Examination of the Extraction Ability of Supercritical Gases - A Physico-Chemical Approach to CO_2-miscible Oil Recovery

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Abstract

CO_2-miscible flooding has become a widely used method for tertiary recovery of light crude oils. The applicability of this process to a particular oil reservoir is usually examined in laboratory experiments, which are PVT-analysis, and flood tests on sand-packed slim tubes or on core material. These experiments yield in the knowledge of the phase behaviour of very complicated multicomponent systems, or in case of flood tests in the information, if the crude oil will be miscible under reservoir conditions or not.

The method introduced in this paper uses a high pressure cell as a rather simple laboratory device on one side, and on the other side the very sophisticated method of gas chromatography. The oil to be investigated is filled into the high pressure cell, together with the gas to be used in the anticipated flood process.

The system is pressurized and the fluid phase, i.e. the supercritical gas together with the oil components extracted by this fluid phase, are drawn from the cell after a time when equilibrium is reached, and the components extracted from the oil are determined in a suitable gas chromatograph.

Experiments were performed with this method for a light crude oil, using CO_2 and N_2 as gases. The difference in the extraction abilities of these two gases was found to be not only in the different minimum miscibility pressure, but also in different components extracted from the oil.

Introduction

The displacement of crude oil from an oil bearing formation by a fluid is called miscible, when no interfacial tensions between the displaced hydrocarbon phase and the displacing phase occur, and thus practically no hydrocarbons are retained in the pore space due to capillary forces. The main miscible fluid displacement processes presently recognized are:

- high pressure dry gas miscible displacement
- enriched gas miscible displacement
- aqueous and oleic miscible slug flooding (such as several of the alcohols)
- carbon dioxide, flue or inert gas displacements

The miscible flood process using carbon dioxide as a displacing agent is very well known, and already being applied commercially in many reservoirs containing light crude oils.

As shown in fig. 1 the displacement efficiency may be raised from about 50 per cent for an immiscible displacement to more than 90 per cent for miscible displacement in a linear experiment. In field cases the recovery of about 20 to 40 per cent for a water flood may be doubled /1/.

Many factors influence the application of a miscible flood process in the oil field, where the most important one is the composition of the crude oil to be displaced. Others are reservoir pressure and temperature, reservoir geology and rock properties.

So the question when are these processes applicable is a very important one in preparing a field project.

The conditions during the miscible displacement using a dry gas may be represented by a diagram as shown in fig. 2. In this ternary phase diagram the crude oil is represented by two fractions: the intermediate fraction C_2-C_6 and a fraction C_{7+}. This diagram from Brigham et al. shows that at a particular pressure and temperature a two phase region exists between the liquid component C_{7+} and the dry gas methane. If a crude oil should be miscible with the dry gas it must have a composition as represented by point B in the region at the right side of a tangent at the critical point parallel to the tie-lines. The displacing phase should have a composition as represented by point D to achieve the so called direct miscibility. If a gas of composition A is injected into the reservoir this gas will be enriched step by step during the flood process until a composition similar to that of point D is achieved at the leading edge of the injected slug. This process is usually called multiple contact miscibility. For a crude oil represented by point C, miscibility can be achieved only if the two phase region is decreased. This can be done by increasing the pressure.

Determination of Miscibility Conditions

As outlined above the miscibility conditions may be determined by laboratory PVT analysis of the reservoir fluid.

Another meaningful and more commonly used method is the displacement test, an experiment which is tried to be carried out quite similar to reservoir conditions. The experimental set up is shown in fig. 3. A slim tube with a length of about 10 m and a diameter of about 1 cm is filled with sand and saturated with the crude oil to be examined. The crude oil is then displaced under high pressure (100 - 300 bar = 10 - 30 MPa = 1500 - 4500 psi) by the miscible fluid, e.g. supercritical carbon dioxide. The recovery at breakthrough of the displacing phase is usually plotted vs. the pressure applied during the experiment. From a curve as shown in fig. 4 obtained from several experiments the minimum pressure where a miscible displacement is possible may be determined.

Extraction with Supercritical Gases

Supercritical gases, expecially carbon dioxide, are not only used for extracting oil in enhanced oil recovery, but have a wide and increasing range of application when a gentle and/or non toxic extraction method is necessary. Examples are the extraction of coffeine from coffee or nicotine from tobacco or other applications in food industry /4/, or the destraction procedure /5/ to remove undesirable impurities from used-oil. The word destraction means a combination of destillation and extraction with supercritical gases, a phenomenon which is known since long, but systematically developed since the early sixties /6/. The physico-chemical fundamentals of fluid mixtures that are important for the extraction with supercritical gases (fluid extraction) and the supercritical fluid phase chromatography (SFC) are presented in detail in several papers /7, 8, 12/.

The results from this research outside petroleum engineering was the impetus for some simple experiments to be presented in this paper.

Experimental Equipment

As already mentioned the basic process in miscible flooding is that some components are extracted from the oil by a high condensed supercritical gas and carried in the fluid phase during the flood.

So one of the most important questions is which components are extracted from the oil, what is the extraction ability of different supercritical gases, and the relationship to miscible flooding.

The extraction ability of carbon dioxide, nitrogen, and several natural gas mixtures was measured at a temperature of 90° C and pressures between 100 and 1000 bar (1 bar = 100 kPa = 1 atm = 14.7 psi).

The setup of the equipment used for the extraction examinations is shown schematically in fig. 5. The live oil to be examined was sucked under pressure by means of a piston pump with mercury as displacing fluid into a steel cell with a volume of 1,000 cm^3 and a nominal pressure of 1,000 bar. Accordingly, a definite gas volume was sucked into the cell in addition to the oil. This should be done at a pressure above the bubble point pressure of the oil, but below the expected minimum miscibility pressure. In the tests described herein, 100 ml oil and 500 ml gas were filled into the cell at a pressure of 150 bar. The whole cell has been heated to 90° C in a water bath.

The cell was allowed to stand for at least 24 h at the pressure to be examined in order to establish equilibrium. Equilibrium was confirmed by the fact that even after 3 to 5 days, no changes had occurred in the composition of the fluid. Sampling was effected by taking a small volume (about 2 cm^3) via two valves from the fluid phase while keeping pressure constant. This gas trap was flushed with N_2, which guaranteed that all gases removed were frozen out in a cooling trap, and that there remained no liquid hydrocarbons in parts of the equipment.

The hydrocarbon gases frozen out in the cooling trap were then analyzed in a gas chromatograph. Analytically it was only possible to determine the hydrocarbons C_5 to C_{30}. The hydrocarbons that can be extracted by the gases (N_2, CO_2, CH_4) in the pressure and temperature range examined lie between C_5 and C_{25}.

For better means of comparison the chromatograms were processed by a calculator, and plotted in a way so that the peak area corresponds to the height of a line as shown in fig. 6. The locations of the lines correspond to the locations of the peaks in the chromatogram.

- 6 -

Experimental results

The first chromatogram in fig. 6 shows the composition of the crude oil examined. The concentration of the individual components is plotted versus relative retention time. An additional scale indicates the retention time of the normal paraffins from C_5 to C_{25}, so that an allocation of hydrocarbons to the number of carbon atoms is possible.

The next two chromatograms show the hydrocarbons that had been extracted from the oil by nitrogen. At 90° C hydrocarbons could be extracted by nitrogen beginning at pressures of 300 bar. At 600 bar hydrocarbons up to C_7 were extracted, at 1000 bar hydrocarbons up to C_{25} were extracted.

These results clearly show that miscibility may be achieved first at a pressure between 600 and 1000 bar, which is far too high to be applied in a petroleum reservoir.

The results also show an advantage of this method in comparison to slim tube tests. To carry out slim tube tests at pressures up to 1000 bar is very difficult, because the equipment for slim tube test is usually only available for pressures up to 350 bar. As one of the objectives of this paper was to examine the potential for miscible flooding with nitrogen, in the following some extraction experiments are presented using mixtures of nitrogen and carbon dioxide and nitrogen and natural gas. The question was, if the high miscibility pressure of nitrogen could be decreased by addition of these gases /9, 10, 11/.

In the next figure (fig. 7) the extraction ability of a gas consisting of 80 mol % CO_2 and 20 mol % N_2 is shown. The pressure range examined is between 150 and 250 bar. In the four chromatograms shown, one clearly discerns the increase in the concentration of higher hydrocarbons with increasing pressure. At a pressure between 200 and 225 bar the minimum miscibility pressure is supposed to be obtained, because hydrocarbons up to C_{20} and above are extracted from the oil. This determination of the minimum miscibility pressure coincides well with former slim tube tests where a minimum miscibility pressure of 210 bar was determined for pure CO_2. The addition of 20 mol % N_2 to the CO_2 shifts the minimum miscibility pressure only negligibly, if at all.

Fig. 8 shows that even at a high nitrogen content of 60 mol %, hydrocarbons are still extracted at a relatively low pressure. At pressures between 200 and 400 bar, two groups of hydrocarbons occur in the chromatograms, one between C_5 and C_{10} with a maximum at C_7, and another between C_{20} and C_{25}. Possibly these two groups may be assigned to the two different gases. At 500 bar first a continous "spectrum" is obtained.

In fig. 9 measurements are shown similar to those shown in the last figure, however, with a mixture of 80 mol % nitrogen and 20 mol % CO_2. Comparing both figures, one sees that the conditions for miscibility further detoriate. The share of components at C_{20} has decreased further.

In the next two figures tests are shown, using mixtures of nitrogen and hydrocarbons. The hydrocarbon gas used in the mixtures consisted of 55 mol % methane, 10 mol % ethane, 15 mol % propane, 10 mol % butane, 6 mol % pentane and 4 mol % hexane.

Fig. 10 shows a test with 40 mol % of this hydrocarbon gas and 60 mol % nitrogen. Like in the previous tests, here too hydrocarbons are extracted at relatively low pressure between 200 and 400 bar, but essentially only between C_5 and C_{10}.

Fig. 11 shows the same test with a mixture of 80 mol % N_2 and 20 mol % of the hydrocarbon gas. There the results are practically the same as before, the only difference being that the extracted components are a bit higher.

A pressure dependence cannot be observed, in the pressure range examined.

Summary of Results

- Pure nitrogen and the live crude oil examined (35 °API) only become miscible at pressures between 500 and 1000 bar at 90° C.

- Addition of up to 20 % N_2 to CO_2 does not increase the minimum miscibility pressure of CO_2 substantially.

- By addition of CO_2, the extraction ability for N_2 is increased strongly, but only for components between C_5 and C_{10}.

- Addition of hydrocarbons also increases the extraction ability for N_2, but again only for hydrocarbons from C_5 to C_{10}. The type of components extracted slighly depends on the quantity of hydrocarbons added.

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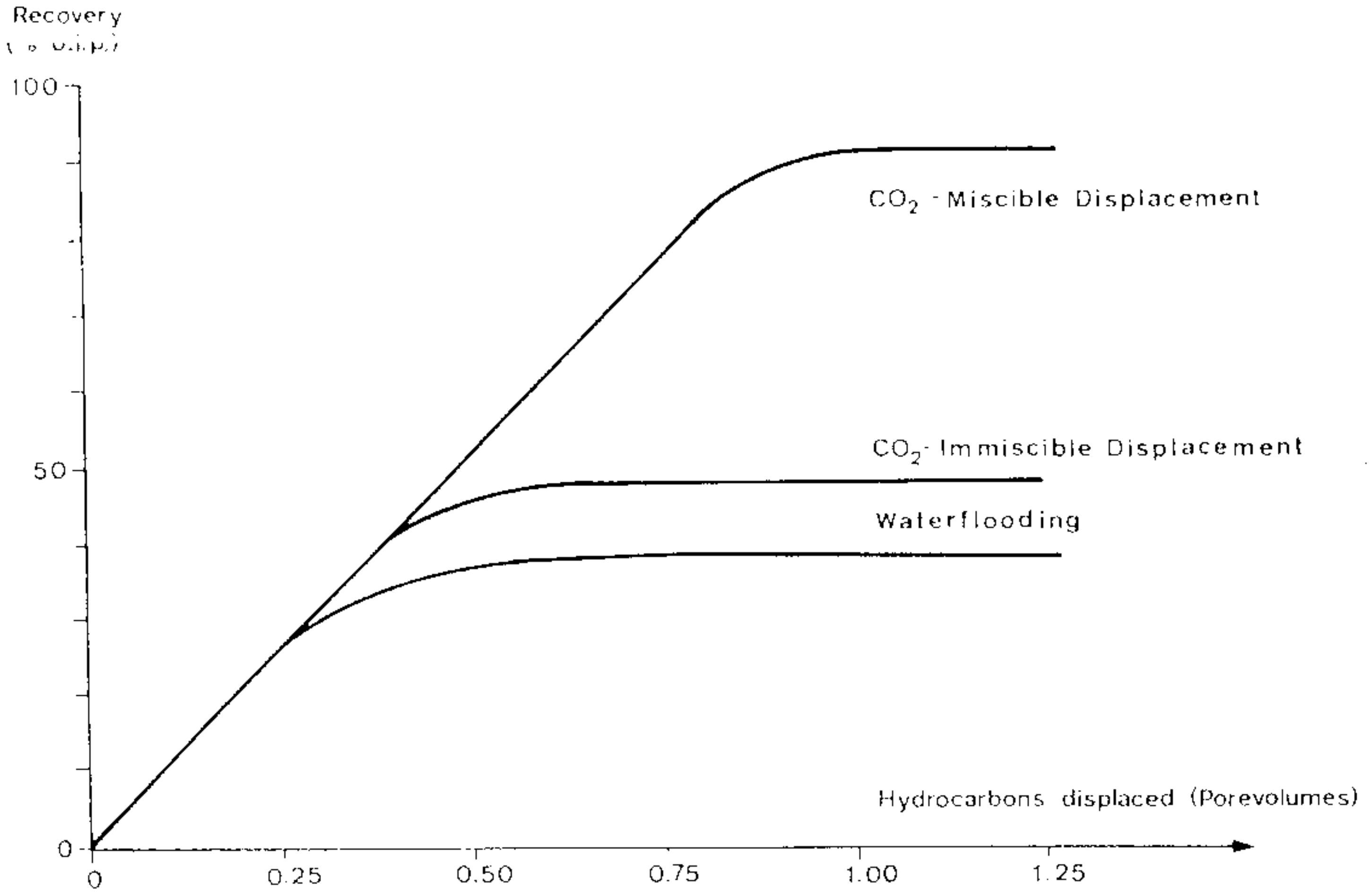
List of figures

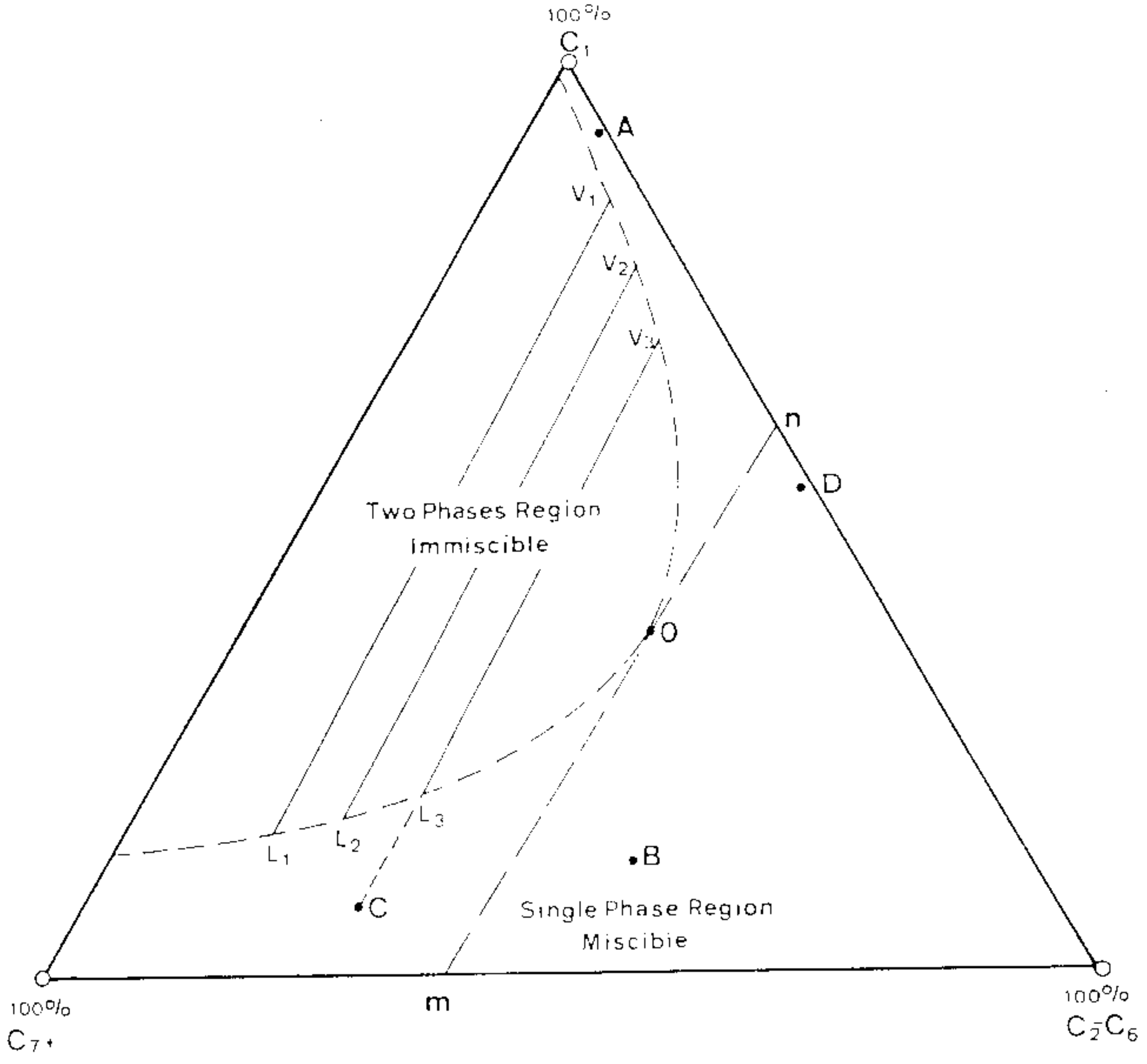
Fig. 1



Immiscible and miscible displacement with CO_2

1981

WL AF

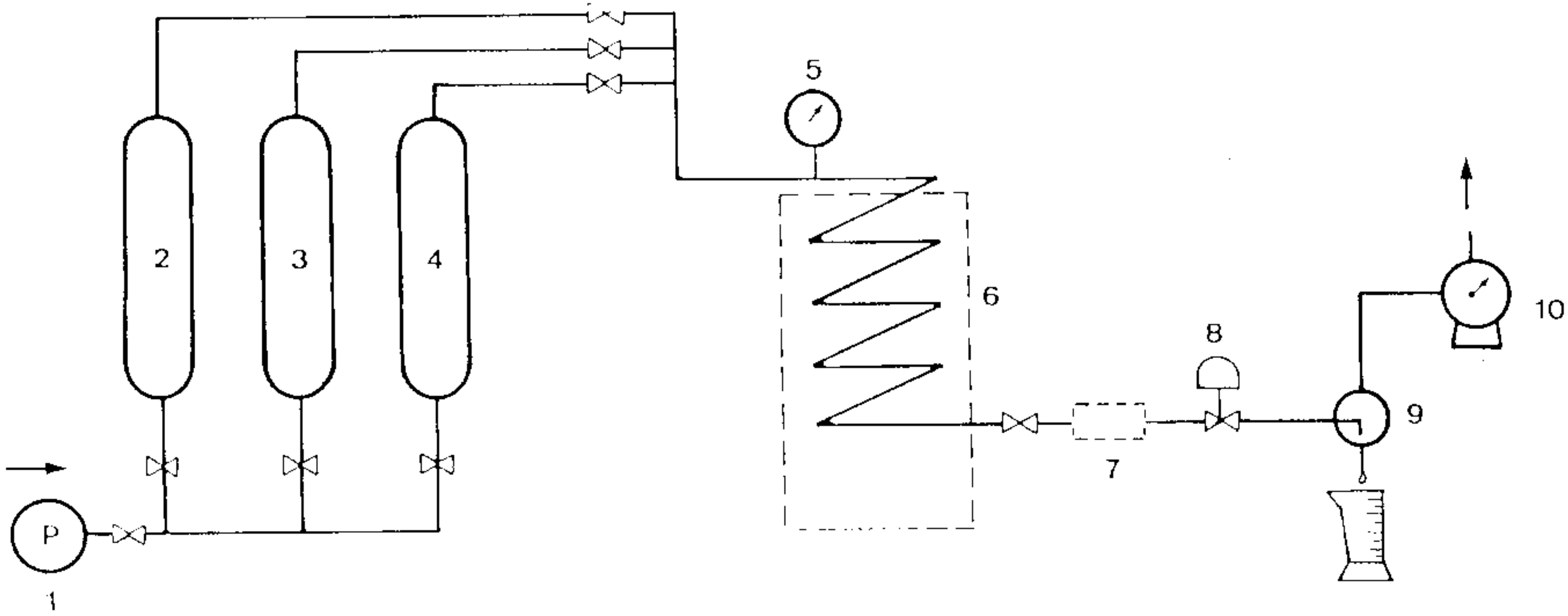


Ternary Diagram Illustrating Conditions Necessary for a Dry Gas Miscible Displacement (from Brigham et al.[2])

1981

WL/BA

Fig. 3



1 – piston pump

2,3,4 – stock for oil, water, CO_2, N_2

5 – pressure gauge

6 – thermostated slim tube

7 – miscible zone detection

8 – back pressure valve

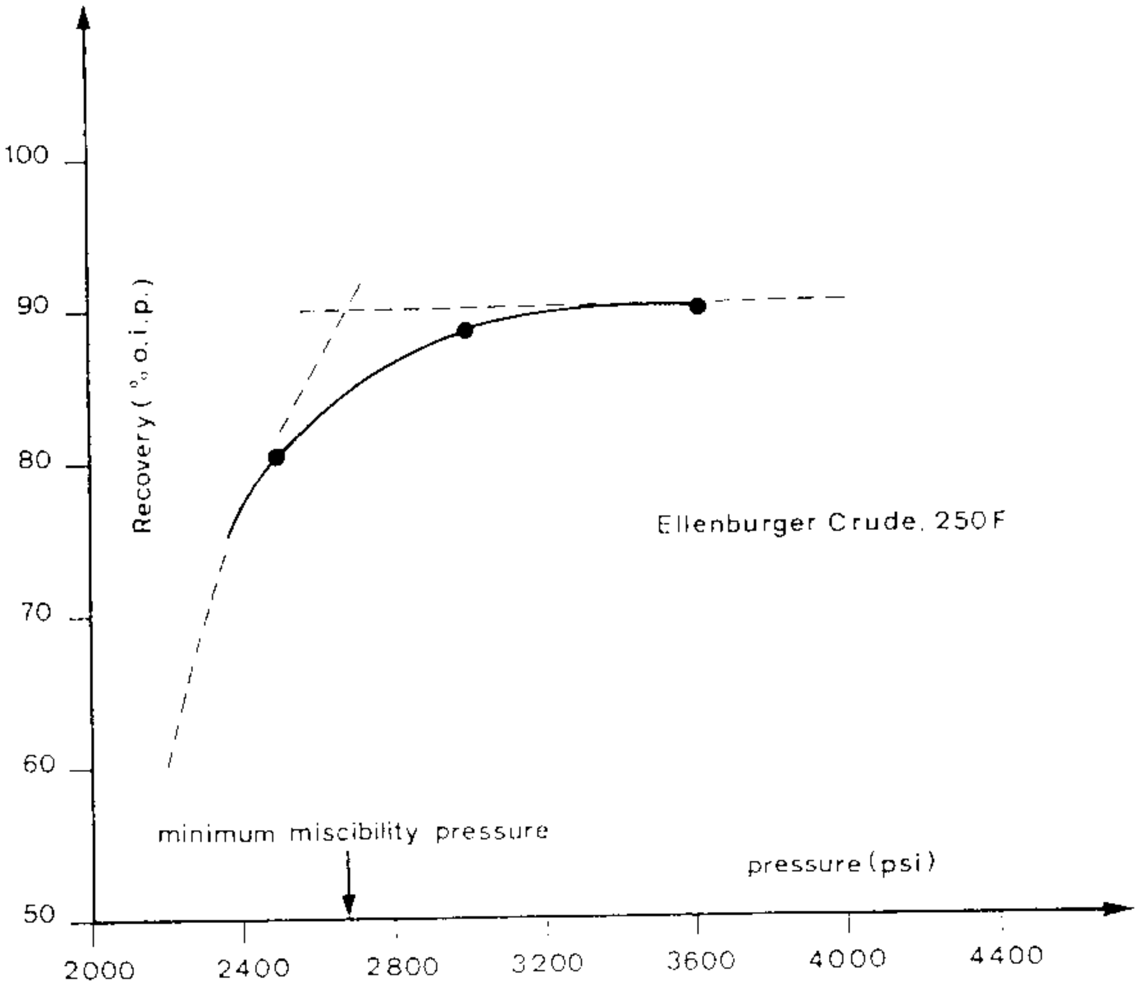
9 – gas separator

10 – gas meter

Slim Tube Test Equipment

1981

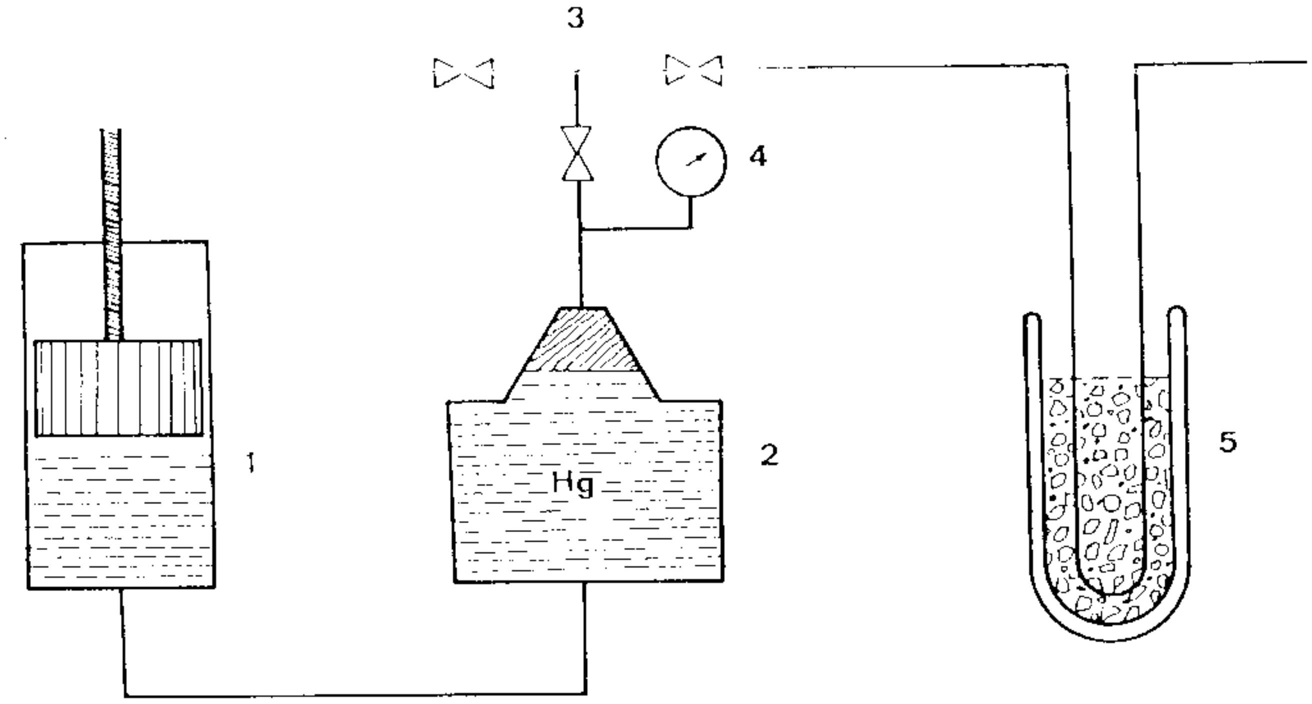
WI MF



(acc to W. W. Aud et al., /3/)

	Determination of Minimum Miscibility Pressure	1981	WL / BA

Fig. 5



1 Hg -high-pressure pump

2 high-pressure cell

3 gas trap

4 pressure gauge

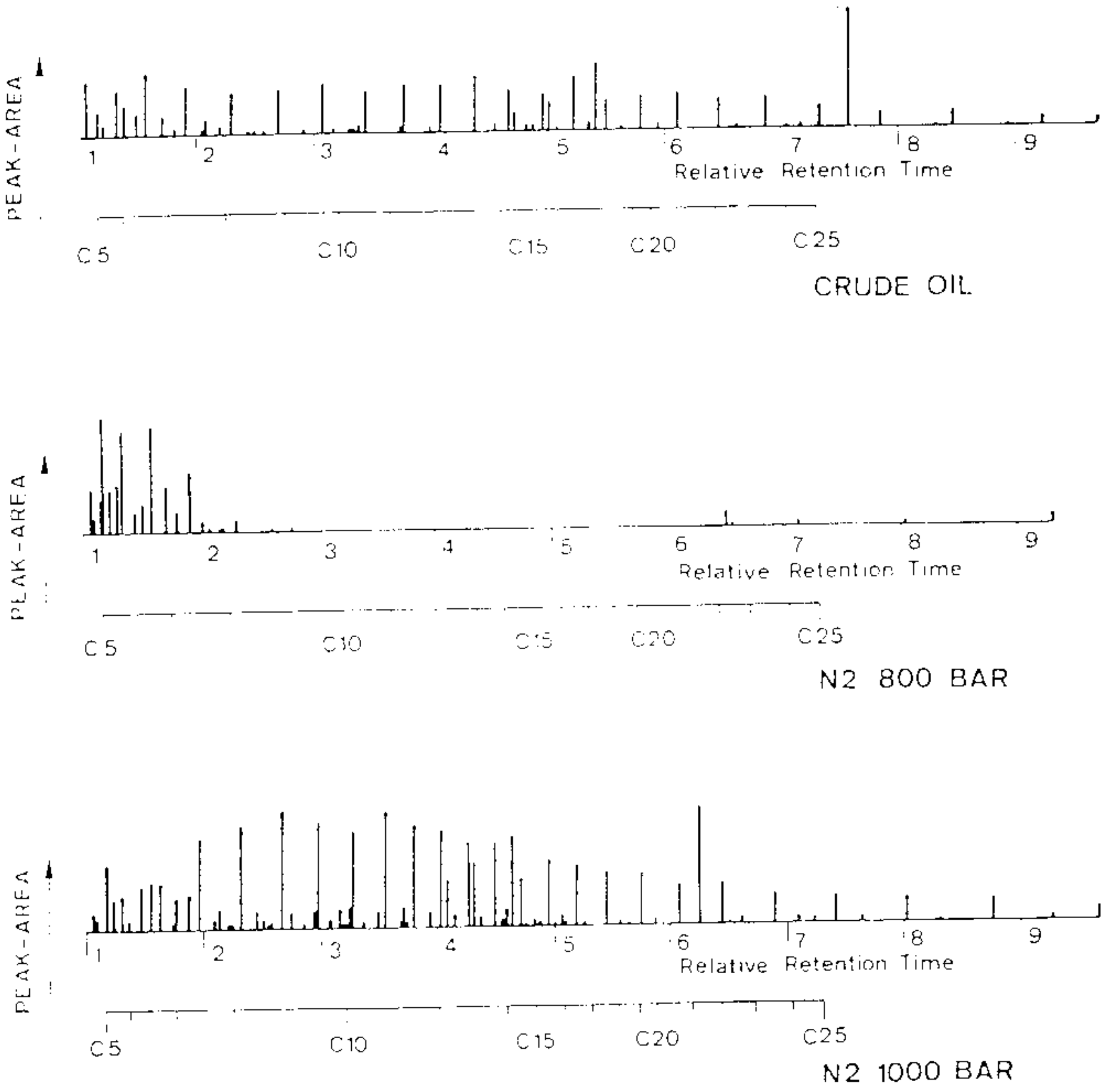
5 cooling trap

Apparatus for the determination of the extraction ability of supercitical gases

1981

WL / MF

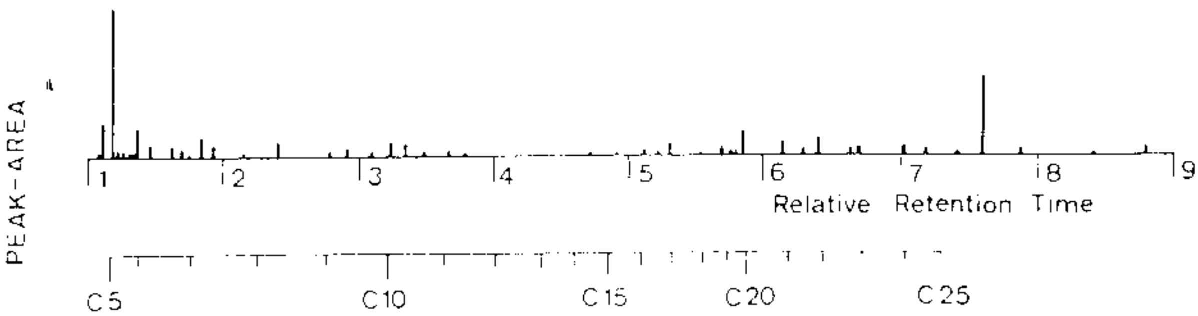
Fig. 6



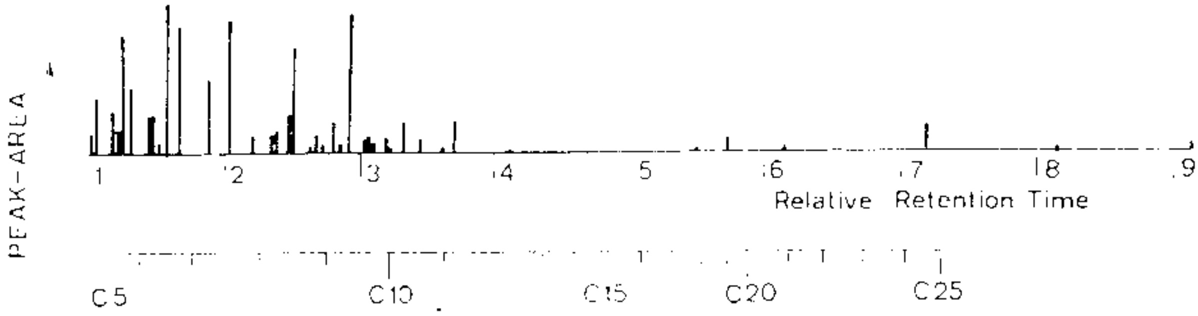
Extraction Ability
of Supercritical Nitrogen
for Live Crude

1981

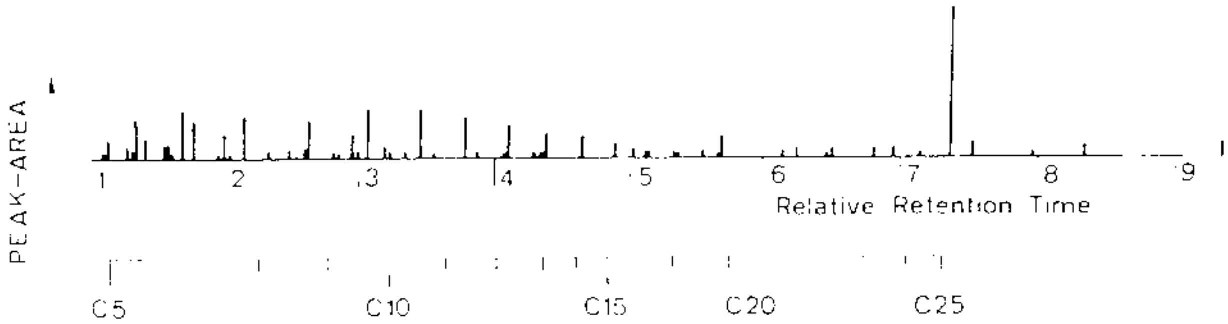
Fig. 7



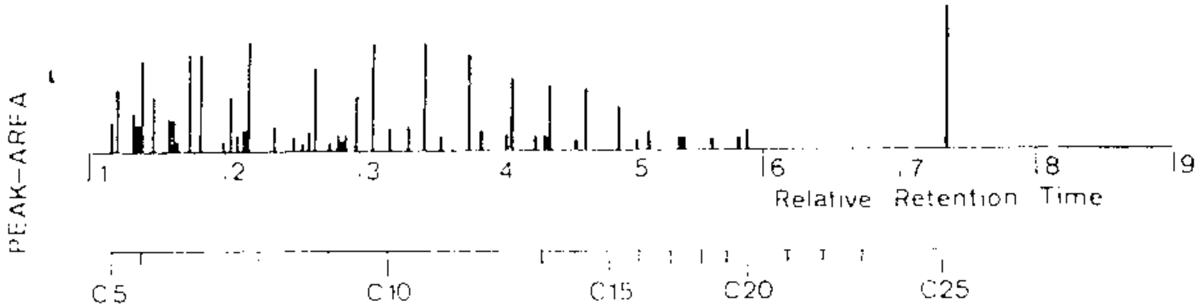
150 BAR



200 BAR



225 BAR

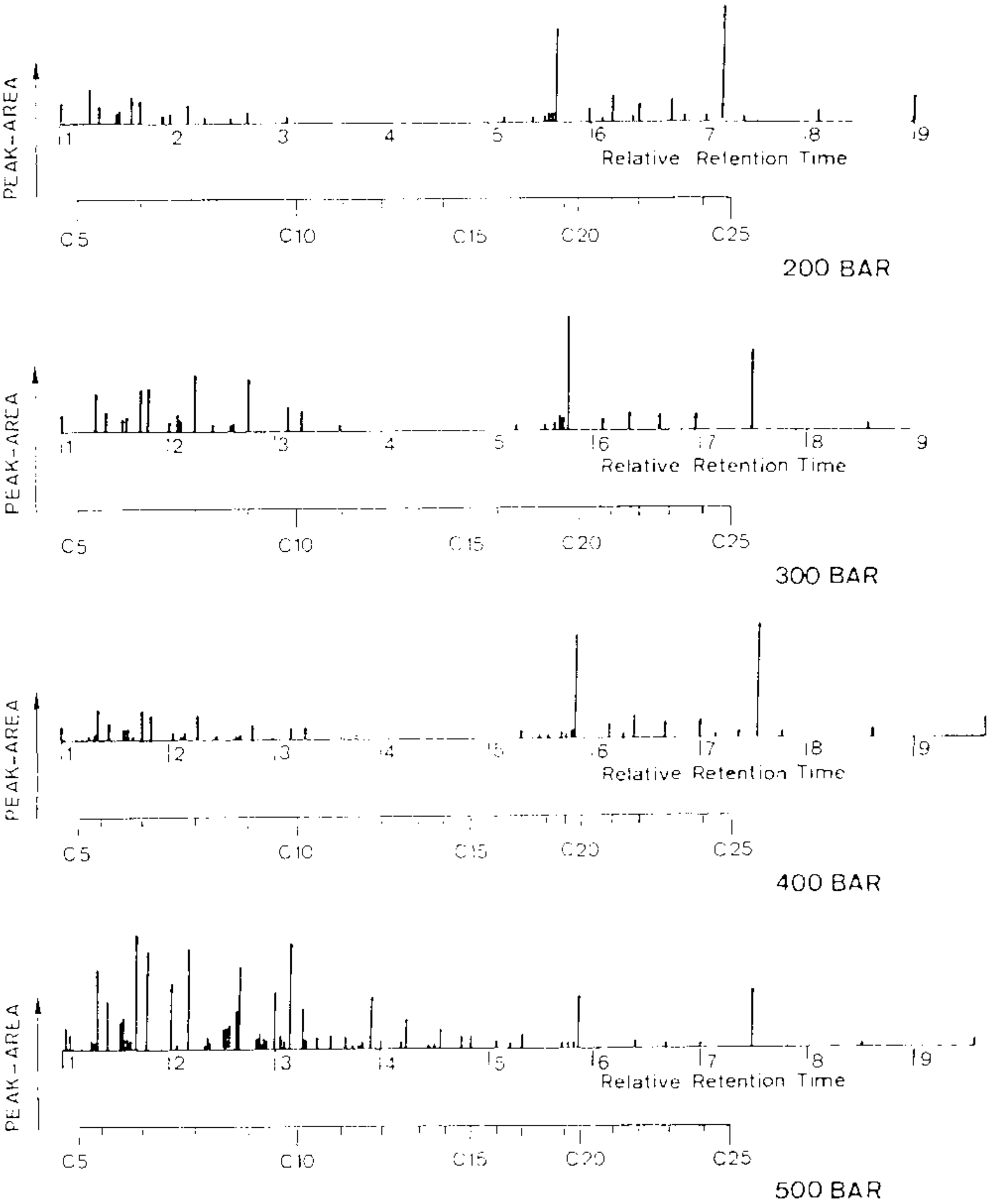


250 BAR

20 % N2 : 80 % CO2

1981

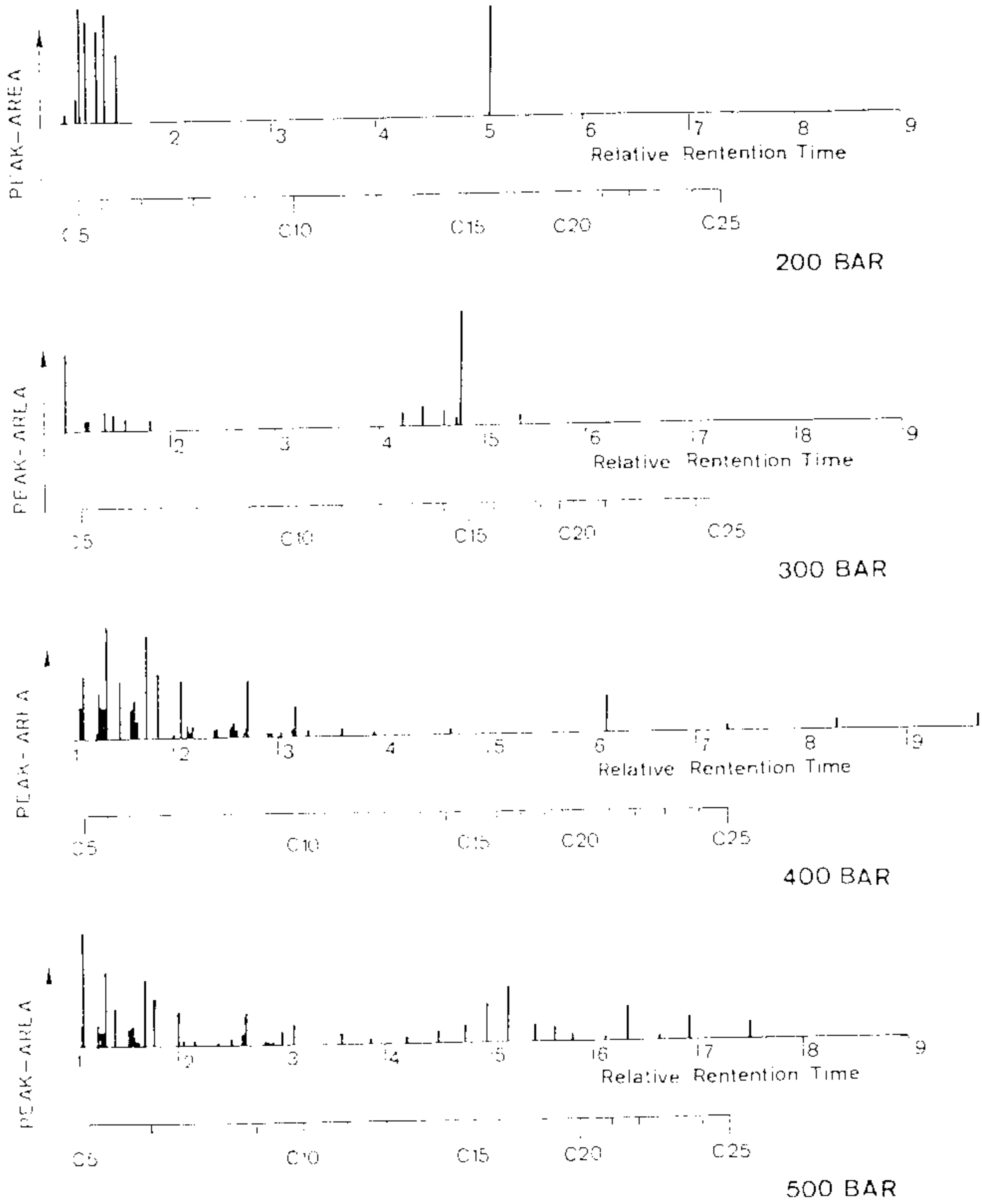
Fig. 8



60% N2 : 40% CO2

1981

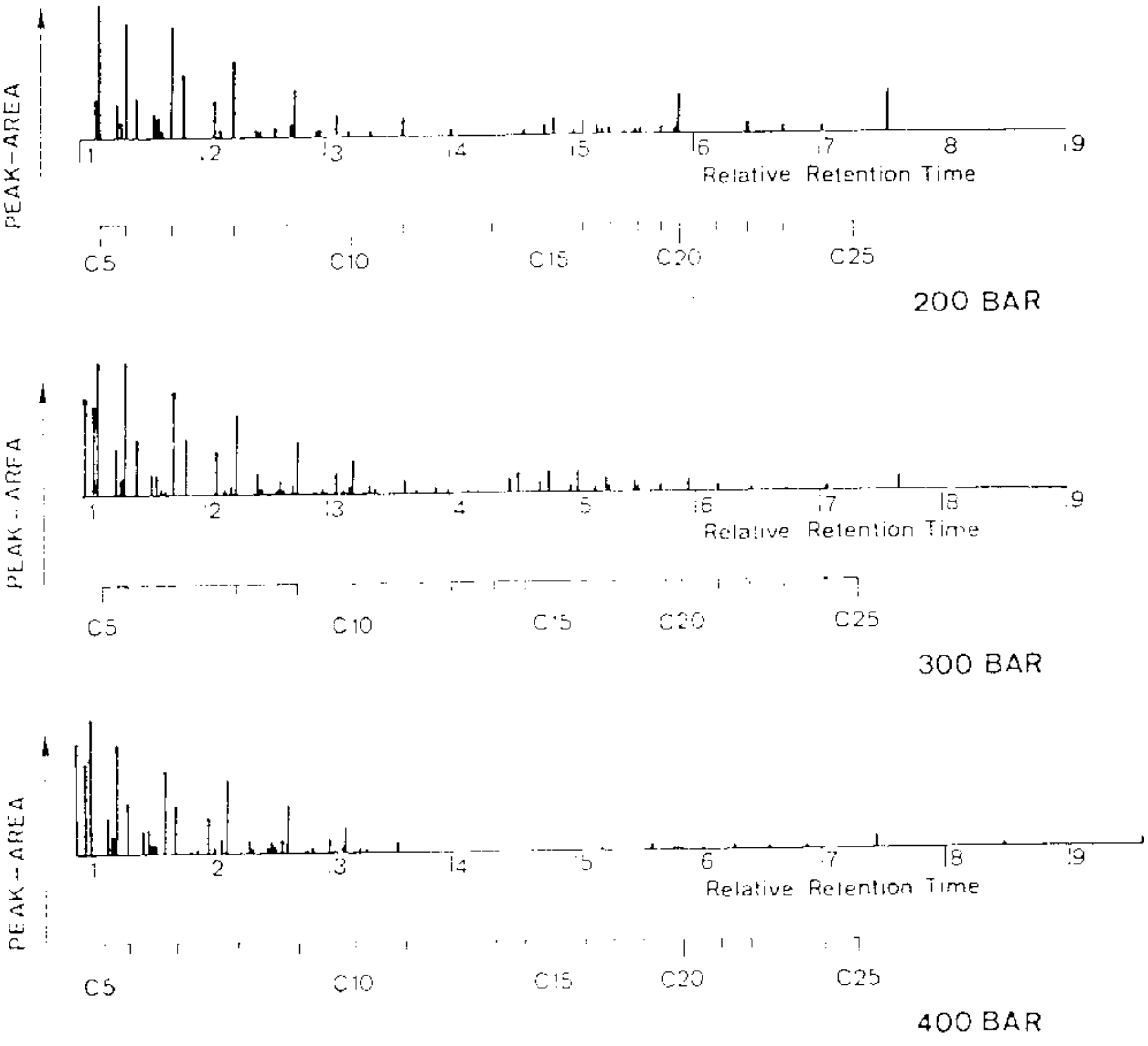
Fig. 9



80% N2 : 20% CO2

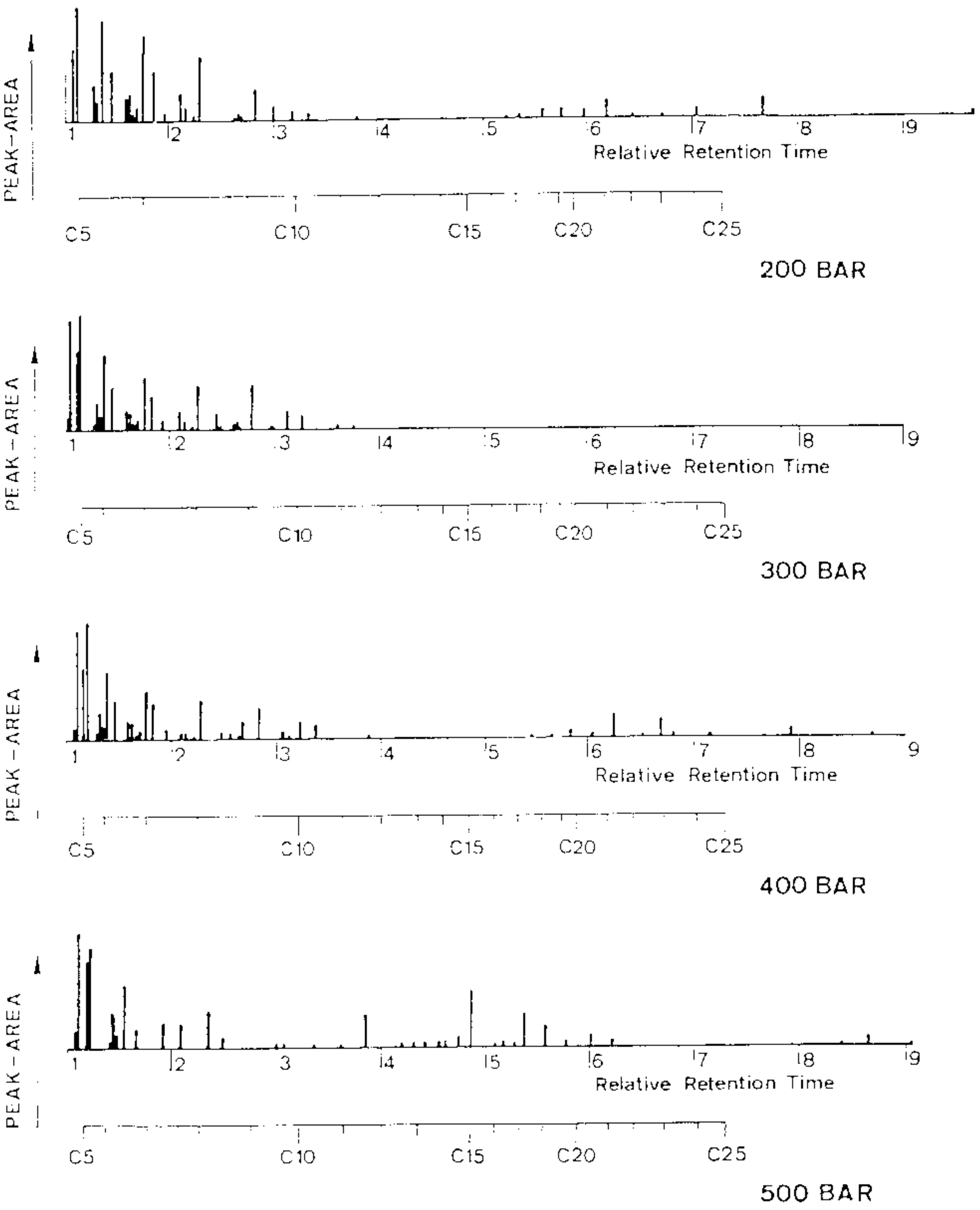
1981

Fig. 10



	60% N2 : 40% HYDROCARBONS	1981

Fig. 11



	80% N_2 : 20% HYDROCARBONS	1981 WL / GR