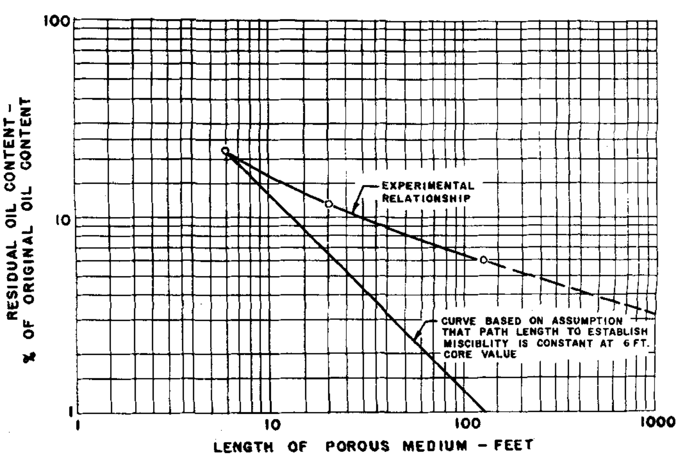
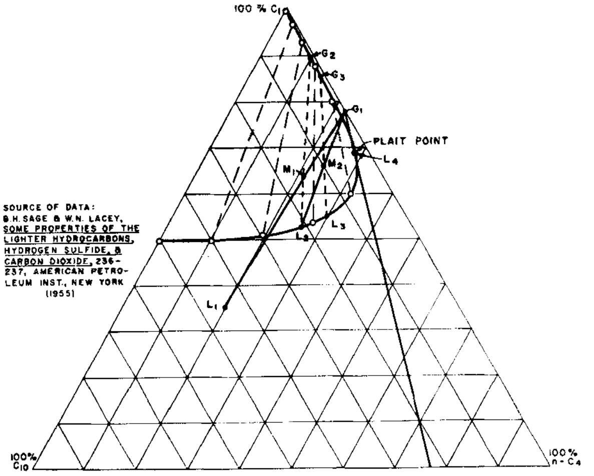
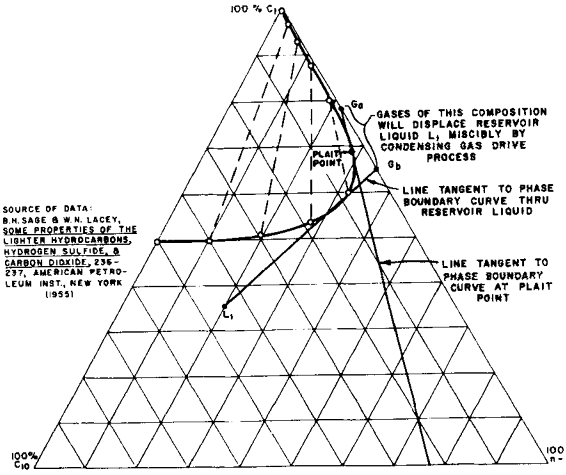


Fig. 12. Oil used up in developing miscible transition zone by high **pressure gas process.**



SOURCE OF DATA: B.H. SAGE & W.N. LACEY, SOME PROPERTIES OF THE LIGHTER HYDROCARBONS, HYDROGEN SULFIDE, & CARBON DIOXIDE, 236-237, AMERICAN PETROLEUM INST., NEW YORK (1955)

Fig. 13*a*. Condensing gas-drive process mechanism demonstrated on triangular phase diagram of analogue system (P = 2,500 lb./sq.in.abs., T = 160°F., mole %).



SOURCE OF DATA: B.H. SAGE & W.N. LACEY, SOME PROPERTIES OF THE LIGHTER HYDROCARBONS, HYDROGEN SULFIDE, & CARBON DIOXIDE, 236-237, AMERICAN PETROLEUM INST., NEW YORK (1955)

Fig. 14. Location of composition limits of injected gas for miscible displacement by the condensing drive process (exemplified by analogue data, P = 2,500 lb./sq.in.abs., T = 160°F., mole %).

other two processes of practical interest is that it can be conducted at lower pressures and therefore has wider applicability. It has one serious disadvantage; once miscibility is lost through the breakdown of the slug from dispersion, it cannot be regenerated.

Pressure Requirements

First examine the pressure requirements for complete miscibility between the injection gas and the slug material by using the phase relations of the methane-*n*-butane system. The phase boundary curves for methane and butane are shown in Figure 15 at several temperatures. All mixtures lying within these curves are immiscible (two-phase region); all other mixtures form a single phase. To assure that the injection gas (methane) and the slug material (*n*-butane) are miscible in all proportions at a given temperature the pressure must be at or above the cricondenbar, for example 1,810 lb./sq. in. abs. at 160°F. A plot of the cricondenbar against the temperature then defines the minimum pressure required for complete miscibility. These relationships for methane and several potential slug materials are given in Figure 16. Propane is the most generally applicable slug material in this group because the pressure required is low.

When the reservoir temperature is above the critical temperature of the slug material, the pressure required for complete miscibility between the slug material and the reservoir oil becomes important. Under these conditions the slug material cannot be liquefied; thus the pressure must be above the cricondenbar for the slug vapor-reservoir oil system at the reservoir temperature. Little is known about the cricondenbar for such systems; it undoubtedly depends on the composition of the reservoir oil and the temperature. It becomes important to know this only when propane is the slug material and the temperature is above 206°F.; it is never a problem for butane because its critical temperature (304°F.) is above the reservoir temperatures normally encountered.

The reservoir temperature is generally below the critical temperature of the slug material. When this is the case and the reservoir pressure is above the vapor pressure of the slug material, the slug material and reservoir fluid will usually be completely miscible because the slug is a liquid. Since the vapor pressure of the slug material is always below the pressure required at the gas-slug boundary, the reservoir pressure will always be above the vapor pressure of the slug material.

The fact that the slug is a liquid does not always mean that it will be completely miscible with the reservoir oil. Materials such as propane and butane are known to cause the precipitation of asphalts from certain crude oils (*18*). As a matter of fact propane has been used as a deasphalting agent in refineries. If all of the oil displaced miscibly in a reservoir were deasphalted by the slug material, this would be a major problem because of the loss of recovery (asphalt) and the plugging of the reservoir rock by the asphalt. However when the oil is displaced by the slug material in a porous medium, a transition-zone fluid is formed between the main body of the slug material and the undeasphalted reservoir oil in much the same way that the transition fluid is formed in the high pressure gas process. This fluid is miscible with the slug material at the rear of the transition zone and with the reservoir oil at the front of this zone. Thus the miscible displacement process

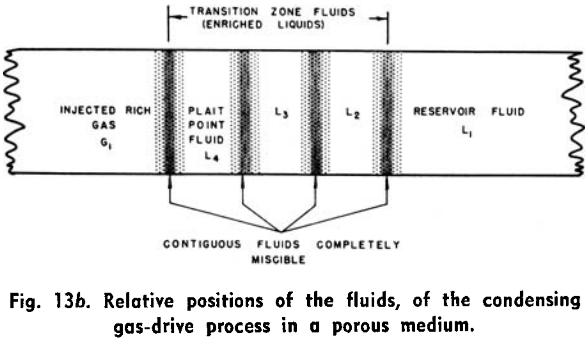
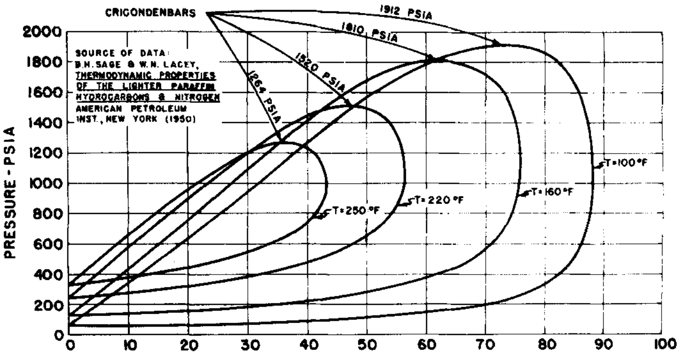
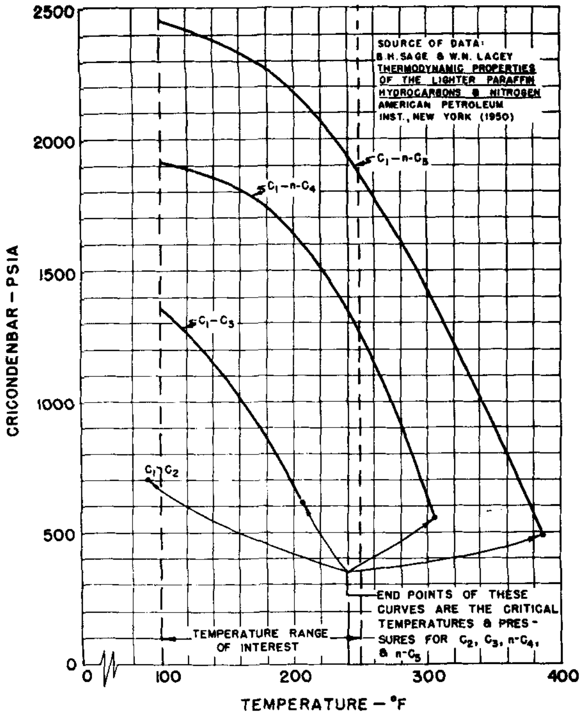


Fig. 13*b*. Relative positions of the fluids, of the condensing gas-drive process in a porous medium.



SOURCE OF DATA: B.H. SAGE & W.N. LACEY, THERMODYNAMIC PROPERTIES OF THE LIGHTER PARAFFIN HYDROCARBONS & NITROGEN AMERICAN PETROLEUM INST., NEW YORK (1950)

Fig. 15. Pressure-composition isotherms for the methane-*n*-butane system.



SOURCE OF DATA: B.H. SAGE & W.N. LACEY THERMODYNAMIC PROPERTIES OF THE LIGHTER PARAFFIN HYDROCARBONS & NITROGEN AMERICAN PETROLEUM INST., NEW YORK (1950)

Fig. 16. Loci of the cricondenbars for methane and potential slug materials (C_2, C_3, n-C_4, n-C_5).

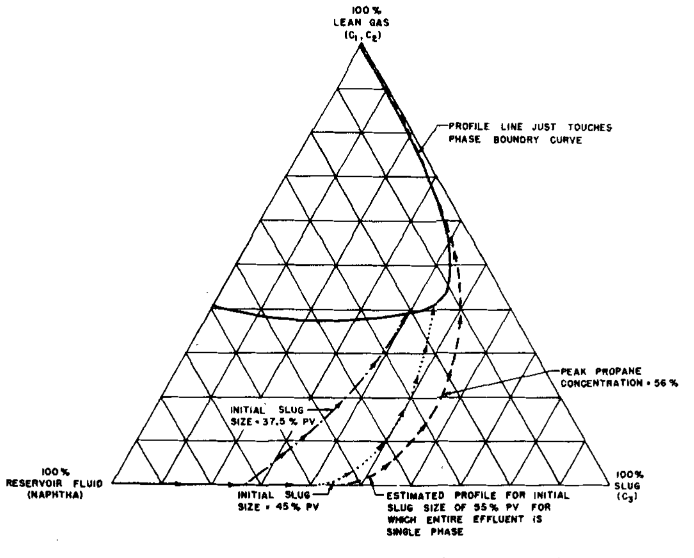


Fig. 18*a*. Composition profile of effluent for the gas miscible slug process in a 3-1/3-ft. sandstone core (P = 1,300 lb./sq.in.abs., T = 77°F., mole %).

proceeds in a normal fashion without further appreciable deasphalting taking place.

Composition of the Slug Material

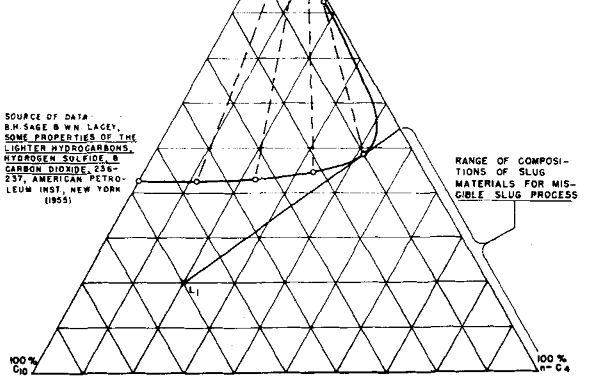
It is not only impractical but unnecessary to use pure components for the slug material. It is possible and perhaps desirable to dilute the slug with injection gas. For a given amount of slug material a larger slug will result, which has some advantage. Dilution with the injection gas is permissible up to a point. This point of maximum dilution is evident from the triangular phase diagram. For example for the analogue system methane-*n*-butane-decane, the slug material can contain up to 54% methane and still be miscible with the reservoir liquid L_1 (Figure 17). This limit of dilution is simply the intersection of the line through the reservoir fluid and tangent to the phase boundary curve with the C_1 to C_4 side of the triangular diagram (Figure 17).

Slug-Size Requirements

When a fluid is displaced miscibly by another fluid in a porous medium, a transition zone containing mixtures of the two fluids is formed. This is caused by two mechanisms. The fluids mix with each other because the velocities in the different pore channels are different; this is dispersion through mixing. The second mechanism is diffusion. The relative contributions of these mechanisms to the total dispersion is a function of the porous medium type, the diffusion coefficient, the average velocity of the fluids (the time for a given length porous medium), and the ratio of the viscosities of the two fluids (*19*).

The engineering of a miscible slug-process application involves first a concern about the phase relations involved and second the determination of the minimum slug size needed. This latter concern involves study of the slug dispersion, or dilution mechanism, and the amount of dilution that can take place before miscibility is lost.

The phase relations on the triangular diagram show the permissible dilution. Since one is interested in the fluid compositions in terms of the three materials involved in this dilution, one lets the apexes of the triangular diagram represent a 100% concentration of the injection gas, the slug material, and the reservoir fluid. An example of the phase relations based on this method of defining composition is shown in Figure 18 for the laboratory analogue system lean gas, propane, and naphtha. From this diagram one can find the minimum propane concentration to maintain a single phase for any naphtha-lean gas ratio. One must know the system composition profile in the reservoir; that is how the oil, gas,



SOURCE OF DATA: B.H. SAGE & W.N. LACEY, SOME PROPERTIES OF THE LIGHTER HYDROCARBONS, HYDROGEN SULFIDE, & CARBON DIOXIDE, 236-237, AMERICAN PETROLEUM INST., NEW YORK (1955)

Fig. 17. Location of the composition limits of the slug material in the gas miscible slug process.

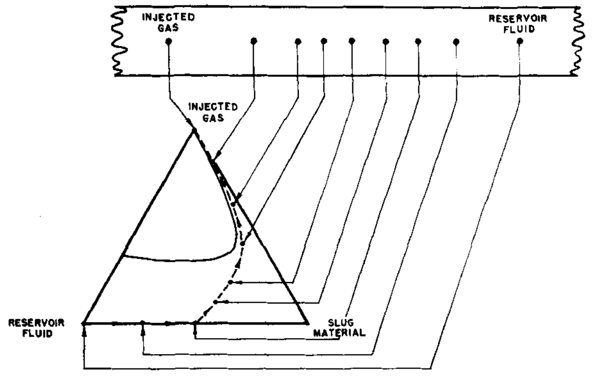


Fig. 18*b*. Relative positions of fluids of gas miscible slug process in a porous medium.

and slug material disperse as the slug progresses from injection well to production well. This then will tell whether or not miscibility is maintained. Figure 18*b* shows schematically the relative positions of fluids in this process in a porous medium.

In one group of experiments the authors determined the composition of the effluent stream from the displacement of naphtha from a 3-1/3 ft. long laboratory porous system by different size propane slugs which were in turn displaced by a lean gas. These composition data are plotted on the triangular diagram of Figure 18*a* to show the relationship between the composition profile through the dispersed slug and the phase boundary curve. For an initial slug size of 37.5% of the core pore volume and for the dispersion characteristic of this system and porous medium the composition profile cuts the phase boundary curve. This indicates that this slug size was not large enough to give a miscible displacement throughout the core. In a like manner two-phase production occurred for the 45% slug-size experiment. For a 55% slug size the entire effluent was single phase with a concentration profile estimated as shown. Since this profile just touches the phase boundary curve, any lower slug size would not yield a miscible displacement throughout the core. This then is the minimum slug size required for a miscible displacement for this length of sandstone core. The peak propane concentration for this slug size was 56%. Since the peak propane concentration in the slug initially was 100% (pure propane was injected), this shows that the peak concentration declined to 56% while the propane traveled through the core. This was the result of the dilution by the lean gas and naphtha.

The results of a series of experiments show that the initial slug length required for a miscible displacement throughout a porous medium is proportional to the square root of the length of the medium (*1*). This means that whereas a 1.83 ft. (55% of the core length) slug of propane was required in the 3.33 ft. core, a slug only 31.7 ft. (3.2% of the total length) would be required for 1000-ft. porous medium, which is a typical reservoir path length. That relatively small slugs are needed in reservoir applications of the miscible slug process makes this process economically promising.

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The Effect of Mixer Design on the Efficiency of a Pump-Mix Mixer-Settler

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The mixing efficiency of simple and pitched paddles, marine propellers, and centrifugal and disk impellers was determined by a heat transfer method in a single stage of a large pump-mix mixer-settler. The mixing devices were from 3 to 5 in. in diameter and were tested with a refined kerosene as the organic phase and water as the aqueous phase.

A heat conductance was calculated from flow parameters and the efficiency and was correlated against impeller design and speed variables .For centrifugal and disk impellers UA was proportional to $n^{1.2}L^{3}b^{0.3}$; for the paddles UA was proportional to $n^{1.67}L^{2.5}b^{0.42}$. At normal operating speeds controlled variation of the internal recirculation of mixed phases through a centrifugal impeller did not change the efficiency.

Horizontal, box type of mixer-settlers are becoming increasingly popular in solvent extraction because of their high efficiency and versatility. A particularly versatile box unit is the pump-mix mixer-settler, described by Coplan and Zebroski (*1*). Excellent operating characteristics have been described in the literature for four pump-mix units, whose sizes are as follows: a miniature