

Simulated distillation of distillates on capillary columns: influence of the polarity of the stationary phase

M. DORBON*, S. LAMAISON and A. CHEVALIER

*Institut Français du Pétrole, Centre d'Étude et de Développement Industriel, B.P. 3, 69390 Vernaison
(France)*

ABSTRACT

Gas chromatographic-simulated distillation gives the boiling range of petroleum products. It has been shown that with capillary columns (as with packed columns), the simulated distillation results of aromatic samples change with the polarity of the stationary phase. Three columns of different polarity, sufficiently thermostable to elute samples having boiling points as high as 600°C were tested. It has been shown that the more suitable column for simulated distillation of vacuum distillates is one with medium polarity.

INTRODUCTION

Simulated distillation is an analytical method widely used in the petroleum industry. It is a gas chromatographic (GC) method which gives the boiling range of complex petroleum mixtures and was first developed on packed columns because it did not require high resolution. More recently, with the development of macrobore columns, papers describing simulated distillation on capillary columns have been published [1–3]. Simultaneously, due to the development of temperature-resistant capillary columns, methods for simulated distillation of heavy petroleum fractions or crude oils have been described [4–8].

The methods previously published on macrobore capillary columns were developed on totally nonpolar columns which were coated with polymethylsilicone-type phases. On these phases, for a given boiling point, the aromatic compounds are eluted before the paraffins [9,10]. Since the calibration of the simulated distillation (transformation of the retention times into boiling points) is done using normal paraffins, the results of simulated distillation should depend on the phase polarity.

With the wide use in refineries of fluid catalytic and thermal cracking units, more and more samples with aromatic content up to 80% as light cycle oils (LCO) and heavy cycle oils (HCO) must be analysed. Consequently, this problem of simulated distillation of aromatic samples is important. In this article, we confirm, on capillary columns, the difference in retention times at a given boiling point between aromatics and paraffins on non-polar phases. It has been shown that on aromatic

distillates the results depend on the polarity of the chromatographic column. Columns coated with phases of different polarity were tested in order to select a phase which is sufficiently polar to elute aromatics and paraffins of the same boiling point at almost the same retention time and which is sufficiently temperature-resistant to elute compounds with boiling points as high as 600°C. A compromise was found with a 1% vinyl, 7% cyanopropyl, 7% phenyl, 85% methylpolysiloxane chemically-bonded phase.

EXPERIMENTAL

Simulated distillation analysis was carried out using a Varian 3500 (Walnut Creek, CA, USA) gas chromatograph equipped with a temperature-programmable column injector.

The analytical columns were a 10 m × 0.53 mm I.D. wall-coated open-tubular (WCOT) fused-silica capillary column coated with a non-polar polydimethylsiloxane phase (wide-bore DB1; J & W, Folsom, CA, USA), a 10 m × 0.53 mm I.D. WCOT fused-silica capillary column coated with a 5% phenyl, 95% methyl polysiloxane phase (wide-bore CP-Sil8 CB; Chrompack, Middelburg, Netherlands) and a 10 m × 0.53 mm I.D. WCOT fused-silica capillary column coated with a 7% cyanopropyl, 7% phenyl, 85% methyl, 1% vinylpolysiloxane phase (wide-bore CP-Sil19 CB; Chrompack). All the phases were chemically bonded.

The carrier gas was helium and the operating conditions were as follows: from 0 to 330°C at 10°C/min for the oven and from 80 to 340°C at 200°C/min for the injector; the carrier gas flow-rate was 18 ml/min.

The principle of the simulated distillation calculation follows standard test method ASTM D2887-89 [10].

Integration was performed on a HP 1000 A 600 computer (Hewlett Packard, Palo Alto, CA, USA). The calculations of the boiling range of the samples were carried out on the same computer using an IFP developed Fortran software.

The samples analysed (A, B, C, D, E and F) were straight run or cracked middle or heavy distillates from different sources. The aromatic content of each sample is shown in Table I.

The pure aromatic compounds were commercially available (Interchim, Paris, France).

TABLE I
AMOUNTS IN WEIGHT PERCENT OF MONO-, DI- AND POLYAROMATICS IN SIX DIFFERENT DISTILLATES

Sample	Monoaromatics	Diaromatics	Polyaromatics	Total aromatics
A	11.1	5.0	0.8	16.9
B	12.2	5.1	4.1	21.4
C	22.4	6.5	3.1	32
D	24.2	41.0	8.7	73.9
E	31.9	25.2	25	82.1
F	33.4	28.8	36.6	98.8

RESULTS AND DISCUSSION

Thermostability of the columns

The three columns were used with temperature programming up to 330°C and a carrier gas flow-rate of 18 ml/min. With such operating conditions, *n*-C₅₀, which has a boiling point of 575°C, is eluted just at the end of the temperature programming. More than 100 analyses were performed on each column with no change of resolution, no increase of bleeding and no shift of retention times. Consequently, the three columns are sufficiently thermostable for the analyses of samples having a final boiling point up to 575°C. Thus the three types of columns are suitable for the analysis of vacuum distillates. At the moment, more polar columns cannot be used at temperatures higher than 300°C.

*Retention of aromatics compared to *n*-paraffins as a function of the stationary phase*

Thirty standard aromatic compounds were analysed on the three different column types. The simulated boiling points of those compounds were calculated by the formula

$$SBP_x = BP_n + (BP_{n+1} - BP_n) \times (RT_x - RT_n) / (RT_{n+1} - RT_n)$$

where SPB_x is the simulated boiling point of compound x ; RT_x is the retention time of compound x ; BP_n and BP_{n+1} are the boiling points of the *n*-paraffins eluted respectively just before and just after compound x ; and RT_n and RT_{n+1} are the retention times of the *n*-paraffins eluted respectively just before and just after compound x .

Table II shows the actual boiling points of the aromatic compounds with their simulated boiling points and Fig. 1 shows the differences between the actual boiling points and the simulated boiling points of the aromatic compounds. The simulated boiling points on the DB1 and on the CP-Sil8 columns are of the same order of magnitude even if they are a little bit higher for the latter. They are higher by about 15°C on the CPSil19 column.

It can be seen that for compounds having boiling points between 80 and 300°C the differences between boiling points and simulated boiling points are between 20 and -20°C on the three columns. Between 300 and 450°C, this difference remains between 0 and 20°C for the CPSil19 column, but is between -20 and -40°C for the two other less polar columns. Beyond a boiling point of 450°C, this difference remains between -20 and -40°C for the more polar column but is around -60°C for the two less polar ones.

On the three columns, the analysis of pure aromatic compounds by simulated distillation shows that, at a given boiling point, the retention of aromatics is different from the retention of paraffins. However, this difference is lower on a medium polar phase such as 7% cyanopropyl, 7% phenyl, 85% methyl, 1% vinylpolysiloxane, mainly for a boiling point beyond 300°C. Since the calibration of the simulated distillation is done using *n*-paraffins, these differences would mean, for very aromatic samples, that the result of simulated distillation depends on the polarity of the column.

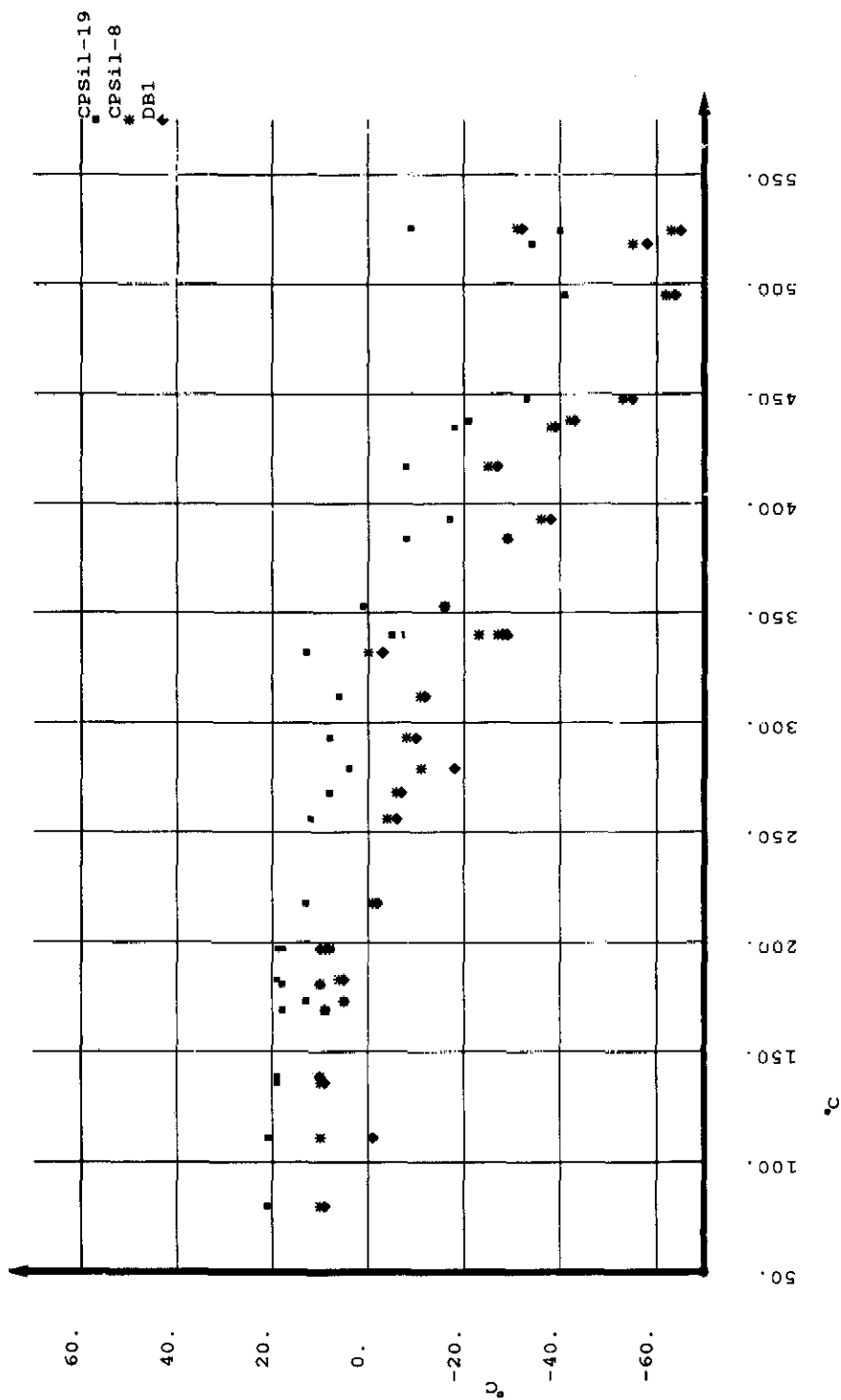


Fig. 1. Differences between boiling points and simulated boiling points on non-polar (DB1), slightly polar (CPS118) and medium polar (CPS1119) columns for 30 different aromatic compounds having boiling points from 80 to 525°C. The aromatic compounds are those listed in Table II.

TABLE II

SURVEY OF THIRTY AROMATIC COMPOUNDS: BOILING POINTS (BP), SIMULATED BOILING POINTS (SBP) IN °C AND DIFFERENCE BETWEEN BP AND SBP ON THE THREE DIFFERENT CAPILLARY COLUMNS (DB1, CPSII8 AND CPSII9)

Compound	BP	DB1		CPSII8		CPSII9	
		SBP	Difference	SBP	Difference	SBP	Difference
Benzene	80	89	+ 9	90	+ 10	101	+ 21
Toluene	111	110	- 1	121	+ 10	132	+ 21
Ethylbenzene	136	145	+ 9	146	+ 10	155	+ 19
<i>m</i> -Xylene	139	149	+ 10	149	+ 10	158	+ 19
Trimethylbenzene	169	178	+ 9	178	+ 9	187	+ 18
Isobutylbenzene	173	178	+ 5	178	+ 5	186	+ 13
Metadiethylbenzene	181	191	+ 10	191	+ 10	199	+ 18
Idene	183	188	+ 5	189	+ 6	202	+ 19
Durene	197	207	+ 10	206	+ 9	216	+ 19
Tetramethylbenzene	197	207	+ 10	205	+ 8	215	+ 18
Naphthalene	218	216	- 2	217	- 1	231	+ 13
Diphenyl	256	250	- 6	252	- 4	268	+ 12
2,3-Dimethylnaphthalene	268	261	- 7	262	- 6	276	+ 8
Acenaphthalene	279	261	- 18	268	- 11	283	- 4
Fluorene	293	283	- 10	285	- 8	301	- 8
9,10-Dihydroanthracene	312	300	- 12	301	- 11	318	- 6
Ortoterphenyl	332	329	- 3	332	0	348	+ 13
Phenanthrene	340	311	- 29	317	- 23	335	- 5
Anthracene	340	312	- 28	313	- 27	333	- 7
4,5-Methylphenanthrene	353	337	- 16	337	- 16	354	- 1
Fluoranthene	384	355	- 29	355	- 29	376	- 8
Pyrene	393	355	- 38	357	- 36	376	- 17
9-Phenylanthracene	417	390	- 27	392	- 25	409	- 8
1,2-Benzanthracene	435	396	- 39	397	- 38	417	- 18
Triphenylene	438	395	- 43	396	- 42	417	- 21
Chrysene	448	393	- 55	395	- 53	415	- 33
Benzo(a)pyrene	495	431	- 64	433	- 62	454	- 41
1,2,3,4-dibenzanthracene	518	460	- 58	463	- 55	484	- 34
1,2,5,6-dibenzanthracene	524	459	- 65	461	- 63	484	- 40
Coronene	525	493	- 32	494	- 31	516	- 9

Influence of the stationary phase of the simulated distillation results

The simulated distillation of six different petroleum products was performed on the three columns. The samples were middle distillates having initial boiling points between ca. 200°C and 350°C, and final boiling points between ca. 400°C and 550°C. They have different percentages of aromatics as shown in Table I.

Fig. 2 shows the simulated distillation results of the three less aromatic samples (A, B and C). With two samples having an aromatic content of about 20% (A and B), the differences between the three columns are very small. Thus for these samples, the three columns are almost equivalent.

With the sample having 32% aromatics (C), the differences are more important. It can be noted that for the same content eluted, the higher boiling point is always with the more polar column, as expected. A small difference between the results

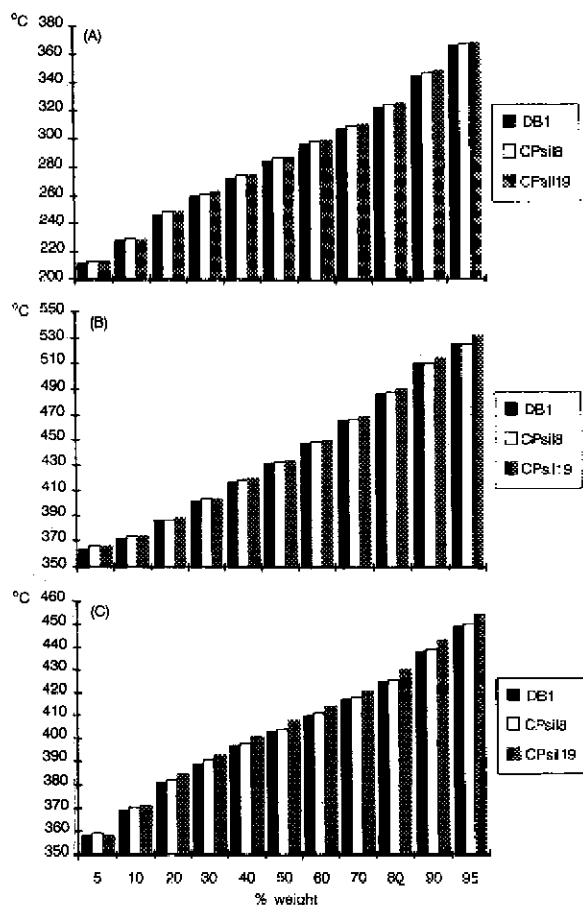


Fig. 2. Comparison of simulated distillation results carried out on non-polar (DB1), slightly polar (CPSil8) and medium polar (CPSil19) columns for three slightly aromatic distillates, A, B and C, the aromaticalities of which are shown in Table I.

obtained on the two less polar columns can also be seen; it means that even for pure compounds the difference in retention times between the two columns is very low (Fig. 1), and thus the difference of polarity between the two phases can cause differences between simulated distillation results for mixtures.

For this sample, the boiling points at $n\%$ on CPSil19 are almost mid-way between the boiling points at $n\%$ and $(n + 10)\%$ on DB1; consequently, even for samples having about 30% aromatic content and more, the differences between the columns cannot be neglected.

On samples containing about 75% aromatic content (D and E), the difference between the three columns are very important (Fig. 3). The boiling points at $n\%$ on the CPSil19 column are almost the same as the boiling points at $(n + 10)\%$ on the less polar column DB1.

A very aromatic samples (F) was also studied (Fig. 3). On this sample, the difference between the three columns is higher. The boiling points at $n\%$ on the

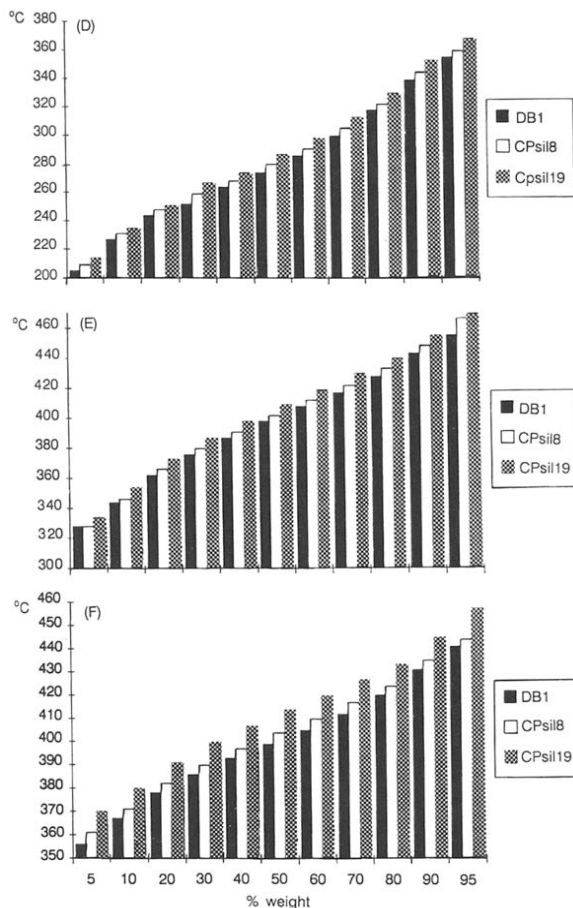


Fig. 3. Comparison of simulated distillation results carried out on non-polar (DB1), slightly polar (CPSil8) and medium polar (CPSil19) columns for three highly aromatic distillates. D, E and F, the aromaticities of which are shown in Table I.

CPSil19 column are almost equal and sometimes higher than the boiling point at $(n + 20)\%$ on the DB1 column; the boiling points at $n\%$ on CPSil8 are close to the boiling point at $(n + 10)\%$ on DB1.

Comparison between simulated distillation and true boiling point distillation (TBP)

The TBP analysis is both a time- and sample-consuming; this is the reason why this analysis was not performed for all the samples. On two of the samples, one with a low aromatic content and one with a high aromatic content, TBP was available. The results and the comparison with simulated distillation are shown in Tables III and IV. As expected, for the low aromatic sample, the TBP and the simulated distillation are very similar, whatever the column. But for the high aromatic sample, the results between the TBP and the simulated distillation on the CPSil19 column are close, but they are different from simulated distillation on the two other columns.

TABLE III

COMPARISON BETWEEN TBP AND SIMULATED DISTILLATION OF SAMPLE B WHICH CONTAINS 21.4% AROMATICS

Temperature (°C)	TBP (% weight)	DB1 (% weight)	CPSil8 (% weight)	CPSil19 (% weight)
399	25.5	28	27	25.5
448	57.5	60	59.5	58
499	84.5	85	85	84
524	93	94.5	94.5	93

TABLE IV

COMPARISON BETWEEN TBP AND SIMULATED DISTILLATION OF SAMPLE D WHICH CONTAINS 73.9% AROMATICS

Temperature (°C)	TBP (% weight)	DB1 (% weight)	CPSil8 (% weight)	CPSil19 (% weight)
247	16.5	22	21	17
298	58.5	68	65.5	60
347	86.5	93	91	88
374	95	98.5	98	96.5

CONCLUSION

The three columns tested, one non-polar, one slightly polar and one of medium polarity, were sufficiently thermostable to analyse petroleum products having boiling points up to 600°C. It has been shown that the difference in simulated distillation results between two columns depends on the aromatic content in the sample and on the polarity of the phase. For non-aromatic samples, the three columns are equivalent. But the difference increases with the aromatic content and is very high for samples having more than 70% aromatics. It appears that the medium polar column is the more suitable for simulated distillation of distillates. It is the one on which the difference in retention between aromatics and paraffins for a given boiling point is the lowest. Moreover, it has been shown for two samples of different aromatic content that it is with the medium polar column that the difference with TBP is the lowest.

REFERENCES

- 1 R. L. Firor, *Am. Lab.*, 21 (1989) 33-33.
- 2 F. Noel, *J. High Resolut. Chromatogr.*, 11 (1989) 837-839.
- 3 N. R. Warren and B. M. Lawrence, *Lab. Pract.*, 36 (1987) 80-81.
- 4 A. Rastogi, *J. High Resolut. Chromatogr.*, 10 (1987) 479-480.
- 5 J. Curvers and P. van den Engel, *J. High Resolut. Chromatogr.*, 12 (1989) 16-22.
- 6 R. L. Firor and R. J. Philips, *J. High Resolut. Chromatogr.*, 12 (1989) 181-183.
- 7 S. Trestianu, G. Zilioli, A. Sironi, C. Saravalle, F. Munari, M. Galli, G. Gaspar, J. M. Colin and J. L. Jovelin, *J. High Resolut. Chromatogr.*, 8 (1985) 771-781.
- 8 L. A. Luke and J. E. Ray, *J. High Resolut. Chromatogr.*, 8 (1985) 193-195.
- 9 N. Petroff, J. M. Colin, N. Feillens and G. Follain, *Rev. Inst. Fr. Petr.*, 36 (1981) 467-484.
- 10 *ASTM Standards*, Vol. 05-02, American Society for Testing and Materials, Philadelphia, PA, 1990, section 5, ASTM D2887-89, pp. 492-499.