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Returneres etter bruk

statoil

Wax analysis

Well 6407/1-3

STATOIL
EXPLORATION & PRODUCTION
LABORATORY

By

Hans Petter Rønningsen

September 1984 LAB 8

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CONTENTS

1. SUMMARY

Pour point, wax appearance point (WAP), total wax content, asphalthene content and dynamic viscosity has been determined for one oil (DST I) and one condensate (DST 2) from well 6407/1-3. The oil has a high wax content, 8.6% by weight, and also high pour point (+15°C), WAP (+25°C) and dynamic viscosity. The asphaltene content, 1,5% by weight, is higher than all other oils from the North Sea which have been tested.

The condensate has a low wax content, only 0.8% by weight.

2. SAMPLES

The samples were taken from two 20 l Jerrycans with stock tank oil, which had been stored at the Norol-store from the arrival on shore. The dates of sampling offshore were 221283 (DST I) and 050184 (DST 2). The cans were slightly heated and shaken before samples were taken out.

3. EXPERIMENTAL

3.1 Wax precipitation

A modification of UOP Method 46-64 (1), as described by Burger et.al.(2), the acetone precipitation technique, was used to precipitate waxy material from the samples. The samples were dissolved in petroleum ether and acetone added. The mixture was kept at -25°C for two hours and then filtered. The precipitated material had to be purified using a 2cm silica cartridge (SEP-PAK).

3.2 Gas chromatographic analysis

To determine the carbon number distribution of the wax material, on - column injection with η -C16 as internal standard was used.

Column: Chemically bonded SE-54, 0.3 mm i.d., 0.30 μm film thickness.

Carrier gas: Helium

Detector: FID. temp. 350°C.

Injection: 1,5 μl of a 1% toluene solution on column

Temperature: 70°C isothermal 1 min,
10°C/min to 200°C
6°C/min from 200 to 340°C.

3.3 Pour point measurement

Pour points were measured according to ASTM method D-97 (1980).

3.4 Wax appearance point (WAP)

WAP was measured optically with polarised light using a LABORLUX 12 microscope with heattable for temperatureregulation. The samples were first heated to 70°C on the heattable to remove all waxcrystals. The temperature was then decreased slowly (about 8-10°/hour) until the first crystals appeared.

3.5 Dynamic viscosity measurement

A Contraves Rheomat 115 rotational viscometer, with a coaxial measuring system operating according to the Searle principle, was used. The viscometer was equipped with a MS 0/115 measuring system, allowing for operation in the shear-rate range 24.2 to 3670 s^{-1}. Dynamic viscosity was measured at 10, 15, 20, 30 amd 40^{o}C.

3.6 Determination of pentane insolubles (asphalthenes)

The crude oil was diluted 1:40 (vol/vol) with pentane, shaked and placed at room temperature overnight before filtration.

Table 1.

Physical properties and results from wax study on oil (DST 1) and condensate (DST 2) from 6407/1-3.

	DST 1	DST 2
Density (g/cm^3, 15^{o}C)*	0.875	0.781
Molecular weigth*	261	146
Weight % C_{10+}*	89.982	59.280
Wax appearance point (^{o}C)	+25	< +8***
Pour point (^{o}C)	+15	-21
Pentane insolubles (wt%)	1.5	0
Wax content (wt%)	8.6	0.84
Σn - alkanes C_{17} - C_{40} (wt%)**	31.11	76.33
Σ other HC C_{17} - C_{40} (wt%)**	21.68	19.17
Σ HC C_{41} - C_{50} (wt%)**	11.90	4.44 (combined with C_{51+})
Σ HC C_{51+} (wt%)**	35.31	

HC = hydrocarbons

* Taken from reports LAB 217 and 218.

** Weight % of total wax

*** Condensation of water on sample cover glass made reliable measurements at lower temperature impossible

4. RESULTS

Oil 6407/1-3 is a very heavy crude oil with a high wax content, 8.6 % by weight, and a relatively high content of pentane insoluble asphaltenes, 1.5 % by weight.

This asphaltene content may, to some degree, be responsible for this oils ability to form stable emulsions. (This aspect of the oil has been studied in detail in the laboratory, and is reported in LAB 84.232).

The high wax content results in a high WAP (+25°C) and a high pour point (+15°C). This is further reflected in a viscosity/temperature curve rising steeply below 20-25°C. At 10°C, still above subsea- temperature, the oil is rather viscous (about 60 mPa.s) and shows pronounced non-Newtonian behaviour (fig 1). At static conditions, where the oil is not influenced by shear forces, it is not pourable at this temperature. This is what might happen during a transport shutdown in a pipeline.

The condensate has, as could be expected, a much lower wax content, 0.8 % by weight. Both pour point (-21°C) and WAP (<8°C) indicate that this condensate will not create problems as far as wax precipitation is concerned. The viscosity is also very low, only 1.5 mPa.s at 10°C (fig. 2). The slightly increasing viscosity with increasing shear rate, is not caused by non-Newtonian behaviour, but by turbulent flow at these high shear-rates.

Fig. 4 and 5 (and tables 4 and 5) show the carbon number distribution of the two wax samples based on gas chromatograhic analysis (chromatograms of wax samples and whole oil/condensate are shown in fig. 6 and 7). The distributions profiles of wax from both oil and condensate have peak at about $n-C_{24}$. But while only 32% of the oil-wax is contained between C_{20} and C_{30}, 79% of the condensate - wax is. The oil wax has a C_{50+} fraction on 35.3 % (representing 3% of the oil), while the condensate has about 4% (0.03% of the oil).

Melting point ranges have not been measured exactly, but microscopic study of the oil-wax indicated that all wax crystals had melted at about 60°C. It is then reasonable to assume that the melting point range of the condensate-wax is shifted appreciably to lower temperatures.

One has to emphasise that all these tests are done on stabilized fluids. Real fluids encountered during production/transportation will be richer in light end components, which will act as solvents for the wax,and reduce the viscosity. On the other hand, higher pressure will tend to increase viscosity.

CONCLUSION

The oil 6407/1-3 DST 1 is a wax-rich oil which certainly will need wax inhibitors/flow improvers to be added during production and transportation. There may also be problems with asphaltene precipitation. Another aspect of this oil is its ability to produce stable water in oil emulsions. The condensate from 6407/1-3 DST 2 will certainly not create serious problems with respect to wax precipitation

Table 2.

Viscosity data of oil 6407/1-3 DST 1 (ν =shear stress, mPa and η = dynamic viscosity, mPa.s). All values at increasing shear rate.

Shear rate (s^{-1})	10°C		15°C		20°C		30°C		40°C	
	ν	η	ν	η	ν	η	ν	η	ν	η
49.6			2689	54.2						
71.0	5968	84.0	3804	53.5	1836	25.8	885	12.5		
101.7	7738	76.1	5279	51.9	2558	25.2	1312	12.9	853	8.4
145.4	10099	69.5	7279	50.1	3607	24.8	1902	13.1	1246	8.6
209	13411	64.2	9968	47.7	4984	23.9	2754	13.2	1836	8.8
298	18100	60.7	13509	45.3	6952	23.3	3935	13.2	2689	9.0
427	24658	57.8	18297	42.9	9837	23.0	5705	13.4	3935	9.2
611	33839	55.4	24986	40.9	13903	22.8	8132	13.3	5705	9.3
875	46103	52.7	33643	38.5	19740	22.6	11673	13.4	8198	9.4
1252	62170	49.7	44988	35.9	28003	22.4	16723	13.4	11804	9.4
1793			60268	33.6	39807	22.2	23937	13.4	16985	9.5
2570					56399	22.0	34200	13.4	24396	9.5
3670					79286	21.6	49119	13.4	35118	9.6

Table 3.

Viscosity data of condensate 6407/1-3 DST 2 (ν = shear stress, mPa and η = dynamic viscosity, mPa.s). All values at increasing shear rate.

Shear rate (s^{-1})	10°C		15°C		20°C		30°C		40°C	
	ν	η	ν	η	ν	η	ν	η	ν	η
49.6										
71.0										
101.7										
145.4										
209										
298										
427	656	1.5								
611	918	1.5			787	1.3	656	1.1	590	1.0
875	1312	1.5			1115	1.3	918	1.1	787	0.9
1252	1836	1.5			1574	1.3	1312	1.1	1180	0.9
1793	2623	1.5			2361	1.3	2230	1.2	2033	1.1
2570	4427	1.7			4066	1.6	3738	1.5	3345	1.3
3670	7476	2.0			6689	1.8	6033	1.6	5443	1.5

Table 4. Carbon number distribution of wax from oil 6407/1-3 DST 1 (based on GC-analysis).

Fraction	Melting point (°C)*	wt% of wax		wt% of fraction	
		n-alkanes	other HC	n-alkanes	other HC
C_{17}	22.0	0.03	0.39	7.1	92.9
C_{18}	28.0	0.07	0.32	17.9	82.1
C_{19}	32.0	0.21	0.29	42.0	58.0
C_{20}	36.8	0.95	0.27	77.9	22.1
C_{21}	40.2	2.04	0.28	87.9	12.1
C_{22}	44.0	2.91	0.29	90.9	9.1
C_{23}	47.5	2.99	0.32	90.3	9.7
C_{24}	50.6	3.26	0.41	88.8	11.2
C_{25}	53.5	2.71	0.56	82.9	17.1
C_{26}	56.3	2.63	0.72	78.5	21.5
C_{27}	58.8	2.20	0.93	70.3	29.7
C_{28}	61.2	2.01	0.98	67.2	32.8
C_{29}	63.4	1.91	1.10	63.5	36.5
C_{30}	65.4	1.60	1.18	57.6	42.4
C_{31}	67	1.31	1.18	52.6	47.4
C_{32}	69	1.06	1.37	43.6	56.4
C_{33}	71	0.83	1.26	39.7	60.3
C_{34}	73	0.64	1.35	21.4	78.6
C_{35}	74.6	0.54	1.30	29.3	70.7
C_{36}	75.9	0.37	1.47	20.1	79.9
C_{37}	77	0.27	1.48	15.4	84.6
C_{38}	78.5	0.23	1.43	13.9	86.1
C_{39}	80	0.19	1.44	11.7	88.3
C_{40}	81	0.15	1.36	9.9	90.1
C_{41-50}	>81	11.90**			
$>C_{50}$		35.31**			

* Melting point of n-alkanes

** Sum of all hydrocarbons

Table 5 Carbon number distribution of wax from condensate 6407/1-3 DST (GC-analysis).

Fraction	Melting point (°C) *	wt% of wax n-alkanes	wt% of wax other HC	wt% of fraction n-alkanes	wt% of fraction other HC
C_{17}	22.0	0.06	0.33	16.2	83.8
C_{18}	28.0	0.16	0.32	33.5	66.5
C_{19}	32.0	0.58	0.28	67.4	32.6
C_{20}	36.8	1.86	0.30	86.2	13.8
C_{21}	40.2	4.22	0.24	94.5	5.5
C_{22}	44.0	2.91	0.29	90.9	9.1
C_{23}	47.5	9.82	0.35	96.6	3.4
C_{24}	50.6	11.37	0.49	95.8	4.2
C_{25}	53.5	9.17	0.72	92.7	7.3
C_{26}	56.3	8.16	1.02	88.9	11.1
C_{27}	58.8	6.05	1.28	82.6	17.4
C_{28}	61.2	4.66	1.44	76.4	23.6
C_{29}	63.4	3.88	1.34	74.3	25.7
C_{30}	65.4	2.86	1.34	7.6	42.4
C_{31}	67	2.04	1.12	64.6	35.4
C_{32}	69	1.44	1.22	54.2	45.8
C_{33}	71	0.98	1.98	49.9	50.1
C_{34}	73	0.65	1.95	40.6	59.4
C_{35}	74.6	0.45	0.78	36.5	63.5
C_{36}	75.9	0.00	1.36	0.4	99.6
C_{37}	77	0.01	0.89	1.5	98.5
C_{38}	78.5	0.04	0.78	4.8	95.2
C_{39}	80	0.02	1.73	2.7	97.3
C_{40}	81	0.03	1.61	4.2	95.8
C_{41-50}	>81	4.44 **			
$>C_{50}$					

* Melting point of n-alkanes

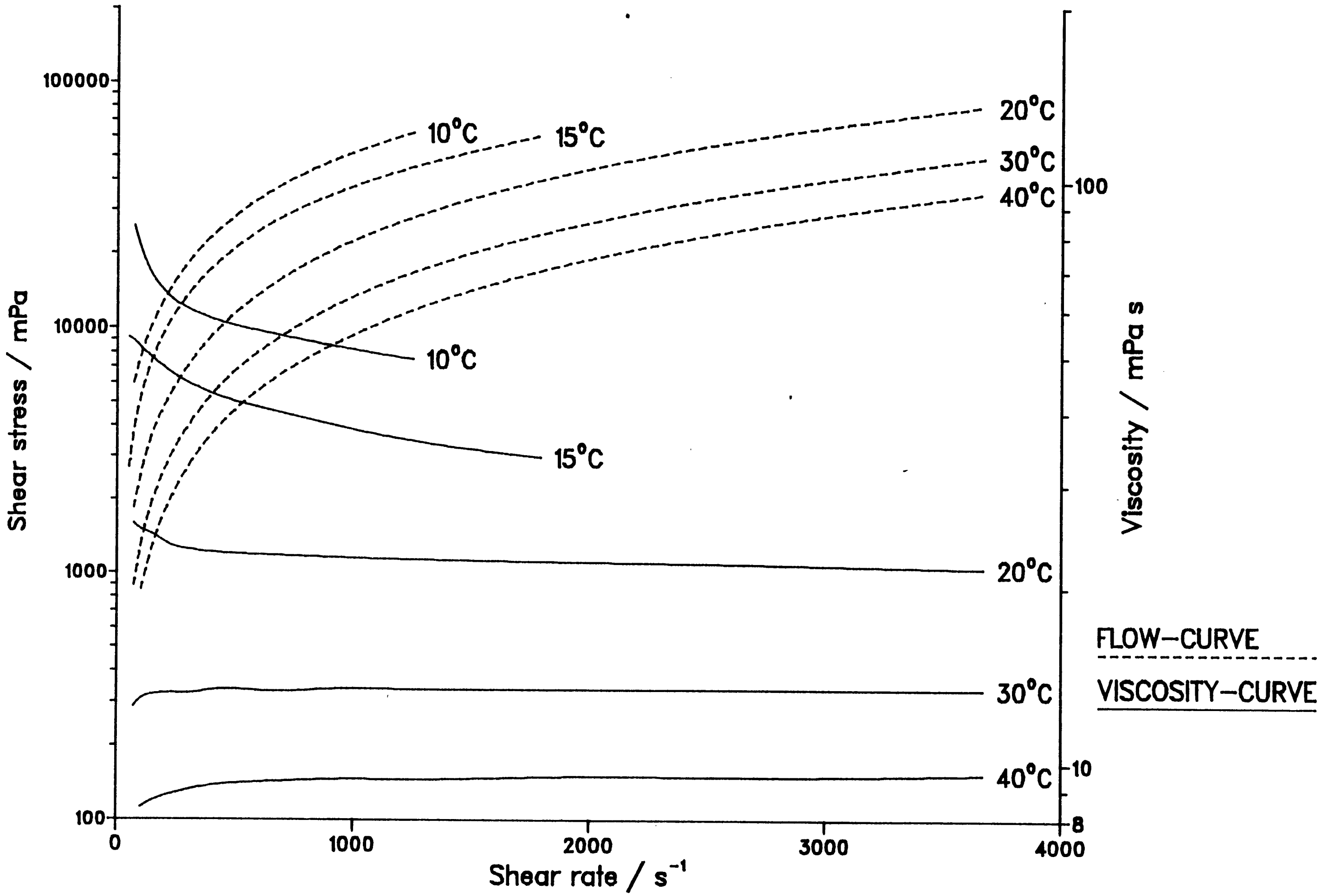
** Sum of all hydrocarbons

REFERENCES

1. "Laboratory Test for Petroleum Oils", Universal Oil Products, Des Plaines, IL (1969).

2. Burger, E.D., Perkins, T.K., Striegler, J.H., Journal of Petroleum Technology, 1075-1086, June 1981.

Fig 1 FLOW AND VISCOSITY CURVES OF OIL 6407/1-3 DST 1.



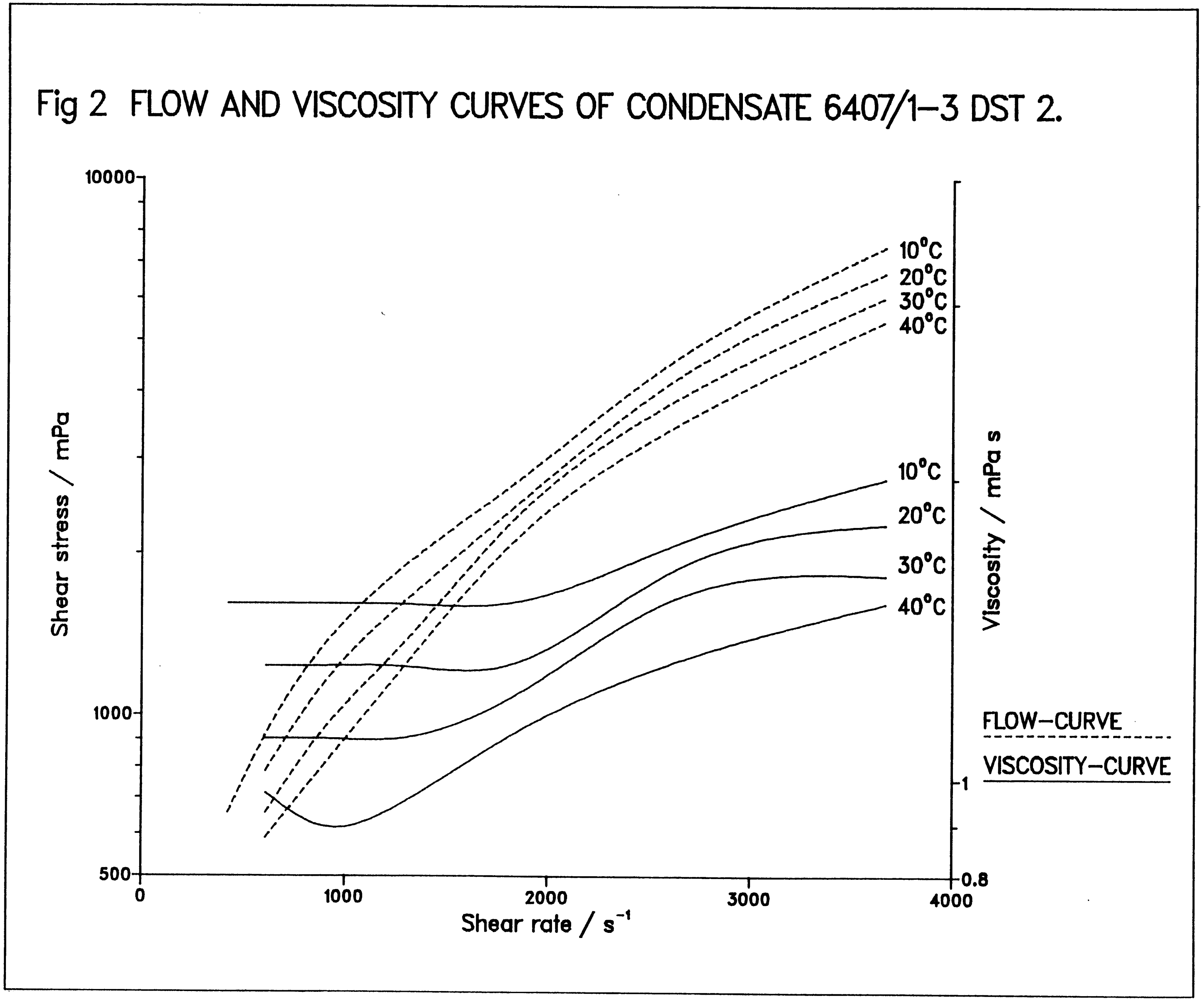


Fig 2 FLOW AND VISCOSITY CURVES OF CONDENSATE 6407/1-3 DST 2.
Shear stress / mPa
Viscosity / mPa s
Shear rate / s⁻¹
10000
1000
500
0
1000
2000
3000
4000
1
0.8
10°C
20°C
30°C
40°C
10°C
20°C
30°C
40°C
FLOW-CURVE
VISCOSITY-CURVE

FIG. 3 VISCOSITY VS. TEMPERATURE OF OIL 6407/1–3 DST 1.

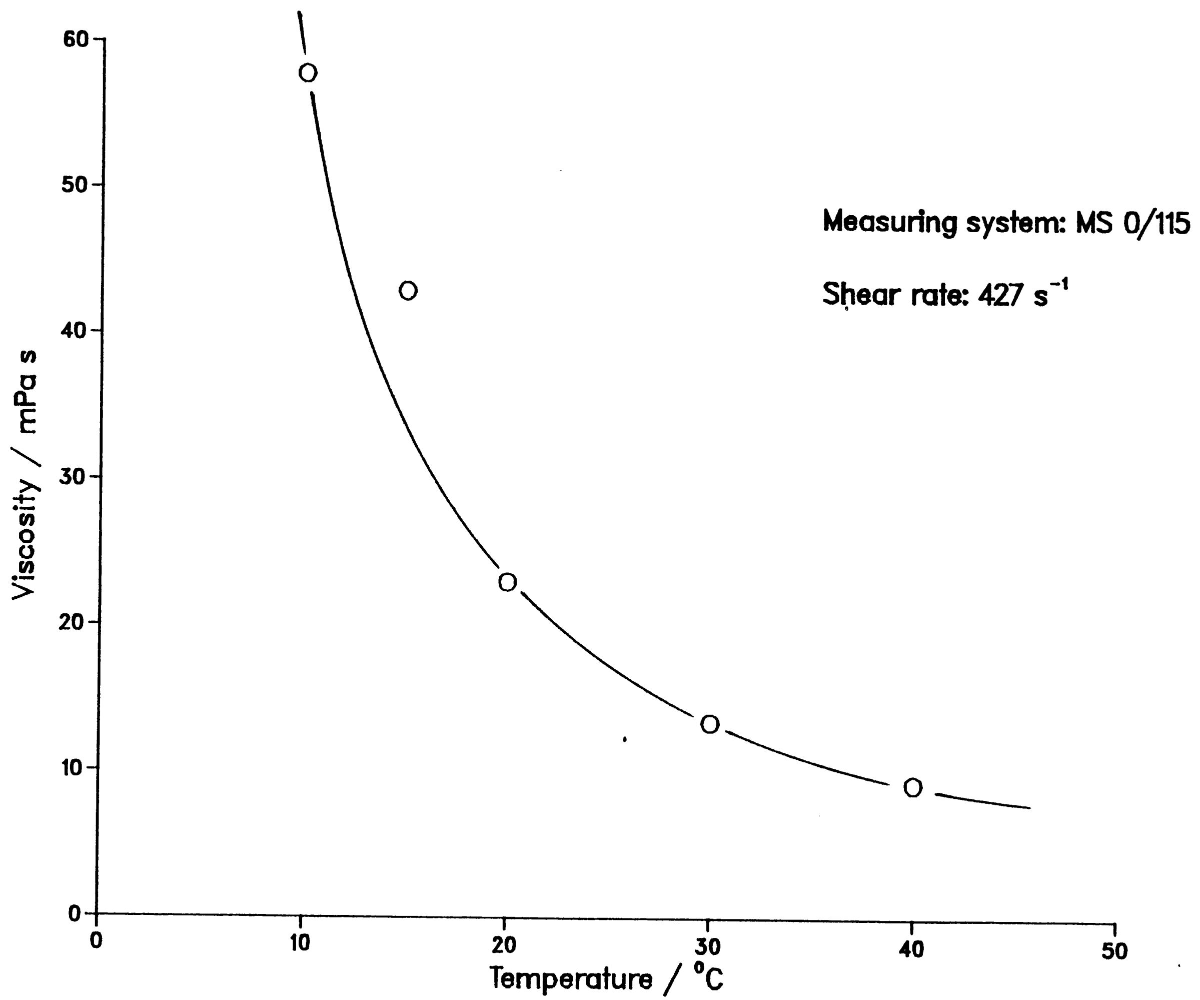


Fig 4. Carbon number distribution of wax from oil 6407/1-3 DST 1.

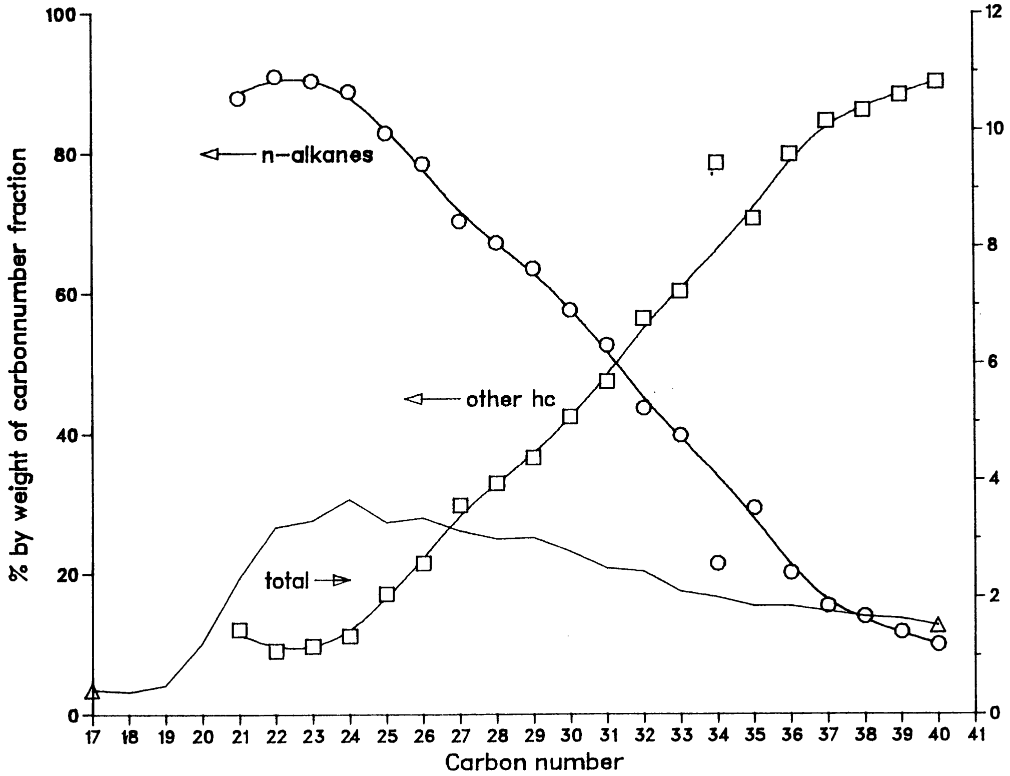
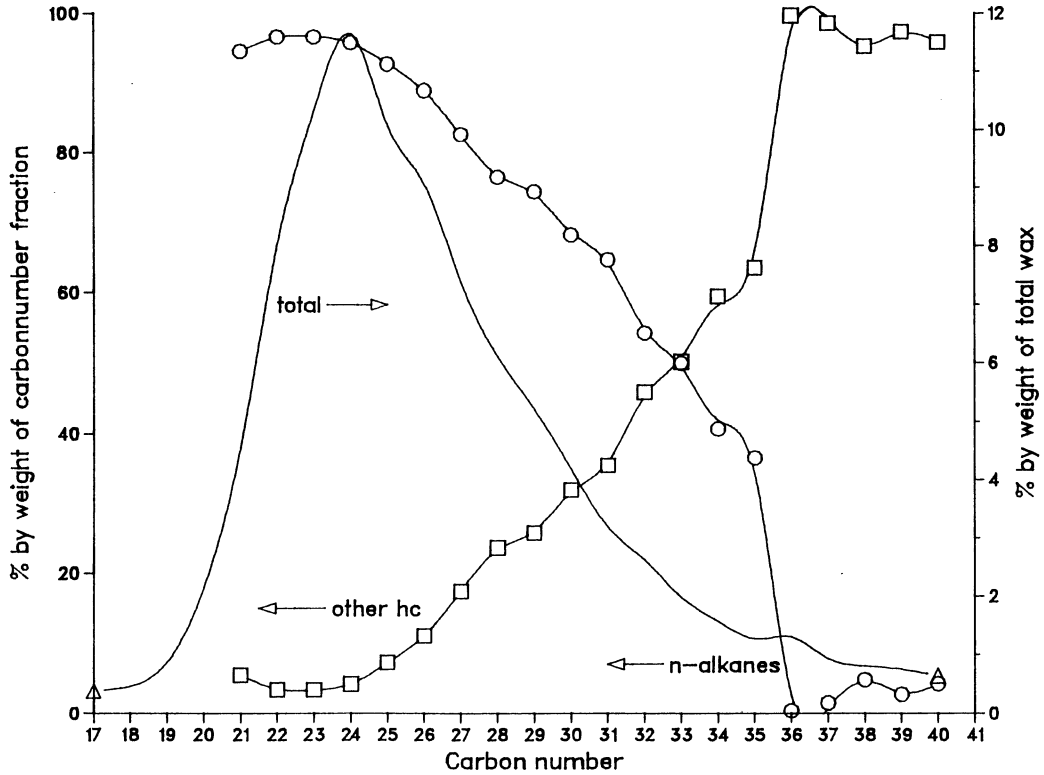


Fig 5. Carbon number distribution of wax from condensate 6407/1–3 DST 2.



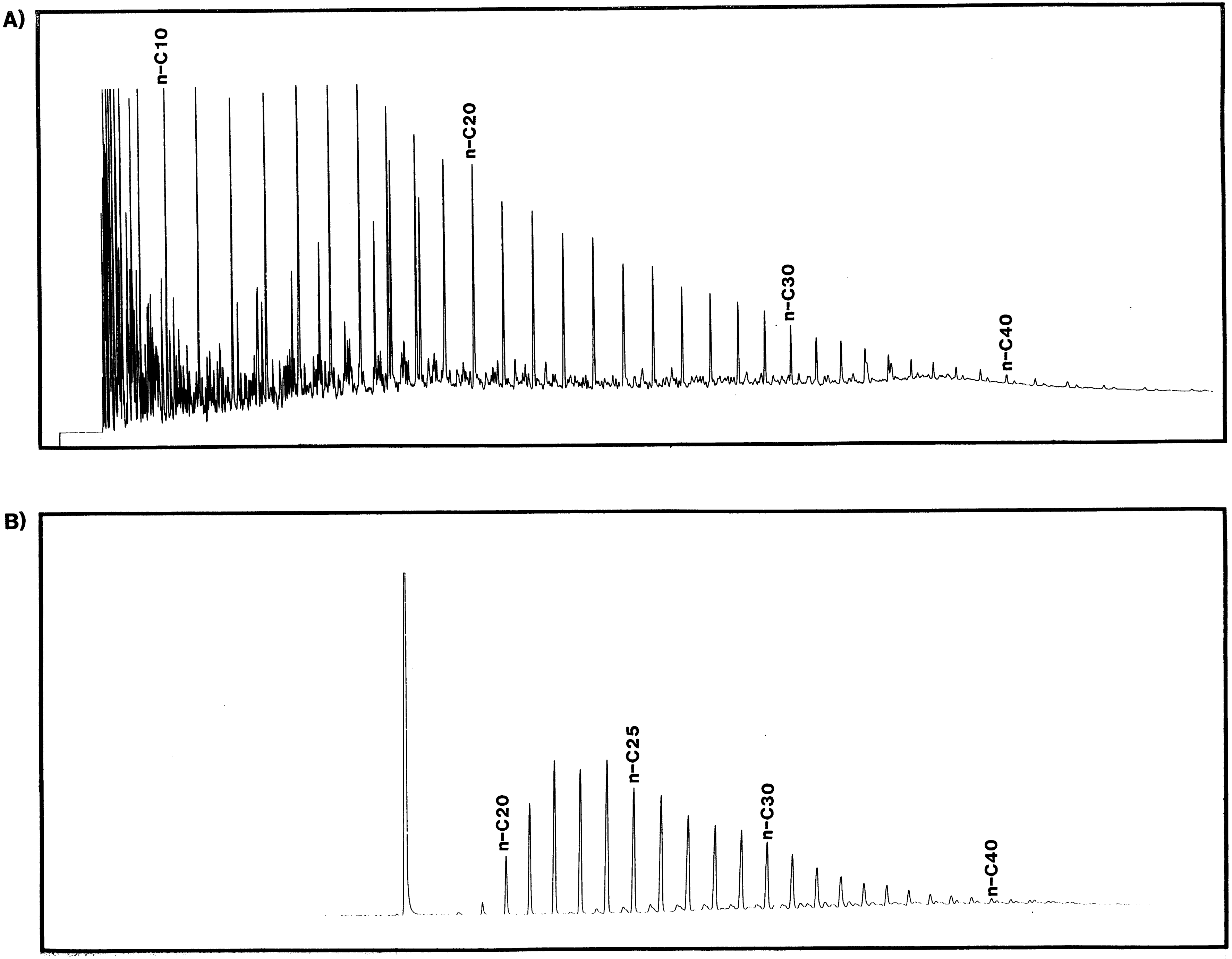


Fig.6 A) Oil 6407/1-3 DST 1 B) Wax from oil 6407/1-3 DST 1

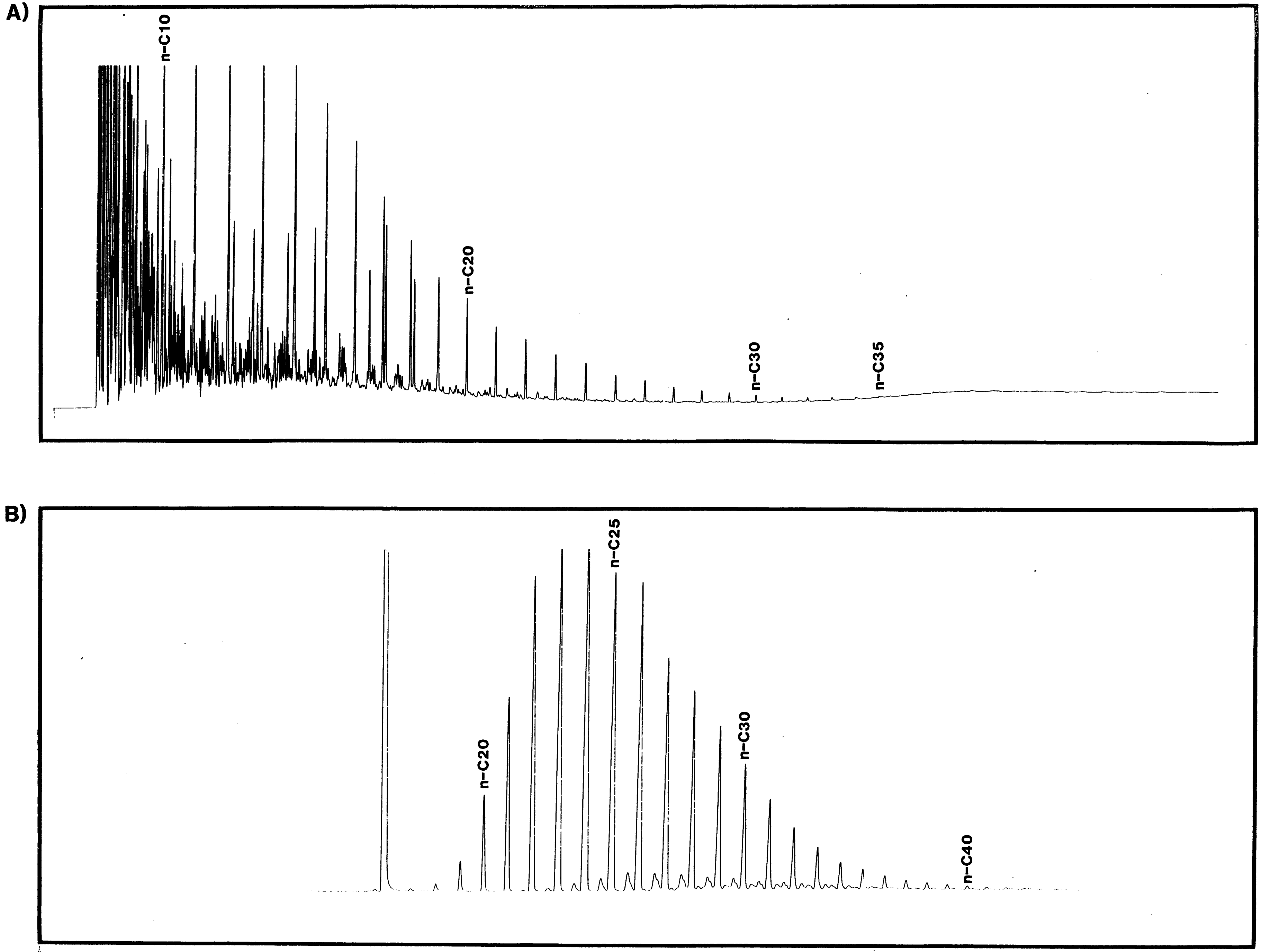


Fig.7 A) Condensate 6407/1-3 DST2 B) Wax from condensate 6407/1-3 DST 2