DETERMINATION OF HYDROCARBONS VOLUMETRIC FRACTIONS BY A HP 5890A GAS CHROMATOGRAPH

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Miscible displacements of waterflood residual oil in packed glass beads were carried out. In the experiments n-hexane was used as solvent to miscibly displaced and recover n-octane, n-decane or mixture of both.

A gas chromatograph model HP 5890A was employed to determine the produced hydrocarbons volumetric compositions. Samples injections were done manually by 1 μL syringe. Flame-Ionization-Detector (FID) with helium and hydrogen as carrier gas was used. The gas chromatograph integrator was Shimadzu C-R3A.

Initially samples of known volumetric fractions of n-hexane, n-octane and n-decane were prepared. These were injected into the gas chromatograph and the respective peak areas were obtained. The known volumetric fractions versus the peak areas obtained from the chromatograms were plotted for each component. These standard curves were later used to determine the volumetric fractions of the produced fluids from the miscible displacements.

The reproducibility of the system was checked four times and found very satisfactory. More than one hundred samples containing mixtures n-hexane, n-octane and n-decane were analysed. The volume of samples range from 6.0 mL to 12 mL. The volumetric fractions and hence the recovery efficiency of the miscible displacements were successfully obtained.

Introduction

One of the methods to increase oil recovery from an oil reservoir is by injecting gases into the reservoir. At the high reservoir pressure and temperature the injected gas is miscible with the oil and is used to miscibly displace the oil towards the production wells. This enhanced oil recovery technique is called miscible flooding. Two gases are normally used; carbon dioxide and nitrogen.

Many experimental and simulation studies have been carried out to investigate the mechanism of miscible displacement and the parameters affecting it [1]. Research in this area is still very active worldwide.

Miscible displacement experiments were conducted in which solvent was used to displace and recover waterflood residual oil. The produced fluids from the displacements were quantitatively analysed by gas chromatograph.

Instrumentation

Gas chromatographic apparatus, HP 5890A with an electronic integrator model Shimadzu C-R3A was used. This gas chromatograph has a very high precision capability and is equipped with an in-built computer control [2].

Helium was used as the carrier gas. Hydrogen and industrial air were also used. Hydrogen flame served as the ionizing source and industrial air was used to support the flame. The pressure for the gases were maintained as follows: helium 185 kpa, hydrogen 500 kpa and air 220 kpa.

Samples were introduced into the column by a 1 μL Hamilton syringe. The oven temperature was programmed to operate with initial temperature of 38 ^{o}C and the final temperature of 300 ^{o}C. The temperature increment was set at 2 ^{o}C per minute. The equilibrium time was 13 minutes.

Flame-Ionization-Detector (FID) was selected because it has the following characteristics [3]:

i) It responds to virtually all organic compounds with roughly the same high sensitivity.
ii) it does not respond to common carrier gas impurities such as water and carbon dioxide.
iii) it has minimal effects from flow, pressure and temperature changes.
iv) very few adjustments are needed.

Experimental Procedures

The schematic flow diagram for the displacement experiments is shown in Figure 1. In the experiments n-hexane represents the injected solvent while n-octane and n-decane represent the residual oils. Prior to the miscible displacement tests, the cores were waterflooded until the hydrocarbons reached residual saturations. N-hexane was injected at various rates to miscibly displace the residual hydrocarbons. Besides injecton rate, other variable parameters in the experiments were types of porous media (water-wet or oil-wet), flow configuration (horizontal and vertical) and types of test fluids used. The produced fluids were collected at regular time intervals and placed in separate bottles. Injections were continued until 1.2 pore volumes of n-hexane had been injected.

A calibration curve of peak area versus volumetric fraction was first obtained. This was done by injecting many standard samples, the compositions and the respective volumetric fractions of which were accurately known. Data on the standard samples and the peak areas are shown in Table 1 and the standard calibration curve is shown in Figure 2. The calibration jobs were done three times to check the validity and the reproducibility of the chromatographic system.

Results

The initial saturation of all the fluids in the core; water, n-octane and n-decane were known. By knowing the core pore volume, the volume of each fluid in the core before the miscible displacement can be calculated,

where;

Fluid volume, ml = fluid saturation x pore volume

The chromatograms give the retention times and the peak areas of each hydrocarbon in the injected sample. The volumetric fraction of hydrocabons can be read from the calibration curve. The volume of water produced can be obtained directly from the graduated collecting bottles.

Samples of the experimental data collected from the displacement experiments are shown in Table 2 and Table 3. The volume of each fluid produced at a particular injection interval was obtained. From there the recovery efficiency of the displacement can be calculated. Result shown in Table 2 and Table 3 were plotted in term of fractions of produced fluids versus pore volumes solvent injected. These plots are shown in Figure 3 and Figure 4.

The curves in Figure 3 and Figure 4 show the fraction of each fluid in the core effluent at a given produced pore volume of the total fluid. The area preceding the curve of the fraction of residual hydrocarbons in the effluent represents the volume of water

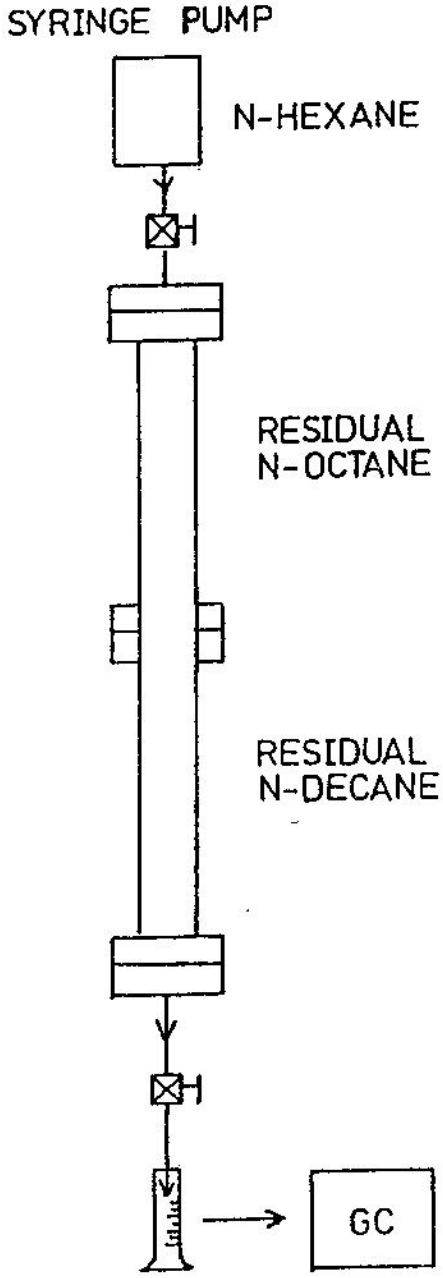


Fig. 1 - Schematic Flow Diagram of Miscible Displacement Run.

Table 1 - Gas Chromatograph Calibration Data

No.	Sample Vol.,ml	n-hexane	n-octane Vol. in sample, ml Vol. fraction peak area	n-decane
1	11.0	7.50 0.68 16.20	2.50 0.23 25.90	1.00 0.09 13.00
2	12.50	2.50 0.20 5.30	7.50 0.60 46.00	2.50 0.20 26.50
3	9.50	1.00 0.11 2.80	1.00 0.11 15.60	7.50 0.79 62.20
4	7.50	2.50 0.33 8.80	2.50 0.33 33.00	2.50 0.33 37.30
5	6.25	1.50 0.24 6.60	2.25 0.36 34.80	2.50 0.40 42.20
6	10.00	1.50 0.15 41.00	7.50 0.75 52.00	1.00 0.10 14.30
7	10.10	7.50 0.74 15.60	1.10 0.11 15.20	1.50 0.15 21.30
8	8.40	0.50 0.16 3.90	1.90 0.20 24.90	6.00 0.64 55.20
9	16.00	13.00 0.81 17.90	1.00 0.06 0.91	2.00 0.13 16.70

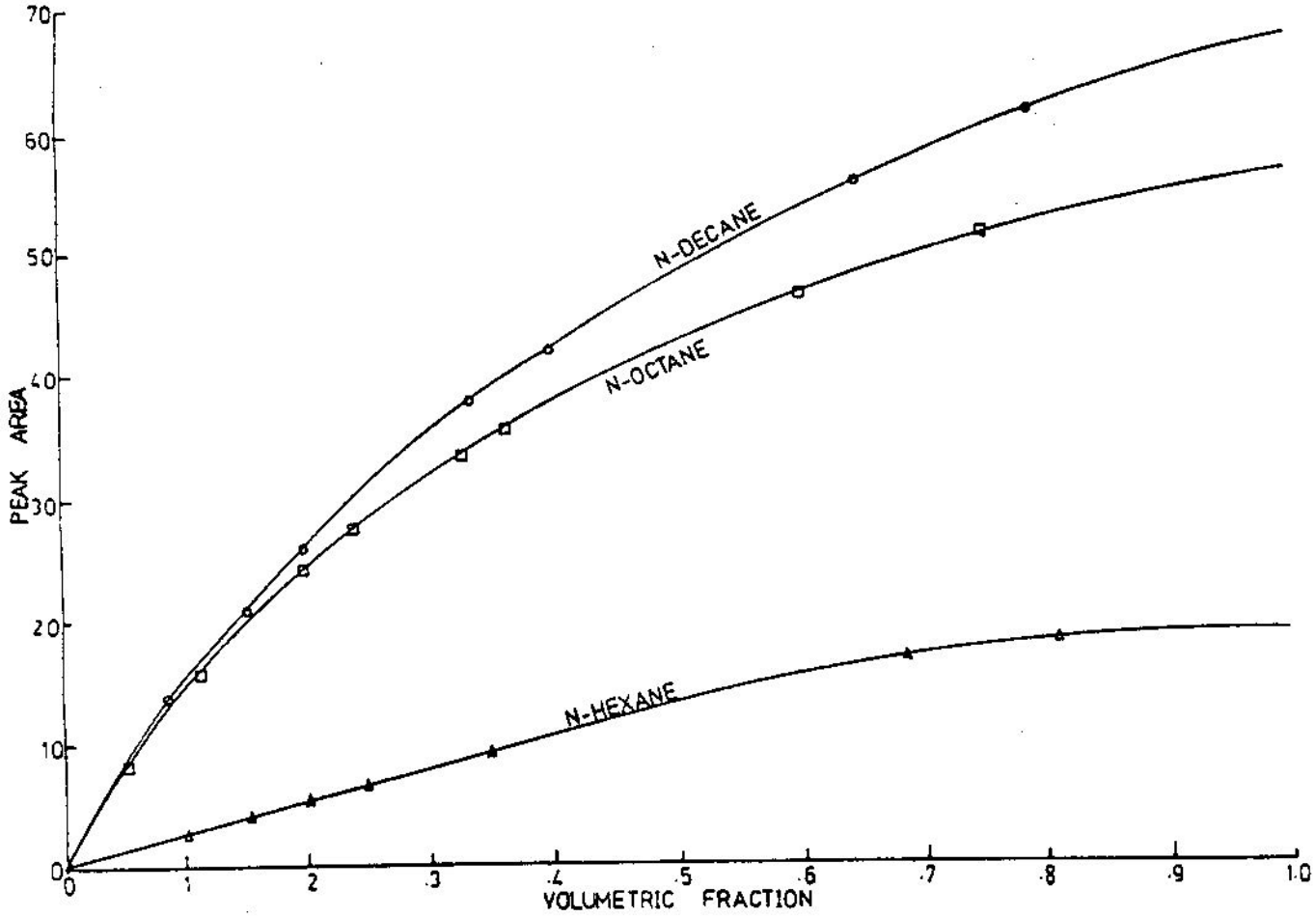


FIG. 2 - GAS CHROMATOGRAPH CALIBRATION **CURVES**

TABLE 2 - Miscible Displacement Of residual N-octane And N- Decane - Run MD 5.

Pore Volume, ml	= 112.0	Flowrate, ml/hr	= 3.0
Wettability	= water-wet	Configuration	= horizontal

No.	Vhi ml	CVi ml	CVi PV	Vwp ml	CVwp ml	Vhcp ml
1	12	12	.11	12	12	0
2	13.5	25.5	.23	13.5	25.5	0
3	22.5	48	.43	4	29.5	18.5
4	5	53	.47	0	29.5	5
5	7	60	.54	0	29.5	7
6	6	66	.59	0	29.5	6
7	6	72	.64	0	29.5	6
8	13	85	.76	0	29.5	13
9	6	91	.81	0	29.5	6
10	30	121	1.08	0	29.5	30
11	3	124	1.11	0	29.5	3
12	11	135	1.21	0	29.5	11

	n-octane peak area	n-octane V.fn	VC8	n-decane peak area	n-decane V.fn	VC10
1						
2						
3	28.7	.28	5.18	38.6	.37	6.85
4	20.6	.15	.75	15.1	.12	.60
5	12.1	.08	.56	7.4	.05	.35
6	5.2	.04	.24	3.6	.02	.12
7	2.5	.02	.12	2.1	.02	.09
8	1.1	.01	.13	1.4	.01	.13
9	.7	.01	.06	1.1	.01	.06
10	.5	traces		1.0	traces	
11	-	0		-	0	

n-octane recovery	= 7.04 ml	n-decane rec.	= 8.20 ml
n-octane rec. eff.	= 60%	n-decane rec. eff.	= 73%

Table 3 - Miscible Displacement Of Residual N-Octane And N-Decane - Run MD 6.

Pore Volume	= 114.0 ml	Flowrate	= 24.0 ml/hr
Wettability	= water-wet	Configuration	= horizontal

No.	Vhi ml	CVi ml	CVi PV	Vwp ml	CVwp ml	Vhcp ml
1	12	12	.11	12	12	0
2	12	24	.21	12	24	0
3	12	36	.32	12	36	0
4	12	48	.42	8	44	4
5	12	60	.53	1	45	11
6	12	72	.63	1	46	11
7	12	84	.74	0	46	12
8	14	98	.86	0	46	14
9	12	110	.96	0	46	12
10	12	122	1.07	0	46	12
11	18	140	1.23	0	46	18

	n-octane			n-decane		
	peak area	V.fn	VC8	peak area	V.fn	VC10
1						
2						
3						
4	25.4	.24	.96	64.5	.67	2.68
5	38.0	.28	3.08	41.7	.26	2.86
6	28.3	.10	1.1	22.1	.06	.66
7	12.7	.09	1.08	8.2	.05	.60
8	3.8	.03	.35	4.9	.04	.49
9	2.1	.02	.18	3.6	.02	.24
10	1.6	.01	.12	2.7	.02	.18
11	1.3	.01	.14	2.1	.01	.18
TOTAL RECOVERY, ml	: 7.01					7.89
RECOVERY EFF.,	: 77%					66%

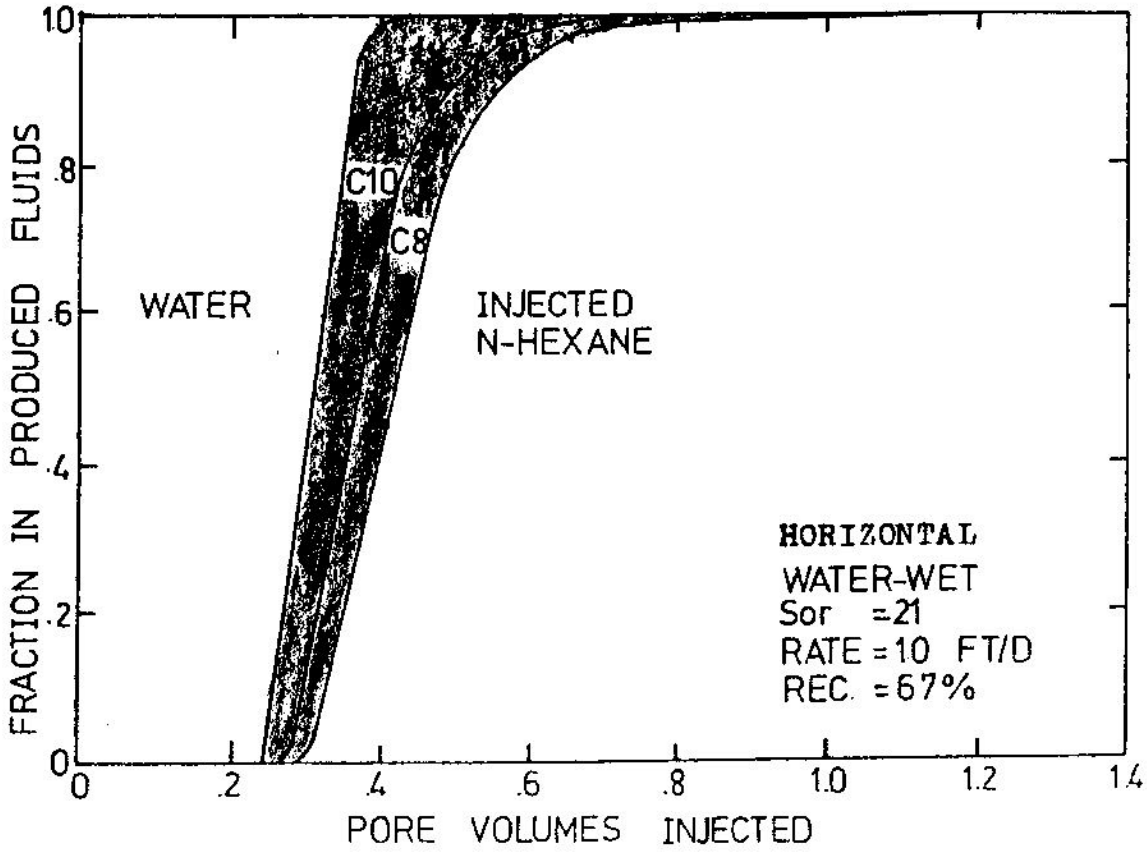


Fig. 3 - N-Hexane Displacing Residual N-Octane and N-Decane in Tandem Packs Experiment - Run MD 5

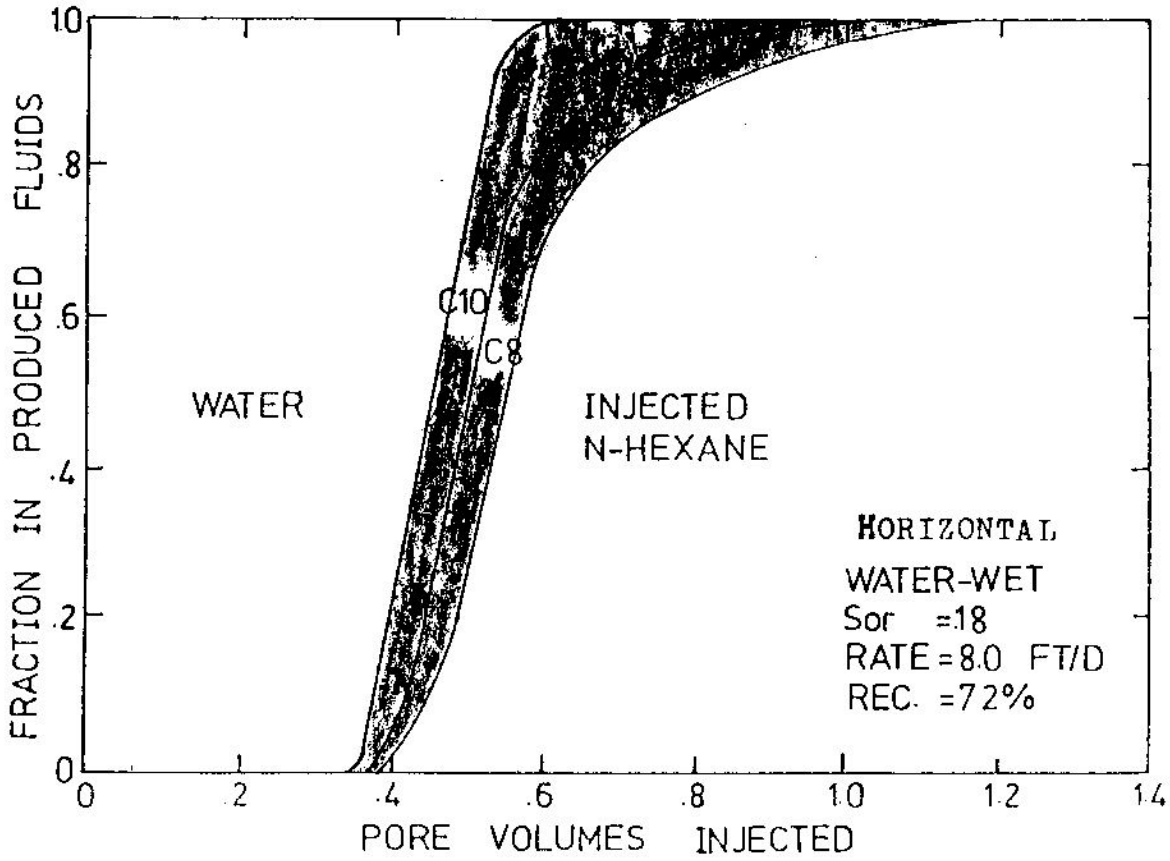


Fig. 4 - N-Hexane Displacing Residual N-Octane and N-Decane in Tandem Packs Experiment - Run MD 6.

produced. The area following the curve of the fraction of injected oil in the effluent represents the volume of injected oil produced. The marked area represents the volume residual oil recovere from the core. Figure 3 and Figure 4 are from two runs having the same variable parameters except the injection rates (1 ft/day and 8 ft/day).

Three chromatogram samples are shown in Figure 5, Figure 6 and Figure 7. These chromatograms were produced by the produced fluid samples taken from different injection periods. The transient time for n-hexane was 4.4 minutes, for n-octane was 11.5 minutes and for n-decane was 20.3 minutes. Figure 5 shows the solvent (n-hexane) first breakthrough. Figure 6 shows the simultaneous producton of the residual oil (n-octane and n-decane) and the injected n-hexane. Figure 6 shows the end of injection period where only traces of residual oils were produced.

Recovery efficiency was calculated for all the miscible displacement tests. Recovery efficiency obtained range from 67% to 99%. These results show that the displacement efficiency is very much influenced by parameters like porous media wettability, injection rates, flow configuration and types of fluid used. From these results as well as from the shapes of the recovery curves shown for example in Figure 3 and Figure 4, one can infer many things concerning relationship between displacement efficiency and reservoir parameters. This will not be discussed here as it is beyond the scope of the paper.

Discussion

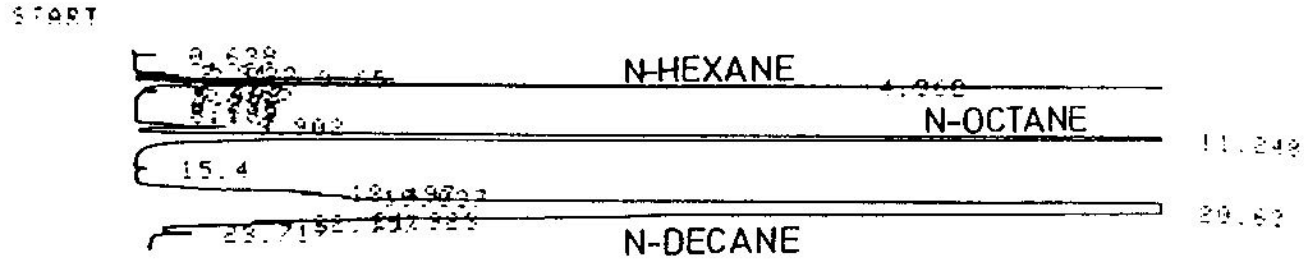
Standard calibration curve was repeated three times and the curves were similar in all of them. This shows that the analytical technique used can be adopted. Volumetric balance between the volume of injected fluid and the volume of produced fluids was done. There was very little difference (of less than 5%) in the volumes of injected and produced fluids. This shows that no significant fluid loss had occurred. Any discrepancy between injected volume and produced volume could be attributed to the injection pump accuracy and the error on the chromatograms analysis.

More than 150 produced fluid samples were analysed. The septum was changed after every ten injections. No technical problem was encountered.

Once the best operating conditions for the gas chromatograph was determined and the injection technique was mastered, the work become easy.

Conclusion

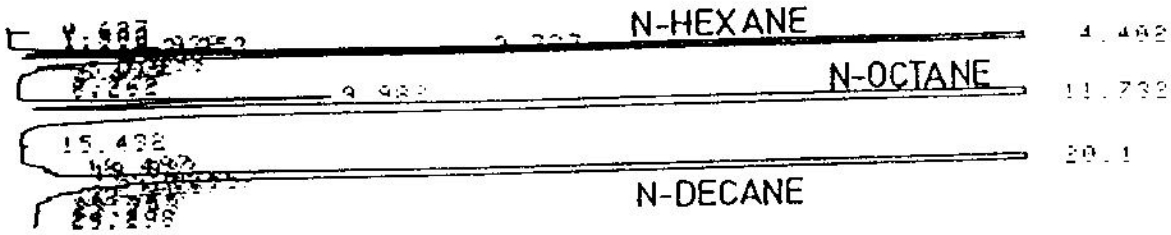
Gas chromatograph HP 5890A was succesfully employed to do quantitative analysis of samples containing n-hexane, n-octane and n-decane.



CHROMATOPAC C-R3A FILE 0
SAMPLE NO 0 METHOD 42
REPORT NO 974

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	0.638	2757				
2	2.91	19873				
3	3.223	30962	V			
4	3.65	191392	V			
5	4.362	1099219	SV	4	15.0203	
6	5.365	13161	T			
7	5.632	1051	TV			
8	9.902	142961				
9	11.248	18763590	V	2	82.3517	
10	15.4	12975				
11	18.497	484201		3	1.5453	
12	19.037	339178	V	3	1.0825	
13	20.63	69486976	SV			
14	21.923	33709	T			
15	22.357	75563	T			
16	23.717	48045	T			
	TOTAL	89655392			100	

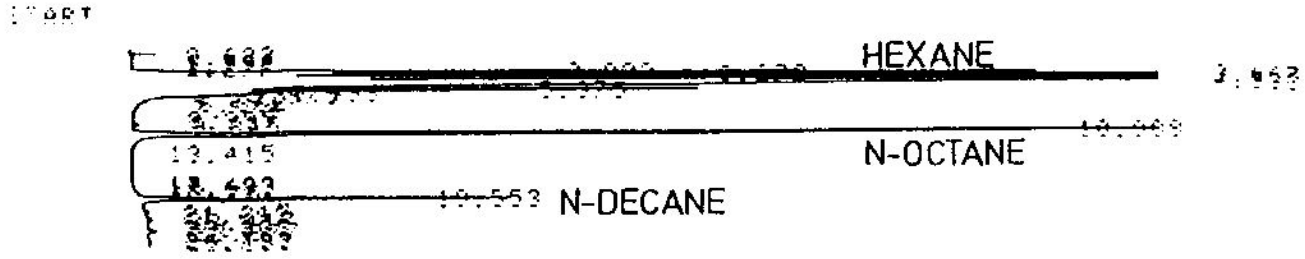
Fig. 5 – A GC Chromatogram Sample From Tandem Pack Experiment Showing Solvent Breakthrough.



CHROMATOPAC C-R3A FILE 0
SAMPLE NO 0 METHOD 42
REPORT NO 964

PEAK NO	TIME	AREA	MK	IDNO	CONC	NAME
1	0.697	3248				
2	2.932	100776				
3	3.253	158225	V			
4	3.727	1016979	V			
5	4.492	4151988	SV	4	99.3401	
6	5.298	40616	T			
7	5.732	5258	TV			
8	6.915	2241	TV			
9	6.992	2509	T			
10	8.262	2559	T			
11	9.992	537229	T			
12	11.732	45511460	SV			
13	15.432	9032	T			
14	18.497	74398		3	0.2817	
15	19.923	54224	V	3	0.2782	
16	20.1	26475282	SV			
17	20.657	5876	T			
18	21.267	12012	T			
19	21.817	3401	T			
20	22.3	12743	T			
21	23.743	8312	TV			
22	25.298	1798	TV			
	TOTAL	79191136			100	

Fig. 6 - A GC Chromatogram Sample From Tandem Pack Experiment Showing the Simultaneous Production of Residual Oils and Solvent.



CHROMATOPAC C-R3A FILE 0
SAMPLE NO 0 METHOD 42
REPORT NO 977

CHNO	TIME	AREA	MK	IDNO	CONC	NAME
1	0.632	3268				
2	2.982	400195				
3	3.272	576149	V			
4	3.667	184417				
5	4.593	15749254		4	96.9269	
6	5.375	312204				
7	5.699	14616				
8	5.975	11102				
9	6.862	5489				
10	7.579	1040				
11	9.845	11264				
12	10.988	1436537	B	2	2.6044	
13	18.75	3558	V	3	0.0047	
14	19.553	427883	V	3	0.5641	
15	21.317	19841	V			
16	21.693	3348	V			
17	22.417	31060	V			
18	23.233	9686	V			
19	23.877	25270	V			
20	24.733	4442	V			
21	25.183	13540	V			
	TOTAL	19242144			100	

Fig. 7 - A GC Chromatogram Sample From Tandem Pack Experiment at the end of Injection.

Nomenclature

eff	=	efficiency
FT/D	=	feet per day
GC	=	gas chromatography
HP	=	Hewlett Packard
mL/hr	=	millilitre per hour
PV	=	pore volume, cm^3
Rec	=	recovery
Sor	=	residual oil saturation
Vhi	=	volume of n-hexane injected, ml
CVhi	=	cumulative volume of n-hexane injected, ml
Vwp	=	volume of water produced, ml
CVwp	=	cumulative volume or water produced, ml
Vhcp	=	volume of residual hydrocarbons produced, ml
V. fn	=	volumetric fraction
VC8	=	Volume of residual n-octane produced, ml
VC10	=	Volumn of residual n-decane produced, ml

Biography

M. H. Yunan is currently teaching at the Petroleum Engineering Department, Universiti Teknologi Malaysia. He did B. Sc Degree at Leeds University and M. Sc. Degree at New South Wales University. His research activities is on enhanced oil recovery by miscible displacement.

Acknowledgements

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