

# Analytical study of heavy crude oil fractions by coupling of the transalkylation reaction with supercritical fluid chromatography

P.-L. Desbène\* and A. Abderrezag

*L.A.S.O.C., Institut Universitaire de Technologie, Université de Rouen, 43 Rue Saint Germain, 27000 Evreux (France)*

B. Desmazières

*Laboratoire de Chimie Organique Structurale, Université P. et M. Curie, URA 455, 4 Place Jussieu, 75005 Paris (France)*

---

## ABSTRACT

Previous work involved the utilization of the transalkylation reaction (retro-Friedel-Crafts reaction to transfer alkyl-substituting chains from the asphaltene aromatic matrix to a light aromatic acceptor) in the analysis of heavy crude oil fractions by coupling it with capillary gas chromatography (GC). In such conditions, a mapping of alkyl chains substituting the complex aromatic matrix of heavy crude oil fractions can be set up. However, it appears from NMR data and quantitative measurements of alkyl chains detected in GC that only about 50% of the transferable chains are effectively involved. This result poses the questions of whether heavy fractions of crude oil contain alkyl chains longer than those evidenced by GC and whether the partial transalkylation is due to an equilibrium. In order to answer these questions, supercritical fluid chromatography (SFC) was used instead of GC. An efficient transfer from model molecules (*n*-alkylnaphthalenes) substituted by alkyl chains up to C<sub>31</sub> was observed, whereas GC did not show evidence for chains longer than C<sub>24</sub>. However, in with various petroleum asphaltene (Boscan, Arabian Light, Maya) no transfer of chains longer than C<sub>21</sub>–C<sub>28</sub> was observed. Moreover, better quantitative results were obtained by SFC, as the analysis limit is well above C<sub>21</sub>. For instance, the global transfer yield of alkyl chains from Boscan asphaltene was 5.2% *versus* 4.6% in GC. The transalkylation yields were significantly increased when successive transalkylations were performed.

---

## INTRODUCTION

Structural studies of heavy crude oils and heavy oil residues are difficult because of the extreme complexity of these mixtures [1]. Methods for separating such materials according to chemical classes have been reported but, even within each separate group, one still finds a complex mixture of compounds [1]. For many of these mixtures, spectroscopic measurements, especially <sup>1</sup>H and <sup>13</sup>C NMR, indicate the presence of alkyl groups and of aromatic and heterocyclic rings [2]. However, obtaining more detailed structural information from NMR is difficult owing to the wide variety of compounds and to the overlapping of peaks corresponding to different chemical structures [3–6].

In order to obtain some information about the nature and abundance of alkyl chains substituting the aromatic matrix of these complex mixtures, we previously used the reversibility of the Friedel-Crafts reaction combined with capillary gas chromatography–mass spectrometry (GC–MS) [7]. After optimizing the operating conditions in order to allow analytical studies, using model molecules and a Boscan atmospheric residue, we found that a satisfactory compromise between an efficient transfer of alkyl chains and the minimum degradation of these chains is possible [8,9]. This result is obtained when benzene is used as an acceptor of alkyl chains, with slightly hydrated aluminium bromide as Lewis acid, and a 4-h reaction time at 60°C. Under these conditions, it becomes possible to obtain relatively

precise mapping of the alkyl chains substituting the aromatic matrix. However, with atmospheric residues, a rough comparison between transfer yields and data resulting from NMR measurements indicates that only about 50% of potentially transferable chains are effectively transferred to the light aromatic acceptor. Hence, in spite of its efficiency, the transalkylation reaction is not quantitative. This relative lack of efficiency was recently confirmed by a comparative study by pyrolysis—GC—MS of various asphaltenes before and after transalkylation [10].

The lack of quantitiveness can originate partly from the limitation of GC analysis because of the low volatility of some compounds such as phenylalkanes possessing C<sub>23</sub>–C<sub>24</sub> or longer alkyl chains, for which GC analysis is difficult or impossible, partly from insufficient reversibility of the Friedel–Crafts reaction, although this phenomenon should be limited under our operating conditions as benzene is used in large excess (solvent), and partly from the poor accessibility of reaction sites in these complex organic matrixes.

In order to answer these questions and to improve the method, we considered the possibility of replacing capillary GC with capillary supercritical fluid chromatography (SFC). We report in this paper an analytical study by SFC of the reaction media obtained after transalkylation of four asphaltenes of various origins but of the same type (type II) according to the classification of Tissot and Welte [11].

## EXPERIMENTAL

### *SFC analyses*

SFC analyses were performed using a Carlo Erba (Milan, Italy) SFC 3000 supercritical fluid chromatograph fitted with a 10 m × 100 μm I.D. fused-silica column coated with SE-52 stationary phase and a flame ionization detector.

Samples were obtained from the mixing of the products obtained from three parallel transalkylations of 150 mg of asphaltenes each time, under the operating conditions reported below. The solution was concentrated to about 5% of the initial volume by evaporating benzene under nitrogen. The residue was weighed, 0.25 wt. % of *n*-hexadecane was added as an internal standard and the mixture was then injected.

The analytical conditions were as follows: eluent, supercritical carbon dioxide (medical grade; Carboxyque Française, Paris, France); oven temperature, 110°C; detector temperature, 310°C; conical restrictor (giving a mobile phase linear flow-rate of 2.0–2.5 cm s<sup>-1</sup>); and pressure programming, isobaric at 100 atm for 10 min, then a linear gradient at 5 atm/min to 280 atm and isobaric at 280 atm for 30 min.

### *Calibration*

The response factors of the series phenylalkanes possessing alkyl chain lengths from C<sub>2</sub> to C<sub>31</sub>, naphthylalkanes substituted by alkyl chains from C<sub>2</sub> to C<sub>31</sub> and 1,ω-dinaphthylalkanes with alkyl chain lengths from C<sub>3</sub> to C<sub>10</sub> were measured in a concentration range 0.05–0.15 wt.% using *n*-hexadecane as internal standard at a fixed concentration (0.25 vol.%).

### *Transalkylation reaction*

In a typical experiment, 150 ± 1 mg of asphaltenes were dissolved in 10 ml of dry benzene in a 20 ml SVL screw-capped tube (Prolabo). Benzene was used both as a solvent and as a light acceptor of alkyl chains. Then 10 μl of distilled water were added using a syringe. A 300-mg amount of aluminium bromide was quickly dissolved in 5 ml of dry benzene and the solution was immediately poured into the benzenic solution of asphaltenes. The tube was sealed and placed in an ultrasonic bath thermostated at 60°C. This last operation represents the zero time of reaction.

After 4 h in the ultrasonic bath, the reaction medium, after addition of 3 ml of benzene to rinse the reactor, was centrifuged at 23 000 g for 10 min. The solid phase was treated with 5 ml of benzene and the suspension was again centrifuged. This second organic phase was combined with the first and hydrolysis and neutralization were performed by adding a 5% aqueous solution of sodium carbonate (15 ml). The organic phase was decanted, washed twice with distilled water and stored in a sealed flask.

### *Samples and reagents*

Asphaltenes were prepared by precipitation with *n*-heptane, according to the NFT 6011S standard [12] from atmospheric residues (340°C+) of Arabian Light (Algeria), Boscan (Venezuela), Kirkouk

(Iraq) and Maya (Mexico) furnished by the IFP-Elf-Total sample bank (Solaize, France).

Anhydrous 98% aluminium bromide from Janssen (Puteaux, France) was used without any further treatment. Benzene (analytical-reagent grade) from Merck (Darmstadt, Germany) was purified by 3–4 successive crystallisations in a deep freezer, until a constant melting point of 4°C was reached and a gas chromatogram showed only the benzene peak. This purification procedure allows for the elimination of impurities such as toluene, and *o*- and *m*-xylene, which are undesirable in analytical transalkylation.

Water was purified by double distillation or by filtration and reversed osmosis using a Milli-Q + Milli-Ro system from Millipore (Molsheim, France).

Calibration graphs were established using either comonomer compounds, *viz.*, *n*-alkanes (C<sub>18</sub> and C<sub>20</sub>), *n*-alkylbenzenes (alkyl chains from C<sub>2</sub> to C<sub>12</sub>) and ethylnaphthalenes of analytical-reagent grade from Janssen, or compounds synthesized as described previously [9], *viz.*, *n*-alkylbenzenes possessing C<sub>16</sub>, C<sub>20</sub>, C<sub>26</sub> and C<sub>31</sub> alkyl chains, *n*-alkylnaphthalenes with C<sub>10</sub>, C<sub>16</sub>, C<sub>22</sub>, C<sub>26</sub> and C<sub>31</sub> alkyl chains and 1, $\omega$ -dinaphthylalkanes with  $\omega = 3, 4, 5, 6, 10$ .

## RESULTS AND DISCUSSION

Using our previous analytical procedure [7,10] it was difficult to obtain evidence for the transfer of alkyl chains longer than C<sub>21</sub>–C<sub>22</sub>. In particular, it was impossible to model the transfer of chains longer than C<sub>22</sub> from alkylnaphthalenes, used as models of the oil aromatic matrix, as these compounds were not eluted by GC beyond C<sub>22</sub>. We used capillary SFC to solve this problem. Effectively this technique should allow the analysis in reaction media obtained after transalkylation of non-volatile compounds possessing alkyl chains of length clearly longer than C<sub>22</sub>, and also a sufficient efficiency to analyse these complex reaction media in a reasonable time.

As a first step we optimized the chromatographic conditions with a mixture of compounds modelling the reaction medium resulting from the transalkylation of an oil aromatic matrix. This model mixture contained alkylbenzenes (from C<sub>2</sub> to C<sub>31</sub>) corresponding to the potential products of transalkyla-

tion and alkylnaphthalenes (C<sub>22</sub>, C<sub>26</sub> and C<sub>31</sub>) used as models of the oil aromatic matrix. As the aim of this study was to obtain both qualitative and quantitative information about the transalkylation products, we added an internal standard to the model mixture at the beginning of optimization. As alkanes are stable in the reaction medium [9], we searched for one that did not interfere with phenylalkanes under our conditions, and *n*-hexadecane was adopted.

As shown in Fig. 1, it is possible to analyse the model mixture in less than 1 h with our SE-52 column (10 m  $\times$  100  $\mu$ m I.D.) at 110°C and with a pressure gradient.

The analysis, under the same conditions, of the reaction medium obtained after transalkylation of a heavy oil fraction is reported in Fig. 2. It must be noted that capillary SFC is less sensitive than capillary GC and we had to concentrate the initial reaction medium to 5% of its initial volume in order to perform this analysis. Using the co-elution technique and extrapolation, it appears that this oil fraction does not contain alkyl chains longer than C<sub>27</sub>–C<sub>28</sub>.

However, as already mentioned, our aim was not only to obtain qualitative information about the composition of heavy crude oil fractions, so we measured the response factors of the main products

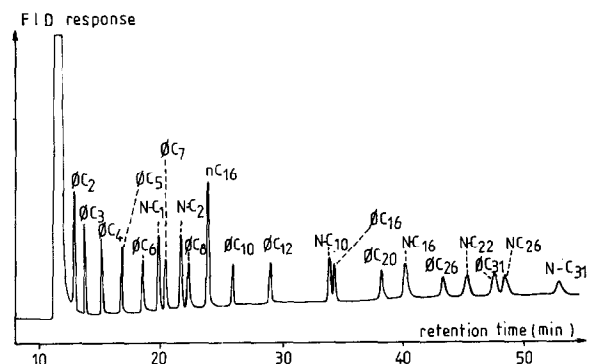


Fig. 1. SFC analysis of a mixture of alkylaromatics modelling the reaction media resulting from the transalkylation of oil heavy fractions. Conditions: SE-52 column (10 m  $\times$  100  $\mu$ m I.D.); eluent, CO<sub>2</sub>, linear flow-rate 2 cm s<sup>-1</sup>; injection volume, 60 nl; split, *ca.* 1:20; temperature 110°C; pressure programme, isobaric at 100 atm for 10 min, linear gradient of 5 atm min<sup>-1</sup> to 280 atm, isobaric at 280 atm for 60 min.  $\Phi$ C<sub>*n*</sub> = Alkylbenzenes; N-C<sub>*n*</sub> = alkylnaphthalenes; nC<sub>16</sub> = internal standard.

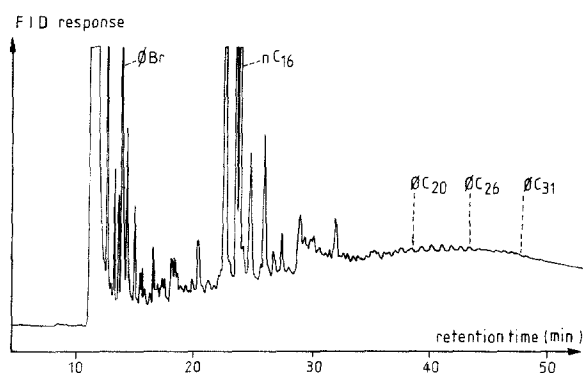


Fig. 2. SFC analysis of the reaction medium resulting from the transalkylation of Kirkouk asphaltenes. Conditions as in Fig. 1.

resulting from the transalkylation prior to the study of asphaltenes from various origins. The response coefficients obtained for a series of phenylalkanes and for the same naphthylalkanes, normalized to those of ethylbenzene and methyl-naphthalene, respectively, are reported in Table I. The results shows that under the conditions used, alkylben-

zenes substituted by alkyl chains from C<sub>2</sub> to C<sub>16</sub> give similar responses, regardless of concentration (in the range 0.05–0.25%, v/v), the responses of alkylbenzenes possessing longer chains decrease when the chain length increases and the detector response is linear in the concentration range 0.05–0.1% (v/v), regardless of the alkyl chain length. At higher concentrations, a deviation from linearity is observed for both short and long alkyl chains. This relatively limited range of linearity is not a problem because the individual concentrations of the transalkylation products remain below 0.1% (v/v) under the conditions used and according to our previous studies [7,10].

From these response factors, it was possible to calculate the overall yield of transalkylation as 7.5% ( $\sigma = 0.8\%$ ) for Kirkouk asphaltenes. This yield is only slightly greater than that obtained by capillary GC for the same asphaltenes (7%,  $\sigma = 0.8\%$ ) [10]. Qualitatively, the comparison of the SFC analysis reported here and of the GC analysis described previously [10] shows that the phenylalkanes found in the reaction media are only slightly

TABLE I

RESPONSE FACTORS OF ALKYL BENZENES AND ALKYL NAPHTHALENES

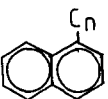
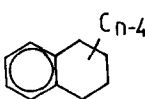

Internal standard: *n*-hexadecane (0.25%, v/v).

Length of alkyl chain	Alkylbenzene concentration (% v/v, <i>n</i> < 16; % w/v, <i>n</i> ≥ 16)						Alkyl-naphthalenes (concentration 0.10% w/v)	
	0.05		0.10		0.25		<i>R</i> / <i>R</i> <sub>Na-C<sub>1</sub></sub> <sup>a</sup>	<i>R</i> / <i>R</i> <sub><i>n</i>-C<sub>16</sub></sub>
	<i>R</i> / <i>R</i> <sub>ØC<sub>2</sub></sub>	<i>R</i> / <i>R</i> <sub><i>n</i>-C<sub>16</sub></sub>	<i>R</i> / <i>R</i> <sub>ØC<sub>2</sub></sub>	<i>R</i> / <i>R</i> <sub><i>n</i>-C<sub>16</sub></sub>	<i>R</i> / <i>R</i> <sub>ØC<sub>2</sub></sub>	<i>R</i> / <i>R</i> <sub><i>n</i>-C<sub>16</sub></sub>		
C <sub>1</sub>							1.00	0.346
C <sub>2</sub>	1.00	0.190	1.00	0.370	1.00	0.755	1.04	0.361
C <sub>3</sub>	1.01	0.191	0.99	0.369	1.09	0.820		
C <sub>4</sub>	1.01	0.191	1.01	0.375	1.22	0.922		
C <sub>5</sub>	1.00	0.190	0.98	0.364	1.29	0.973		
C <sub>6</sub>	1.01	0.191	0.94	0.349	1.34	1.02		
C <sub>7</sub>	0.95	0.181	0.92	0.340	1.29	0.971		
C <sub>8</sub>	0.89	0.179	0.93	0.343	1.34	1.01		
C <sub>10</sub>	0.94	0.178	0.97	0.359	1.33	1.00	0.83	0.287
C <sub>12</sub>	0.91	0.173	0.98	0.363	1.38	1.04		
C <sub>16</sub>	0.94	0.179	1.01	0.373	0.63	0.477	0.78	0.270
C <sub>20</sub>	0.79	0.150	0.86	0.319	0.52	0.393		
C <sub>22</sub>							0.68	0.234
C <sub>26</sub>	0.64	0.121	0.69	0.255	0.360	0.272	0.63	0.218
C <sub>31</sub>							0.56	0.194
<i>n</i> -C <sub>16</sub>	5.26	1.00	2.70	1.00	1.32	1.00	2.89	1.00

<sup>a</sup> Na-C<sub>1</sub> is 1-methylnaphthalene.

TABLE II

TRANSALKYLATION YIELDS OF ALKYLNAPHTHALENES USED AS MODEL COMPOUNDS OF ASPHALTENES AROMATIC MATRIX

Alkyl-naphthalene transalkylated	% of alkyl chain transferred as:	
		
$n = 22$	10	22
$n = 26$	8	32.5
$n = 31$	12.5	32

longer than those previously identified ( $C_{27}$ – $C_{28}$  by SFC versus  $C_{22}$ – $C_{23}$  by GC).

Some questions arise from these observations: are aromatic matrices of oil substituted by alkyl chains no longer than  $C_{27}$ – $C_{28}$ , or is transalkylation inefficient in the case of long alkyl chains? In order to solve this problem, we analysed by SFC reaction media obtained after transalkylation of alkyl-naphthalenes substituted by  $C_{22}$ ,  $C_{26}$  and  $C_{31}$  alkyl chains. These compounds were used as model molecules of the asphaltene matrices and the analytical conditions were the same as those for Kirkouk asphaltene.

The results of these transalkylations are given in Table II, and the chromatogram obtained by SFC for the transalkylation reaction media of  $n$ - $C_{31}$ -alkyl-naphthalene is reported in Fig. 3.

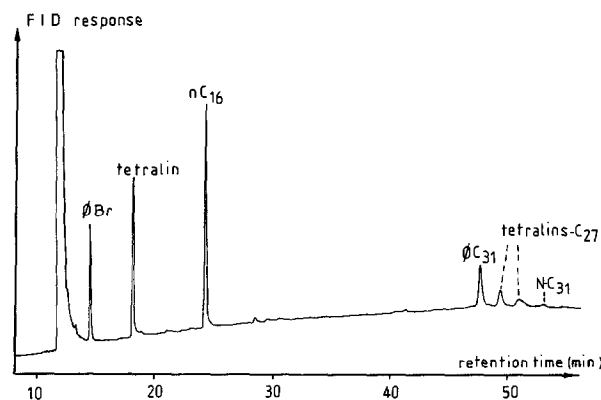


Fig. 3. SFC analysis of the reaction medium resulting from the transalkylation of  $n$ - $C_{31}$ -alkyl-naphthalene. Conditions as in Fig. 1.

These results indicate some of the main features of the aptitude of long alkyl chains to undergo transalkylation and the stability of the reaction products. As previously observed with shorter alkyl chains ( $C_{10}$  and  $C_{12}$  [9]),  $C_{22}$ -,  $C_{26}$ - and  $C_{31}$ -alkyl-naphthalenes are transalkylated. The percentage of chains transferred (between 30 and 45%) is close to the values obtained with  $C_{10}$ - and  $C_{12}$ -alkyl-naphthalenes (about 40%). As with the shorter chains, the alkyl chain is partly rearranged by cyclization during the transfer, producing tetralins substituted by  $C_{n-4}$  alkyl chains. Hence, in the transalkylation of  $C_{22}$ -alkyl-naphthalene, the reaction media can still be analysed by GC-MS, allowing the identification of the transalkylation product. The transalkylation yield is in fact greater for the transalkylation of model molecules [9], indicating that the stability of alkylbenzenes in the reaction media decreases when the chain length increases. It was concluded that the aromatic matrix of Kirkouk asphaltene does not possess  $n$ -alkyl chains longer than  $C_{27}$ – $C_{28}$  in detectable amounts.

We verified this conclusion by the SFC analysis of reaction media from the transalkylation of various asphaltene. The chromatograms obtained for Arabian Light, Boscan and Maya asphaltene are reported in Fig. 4.

Comparison of Fig. 2 and 4 shows that slightly longer chains are transferred from the Kirkouk asphaltene aromatic matrix to the light acceptor (benzene) than from the other asphaltene. In Kirkouk asphaltene, the longest alkyl chain transferred is  $C_{27}$ – $C_{28}$ , versus  $C_{23}$ – $C_{24}$  for Boscan, Maya and Arabian Light asphaltene. As SFC provides evidence for the transfer of alkyl chains appreciably longer than those previously detected by GC, we can now confirm that the length of alkyl chains substituting the aromatic matrix of asphaltene is not greater than  $C_{23}$ – $C_{28}$ , depending on the origin of the oil.

Consequently, the lack of quantitiveness of the transalkylation reaction results from some cause other than the inadequacy of the technique used to analyse the reaction media obtained after the transfer of alkyl chains from the oil aromatic matrix to benzene. The comparison of the overall yields of transalkylation obtained by SFC and in GC for various asphaltene, reported in Table III, clearly proves this point.

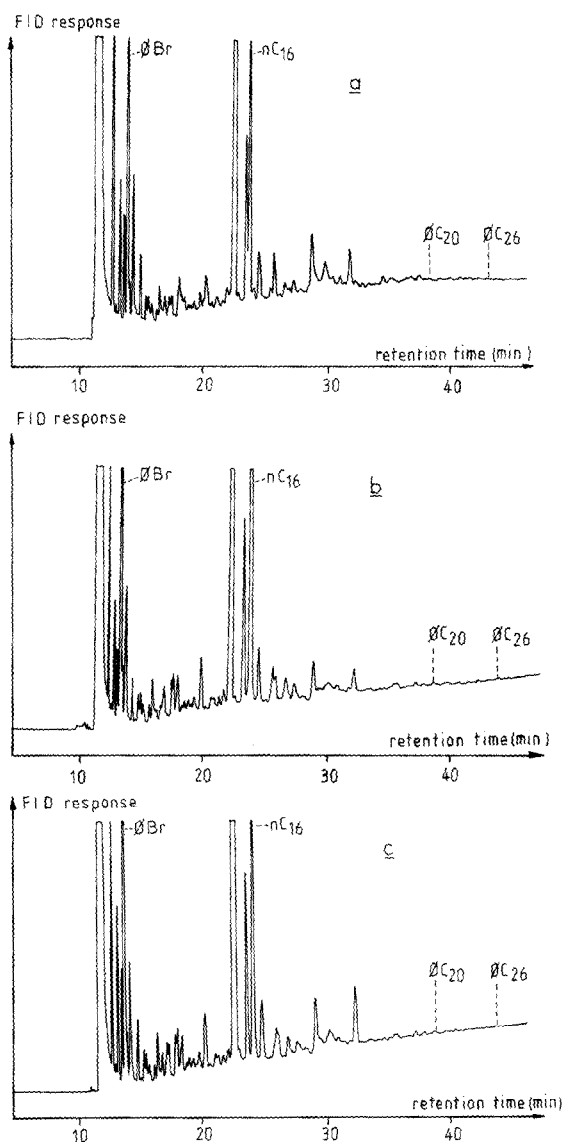


Fig. 4. SFC analysis of reaction media resulting from the transalkylation of various asphaltenes: (a) Arabian Light (Algeria); (b) Boscan (Venezuela); (c) Maya (Mexico). Conditions as in Fig. 1.

As transalkylation is a reaction which on the one hand is, in principle, an equilibrium (retro-Friedel-Crafts), and on the other is applied to very complex structures, reaction sites of which can be hindered, we concluded this study by examining the impact of one or more recyclings on the overall yields of transalkylation. Table IV reports the results ob-

TABLE III

OVERALL YIELDS OF TRANSALKYLATION PRODUCTS FROM VARIOUS ASPHALTENES DETERMINED BY CAPILLARY SFC AND CAPILLARY GC ANALYSES

The standard deviation is calculated from five independent transalkylations.

Asphaltenes	Overall yield (%)	
	SFC	GC
Arabian Light	7.5 ± 0.9	6.9 ± 0.3
Boscan	5.2 ± 0.2	4.6 ± 0.9
Kirkouk	7.5 ± 0.8	7.0 ± 0.8
Maya	5.9 ± 0.6	5.7 ± 0.8

tained by SFC analysis after one recycling of Kirkouk, Boscan, Maya and Arabian Light asphaltens and after recycling Kirkouk asphaltens twice.

These experiments show clearly that one transalkylation is not sufficient to transfer efficiently the totality of alkyl chains substituting the aromatic matrix of heavy crude oil fractions. The yields obtained in the second and third transalkylations are far from negligible. However, SFC and GC-MS analyses indicate clearly that almost no long chains are transferred in the course of these further transalkylations. Hence it appears that the transfer of

TABLE IV

EVOLUTION OF OVERALL TRANSALKYLATION YIELDS OF VARIOUS ASPHALTENES AS A FUNCTION OF RECYCLING

Asphaltens	Transalkylation number	Overall yield by SFC (%)
Boscan	1	5.2
	2	4.3
	3	0.9
Arabian Light	1	7.5
	2	3.5
Maya	1	5.9
	2	3.9
Kirkouk	1	7.5
	2	3.2

long alkyl chains substituting aromatic matrices was efficient in the first transalkylations.

The short chains transferred in the first and second recyclings give mainly di- and triphenylmethanes and were previously considered to be responsible for the distribution of aromatic entities in the composition of heavy crude oil fractions [7]. They can also be attributed to the fragmentation of longer or branched alkyl chains substituting heteroaromatic molecules (in place of simple aromatics), which are also present in heavy oil fractions [13,14].

Because of the lack of studies concerning the behaviour of alkyl heteroaromatics under transalkylation conditions, we cannot answer this fundamental question at present.

#### CONCLUSIONS

SFC, which is well adapted to the study of the transalkylation of alkyl chains substituting the complex aromatic matrices of heavy crude oil fractions (regardless of chain length), allowed us to confirm that if relatively long linear alkyl chains are present, their length does not exceed  $C_{27}$ – $C_{29}$ .

The study of asphaltenes of various origins by combining transalkylation and SFC indicated that in spite of the differences observed in the distribution of alkyl chains substituting the aromatic matrices as a function of the origin of the asphaltenes, the length of the longer chains varies only slightly in the different asphaltenes. The maximum chain length is greater in Kirkouk asphaltenes than in Boscan, Maya and Arabian Light asphaltenes. As the alkyl chains substituting the oil aromatic matrix are only slightly longer than those previously identified by capillary GC, the non-quantitativeness of the alkyl chain transfer must have a cause other than the analytical procedure. Using successive transalkylations of the same asphaltenes we proved that an efficient transfer of alkyl chains cannot be obtained after only one transalkylation. This may

be due to an equilibrium (in spite of the excess of light aromatic acceptor) or to poor accessibility of reaction sites in oil aromatic matrices which are very complex.

The nature of the alkyl chains transferred after recycling, which are relatively short, raised the question of whether they are short chains distributed in heavy crude oil fractions or degradation products of longer linear or branched chain substituted heteroaromatic molecules (containing nitrogen, oxygen and mainly sulphur) which constitute part of heavy oil fractions. In order to answer this last question, we are currently studying the transalkylation of *n*-alkyl heteroaromatic molecules.

#### REFERENCES

- 1 J. G. Speight, *The Chemistry and Technology of Petroleum*, Marcel Dekker, New York, 1980.
- 2 L. Petrakis and D. Allen, *N.M.R. for Liquid Fossil Fuels*, Elsevier, Amsterdam, 1984.
- 3 A. A. Herod, W. R. Ladner and C. E. Snape, *Philos. Trans. R. Soc. London, Ser. A*, 300 (1981) 3.
- 4 C. E. Snape, *Fuel*, 62 (1983) 621.
- 5 C. E. Snape, W. R. Ladner, L. Petrakis and B. C. Gates, *Fuel Process Technol.*, 2 (1984) 155.
- 6 C. E. Snape, W. R. Ladner, K. D. Bartle and N. Taylor, *Characterization of Heavy Crude Oils and Petroleum Residues (Collection Colloques et Séminaires, Vol. 40)*, Technip, Paris, 1984, p. 315.
- 7 P. L. Desbène, N. Jauseau-Pierre, B. Desmazières and J. J. Basselier, *Chromatographia*, 26 (1988) 70.
- 8 P. L. Desbène, N. Jauseau-Pierre, B. Desmazières and J. J. Basselier, *Anal. Chim. Acta*, submitted for publication.
- 9 P. L. Desbène, N. Jauseau-Pierre, A. Abderrezag and B. Desmazières, *Bull. Soc. Chim. Fr.*, submitted for publication.
- 10 P. L. Desbène, A. Abderrezag, B. Desmazières, J. J. Basselier, F. Béhar and M. Vandenbroucke, *Org. Geochem.*, 16 (1990) 969.
- 11 B. Tissot and D. Welte, *Petroleum Formation and Occurrence*, Springer, Berlin, 1978.
- 12 *French Standard*, NFT 6011S, AFNOR, Paris, 1970.
- 13 F. Béhar and M. Vandenbroucke, *Org. Geochem.*, 11 (1987) 15.
- 14 J. L. Faulon, M. Vandenbroucke, J. M. Drappier, F. Béhar and M. Romero, *Org. Geochem.*, 16 (1990) 981.