

PAH`s in bitumen: many paths - one destination

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ABSTRACT

Polycyclic Aromatic Hydrocarbons (PAH), a sub-group of Polycyclic Aromatic Compounds (PAC), often play a key role in the hazard evaluations of materials and their regulation with respect to the impact on health and the environment. This is reflected by the large number of existing inventory lists of PAHs by regulators and advisory bodies. However, in chemically complex materials or less well defined substances the test method used for determination and quantification of PAC/PAH may influence the outcome significantly.

Recently, PAHs have played an important role in the outcome of the cancer hazard assessment of occupational exposure to bitumen and its emissions. Bitumen is a complex substance manufactured from the distillation of crude oil. It can generally be described as a complex mixture of hydrocarbons containing a large number of different chemical compounds of relatively high molecular weight. Under REACH it is a non-hazardous substance and a so called UVCB, a material "of Unknown, of Variable Composition, or of Biological Origin". Crude oils contain low parts of PAH/PAC and as such low (ppm) levels may be present in bitumen.

This article presents results of PAH quantifications carried out in four analytical institutes on a variety of (intermediate) substances along the bitumen manufacturing process: from crude oil to final bitumen product. It provides an insight in the development of PAH content during the manufacturing process of bitumen. The different analytical methods applied in this study are discussed. Conclusions are drawn focussing on the PAH in the EPA PAH-list.

It is shown that the different (standard) analytical techniques on the complex petroleum substances tested in this study lead to different results. This in turn stresses the need for standardising test conditions and/or analytical preparation techniques in order to allow fair comparison of materials.

Keywords: Polycyclic Aromatic Hydrocarbon

1. INTRODUCTION

By doing the work presented in this paper the authors have ventured along a number of paths of investigation with one destination in mind: to learn some more about Polycyclic Aromatic Hydrocarbons (PAHs) in bitumen. One path explores ‘standard’ analytical techniques to determine the PAH content of bitumen. It was discovered that although analytical techniques by themselves are quite accurate and well advanced, application to complex mixtures of substances such as bitumen can produce unexpected results. A second path follows PAHs through the principle bitumen manufacturing processes of atmospheric and vacuum distillation. It is shown that distillation removes PAHs from crude oil leaving only low concentrations of PAHs in bitumen. A third path follows PAHs in two other manufacturing processes air rectification and oxidation. It is shown that both processes leave the PAH content of bitumen essentially unaltered. The manufacturing path of oxidation to produce oxidised industrial bitumen grades shows that the PAH content of the final product depends on the PAH content of the raw materials used. In reading this paper, please enjoy the journey with us.

2. EXPERIMENTAL

2.1. Background

Bitumen, in very general terms, can be described as a complex mixture of hydrocarbons containing a large number of different chemical compounds of relatively high molecular weight. Under REACH, bitumen is a non-hazardous substance and a so called UVCB, a material “of Unknown, of Variable Composition, or of Biological Origin”. Bitumen is manufactured from the distillation of crude oil. Crude oils contain low parts of PAH/PAC and as such low (ppm) levels may be present in bitumen.

Polycyclic Aromatic Hydrocarbons (PAH), a sub-group of Polycyclic Aromatic Compounds (PAC), often play a key role in the hazard evaluations of materials and their regulation with respect to the impact on health and the environment. Consequently, PAHs feature on many regulatory lists such as the EPA list [1]. More and more quantitative limits are defined for PAH in materials in order to protect consumers and/or workers from potential adverse health effects that may arise from exposure to these substances. In order to set such occupational or environmental limits robust analytical techniques are required. The chemical complexity of bitumen provides a challenge for (standard) laboratory analytical techniques. We show this by presenting a comparison of results from four different analytical laboratories.

The principle refinery process used for the manufacture of bitumen is a two step distillation: atmospheric distillation followed by vacuum distillation. This is sometimes followed by airrectification (mild oxidation) and/or oxidation (severe oxidation) depending on the required final product properties [2]. In this paper we follow the path of PAHs throughout the three principle bitumen production processes distillation, airrectification and oxidation.

2.2. The 16 EPA PAH

We focussed on the 16 EPA PAH, see Table 1.

Table 1: 16 EPA PAH names, number of aromatic rings and boiling points

	Names	Number of rings	Boiling Ponto [°C]		Name	Number of rings	Boiling Point [°C]
1.	Naphthalene	2	218	8.	Pyrene	4	404
2.	Acenaphthylene	2	280	9.	Benzo[a]anthracene	4	438
3.	Acenaphthene	2	279	10.	Chrysene	4	448
4.	Fluorene	2	295	11.	Benzo[b]fluoranthene	4	481
5.	Phenanthrene	3	332	12.	Benzo[k]fluoranthene	4	480
6.	Anthracene	3	340	13.	Benzo[a]pyrene	5+	495
7.	Fluoranthene	3	375	14.	Indeno[1,2,3-cd]pyrene	5+	536
				15.	Dibenzo[a,h]anthracene	5+	524
				16.	Benzo[ghi]perylene	5+	500

The principle refining process for bitumen is distillation, a technique that separates substances based on their boiling point. Therefore it is informative to review the boiling points of the 16 EPA PAHs provided in Table 1. The 16 EPA PAHs can be grouped into four categories 2, 3, 4 and 5+ ring substances with respective boiling points broadly between 200 and 300°C, 300 and 400°C, 400 and 495°C and above 495°C. We will compare these with typical process temperatures that occur in bitumen production.

2.3. Materials

A total number of 44 products have been analysed for the PAH content in the preparation of this paper. The analytical gaschromatography (GC) techniques applied can detect a large number of PAH compounds, but we have focussed on the 16 EPA PAHs.

2.3.1. PAH analytical methods ‘path 1’

PAH content is measured on 25 samples involving 4 different laboratories in three separate rounds. Not all laboratories tested all products as this was not a formal round robin in a statistical sense. The materials tested were from both refinery production and laboratory (scale) pilot plants. It included straight run (13) and airrectified (1) paving grades, oxidised industrial grades (4), crude oil (1) and various distillates and refinery intermediates (6).

2.3.2. Bitumen manufacturing: ‘path 2 & 3’

Two separate crude oils CX and CY are distilled in the laboratory into paving grade bitumens giving the following (intermediate) products:

- Atmospheric residue at 200°C, distillate at 400°C and vacuum residue distilled at 400°C giving a 100/150 penetration grade bitumen from crude oil CX
- Atmospheric residue and distillate at 200°C, and five vacuum residues down to 35/50 penetration grade bitumen and associated distillates at five different distillation temperatures from crude oil CY

We compared the PAH content on all samples from crude to final product – ‘path 2’. Furthermore, three airrectified bitumens (10/20 grade) from two different refineries including their corresponding vacuum residues, used as blowing unit feedstocks, are studied comparing the effect of airrectification on the PAH content.

Five oxidised industrial bitumens (100/40, 100/25 and 95/40 grade), both laboratory and refinery produced were studied. We compared the PAH content with the raw material components used in their production (i.e. vacuum residue and flux/distillate). To avoid potential variation caused by analytical test methods, the PAH content of materials from path 2 & 3 were tested in one single laboratory (A).

2.4. Methods

Analytical Path 1: In total 25 different samples of penetration grade and industrial grade bitumen were investigated in four laboratories. Each laboratory used own in-house methods. A brief summary of these methods is give in Table 2

Table 2: PAH analytical method summary

	Institute	Solvent	Measurement	Detection	Method guidelines
1.	A	cyclohexane	GC	*MSD in SIM mode	acc. Grimmer Method SOP PAH-0397
2.	B	cyclohexane	GC	MSD	acc. DIN ISO 18287:2006-05
3.	C	hexane	GC	TOFMS	EPA SW-846 8270C[1] by Kriech at al.
4.	D	dichlormethane	GC	MS in EI SIM mode	house method

*MSD - Mass Selective Detector, SIM - Selective Ion Monitoring, TOFMS - Time of Flight Mass Spectrometry, MS - Mass Spectrometry, EI - Electron Ionisation

Bitumen Manufacturing: Figure 1 schematically details the principle bitumen refining processes considered in this paper. See also ‘The Bitumen Industry – a global perspective’. [2]

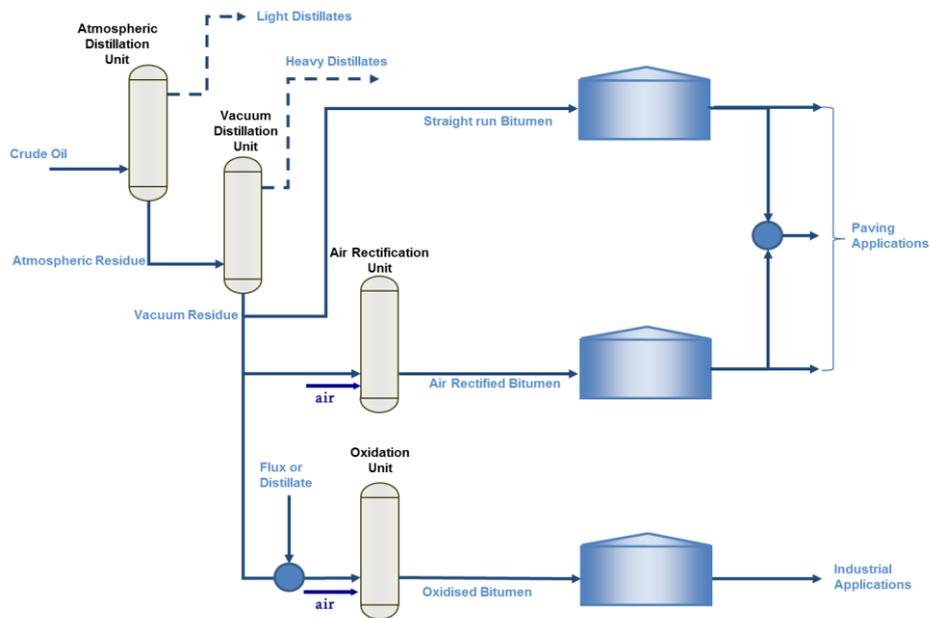


Figure 1: Schematic of principle bitumen production processes.

Laboratory bitumen manufacturing processes were done in custom built small scale pilot plants. These laboratory scale plants are known to be able to replicate refinery bitumen production processes very well for those refineries whose products are included into this investigation.

Path 2: Distillation is the principle and most common refining process used to produce bitumen. It usually occurs in two steps, atmospheric distillation followed by vacuum distillation. This results in an end-product consisting of a vacuum residue distilled up to 535°C (Atmospheric Equivalent Temperature, AET) which is a product with very low volatility. Samples for this report were obtained by laboratory distilling crude oils and/or samples directly from the refinery vacuum distillation units.

Vacuum distillation temperatures in this paper are expressed in terms of Atmospheric Equivalent Temperature. This is the actual vacuum distillation temperature recalculated to a pressure of one atmosphere giving the equivalent distillation temperature at atmospheric pressure assuming no thermal decomposition takes place [3, 4]. The vacuum distillation of the atmospheric residue of crude oil CY at five different temperatures (410, 480, 495, 505 and 520°C) was done in sequential, incremental steps. In other words, atmospheric residue from crude oil CY was distilled from low to high AET in steps whereby each vacuum residue was distilled further from the previous step. Standard bitumen properties and PAH content were measured on all distillate and residue fractions, see Table 3. The vacuum distillation of CX was done only at one temperature, 400°C (AET). PAH contents were determined in one single laboratory (A).

Table 3: Standard properties of laboratory produced vacuum residue and distillate fraction of CX and CY

Sample	Crude Oil CX	Residue 200	Distillate 400	Residue 400	Crude oil CY	Distillate 200	Residue 200	Distillate 410	Residue 410	Distillate 480	Residue 480	Distillate 495	Residue 495	Distillate 505	Residue 505	Distillate 520	Residue 520
AET [°C]		200°C	400°C	400°C		200°C	200°C	410°C	410°C	480°C	480°C	495°C	495°C	505°C	505°C	520°C	520°C
Penetration (1/10)				113							343		144		94		52
Softening Point (°C)				42.4							37.4		41.8		46.4		51.6
PAH	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)
Naphthalene 2-Ring	128.04	117.24	206.93	0.10	220.54	971.57	58.01	113.85	0.06	0.11	0.15	0.15	0.07	0.33	0.08	0.88	0.26
Acenaphthylene 2-Ring	3.84	3.65	12.01	<0.001	1.39	0.67	0.66	2.60	<0.001	0.02	<0.001	0.07	<0.001	0.15	<0.001	0.29	<0.001
Acenaphthene 2-Ring	3.48	4.29	13.94	<0.001	8.07	8.47	6.32	29.83	<0.001	0.08	<0.001	0.17	<0.001	0.51	<0.001	1.55	<0.001
Fluorene 2-ring	16.04	16.95	57.94	0.15	14.91	12.61	15.02	59.70	0.04	0.18	0.12	0.28	0.03	0.62	0.03	1.73	0.12
Phenanthrene 3-Ring	75.28	83.88	297.60	2.50	58.29	25.52	63.40	298.91	0.68	7.02	<0.001	0.27	0.02	0.55	0.02	2.00	0.04
Anthracene 3-Ring	<0.001	0.75	4.85	0.05	0.58	0.51	2.62	15.87	0.13	0.47	<0.001	0.29	0.04	0.58	0.03	1.63	<0.001
Fluoranthene 3-Ring	4.30	4.65	12.28	1.84	1.32	0.21	1.53	5.36	0.41	4.19	<0.001	0.15	<0.001	0.17	<0.001	0.60	<0.001
Pyrene 4-Ring	10.12	11.21	25.17	5.82	3.52	0.49	4.11	13.88	1.58	15.00	0.03	0.70	<0.001	0.36	0.01	1.35	0.02
Benzo[a]anthracene	1.75	2.35	2.70	2.11	1.84	0.06	2.06	4.62	2.05	14.78	0.25	5.98	0.02	0.49	<0.001	0.63	<0.001
Chrysene	6.56	7.24	6.40	7.22	4.63	0.20	5.76	8.69	5.31	32.22	0.82	11.70	0.05	0.93	<0.001	0.37	<0.001
Benzo[b]fluoranthene	6.01	6.83	2.37	9.02	1.65	0.02	1.92	1.50	2.54	10.02	1.07	15.52	0.41	7.02	0.02	0.73	<0.001
Benzo[k]fluoranthene	0.42	0.56	0.19	0.81	0.43	<0.001	0.38	0.56	0.85	3.26	0.33	2.34	0.12	2.67	<0.001	0.15	<0.001
Benzo[a]pyrene 5-Ring	1.94	2.31	0.57	3.06	0.74	<0.001	0.95	0.55	1.35	4.19	0.66	7.06	0.35	5.30	0.04	1.50	<0.001
Indeno[1,2,3-cd]pyrene	0.41	0.41	0.04	0.67	0.19	<0.001	0.28	0.07	0.48	0.45	0.24	1.63	0.34	2.19	0.15	2.51	<0.001
Dibenzo[a,h]anthracene	0.22	0.25	0.03	0.36	0.05	<0.001	0.09	0.04	0.18	0.14	0.08	0.87	0.13	1.40	0.06	0.81	<0.001
Benzo[ghi]perylene	3.62	4.12	0.30	6.00	2.78	<0.001	3.34	0.59	4.70	4.68	4.18	15.09	3.71	26.25	2.14	25.14	0.58
TOTAL EPA-16 PAH	262.01	266.69	643.30	39.72	320.92	1020.32	166.44	556.62	20.36	96.80	7.92	62.28	5.28	49.51	2.59	41.87	1.02
2-Ring	151.39	142.13	290.82	0.25	244.91	993.32	80.02	205.98	0.10	0.38	0.28	0.67	0.10	1.60	0.10	4.45	0.38
3-Ring	79.58	89.29	314.72	4.39	60.19	26.23	67.84	320.14	1.22	11.68	0.00	0.72	0.05	1.29	0.05	4.23	0.04
4-Ring	24.85	28.19	36.82	24.98	12.07	0.77	14.23	29.25	12.32	75.28	2.49	36.24	0.60	11.47	0.03	3.22	0.02
5-ring	6.19	7.09	0.93	10.10	3.76	0.00	4.66	1.24	6.72	9.46	5.15	24.65	4.53	35.14	2.40	29.96	0.58

Path 3: Airrectification – three airrectified bitumen production samples from two different refineries were analysed together with their respective vacuum residue feeds of the airrectification units. Table 4 provides the results. PAH contents were determined in one single laboratory (A).

Table 4: Results of refinery produced airrectified bitumen and vacuum residue feeds used to produce them

Sample	Vacuum Residue Feed (a)	Airrectified Bitumen (a)	Vacuum Residue Feed (b)	Airrectified Bitumen (b)	Vacuum Residue Feed (c)	Airrectified Bitumen (c)
Origin	a	a	b	b	c	c
PAH	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)
Naphthalene 2-Ring	0,18	0,16	0,53	0,12	0,24	0,05
Acenaphthylene 2-Ring	<0,001	<0,001	<0,001	<0,001	<0,001	<0,001
Acenaphthene 2-Ring	0,05	<0,001	<0,001	<0,001	0,11	<0,001
Fluorene 2-ring	0,11	0,50	0,17	0,28	0,15	0,07
Phenanthrene 3-Ring	0,08	0,16	0,32	0,39	0,47	0,19
Anthracene 3-Ring	0,04	0,03	0,03	0,05	0,05	0,03
Fluoranthene 3-Ring	0,02	0,06	0,03	0,06	0,03	0,03
Pyrene 4-Ring	0,04	0,08	0,05	0,08	0,08	0,07
Benzo[a]anthracene	0,04	0,14	0,02	0,04	0,03	0,03
Chrysene	0,07	0,32	0,05	0,09	0,10	0,08
Benzo[b]fluoranthene	0,13	0,22	0,07	0,10	0,08	0,08
Benzo[k]fluoranthene	0,02	0,03	<0,001	0,02	0,01	<0,001
Benzo[a]pyrene 5-Ring	0,13	0,17	0,07	0,07	0,06	0,06
Indeno[1,2,3-cd]pyrene	0,18	0,11	0,05	0,05	0,05	0,05
Dibenzo[a,h]anthracene	0,05	0,04	0,02	0,02	0,01	0,02
Benzo[ghi]perylene	0,89	0,74	0,66	0,64	0,70	0,64
TOTAL EPA-16 PAH content	2,02	2,74	2,06	2,00	2,18	1,40
2-Ring	0,33	0,65	0,70	0,40	0,49	0,12
3-Ring	0,13	0,25	0,38	0,50	0,55	0,25
4-Ring	0,30	0,77	0,20	0,33	0,30	0,26
5-ring	1,26	1,07	0,80	0,78	0,83	0,77

Oxidation – oxidised industrial bitumens are mixtures of vacuum residue with (optional) flux or distillate that are severely blown in an oxidation unit. Table 5 provides the PAH content of the individual oxidation unit feedstock components (in this case flux and vacuum residue) and final 100/40 product made in the laboratory, oxidised bitumen a, and a typical equivalent refinery produced 100/40, oxidised bitumen b, using similar materials. The fluxes used in the laboratory and the refinery were identical.

Table 5: Results of oxidised bitumen and the raw materials used.

Sample	Vacuum residue feed a	Flux	Blowing feed (calculated from vacuum residue + flux)	Oxidised bitumen a [laboratory produced]	Vacuum residue feed b	Flux	Blowing feed (calculated from vacuum residue + flux)	Oxidised bitumen b [refinery produced]
	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)
PAH								
Naphthalene 2-Ring	0.114	2.773	0.779	0.264	0.512	2.773	1.077	0.404
Acenaphthylene 2-Ring	<0,001	1.012	0.253	<0,001	<0,001	1.012	0.253	<0,001
Acenaphthene 2-Ring	<0,001	1.131	0.283	<0,001	<0,001	1.131	0.283	<0,001
Fluorene 2-ring	0.11	3.307	0.909	0.275	0.132	3.307	0.926	0.294
Phenanthrene 3-Ring	0.045	30.237	7.593	2.411	0.051	30.237	7.598	2.525
Anthracene 3-Ring	0.028	5.031	1.279	0.397	0.031	5.031	1.281	0.301
Fluoranthene 3-Ring	0.011	7.613	1.912	1.267	0.019	7.613	1.918	1.32
Pyrene 4-Ring	0.013	14.691	3.683	2.601	<0,001	14.691	3.673	2.948
Benzo[a]anthracene	0.07	6.936	1.787	1.56	0.013	6.936	1.744	1.248
Chrysene	0.213	5.411	1.513	1.544	0.021	5.411	1.369	1.064
Benzo[b]fluoranthene	2.076	3.792	2.505	2.949	0.318	3.792	1.187	1.011
Benzo[k]fluoranthene	0.418	0.647	0.475	0.521	0.061	0.647	0.208	0.175
Benzo[a]pyrene 5-Ring	2.605	5.279	3.274	3.29	0.377	5.279	1.603	1.084
Indeno[1,2,3-cd]pyrene	3.51	3.639	3.542	2.906	0.276	3.639	1.117	0.838
Dibenzo[a,h]anthracene	0.805	0.674	0.772	1.094	0.042	0.674	0.200	0.171
Benzo[ghi]perylene	12.269	7.491	11.075	9.873	2.532	7.491	3.772	3.515
TOTAL EPA-16 PAH content	22.287	99.664	41.631	30.952	4.385	99.664	28.205	16.898
2-Ring	0.22	8.22	2.22	0.54	0.64	8.22	2.54	0.70
3-Ring	0.08	42.88	10.78	4.08	0.10	42.88	10.80	4.15
4-Ring	2.79	31.48	9.96	9.18	0.41	31.48	8.18	6.45
5-ring	19.19	17.08	18.66	17.16	3.23	17.08	6.69	5.61

3. RESULTS AND DISCUSSION

In the next three subsections we present and discuss results from the three paths of investigation: ‘Path 1’ exploring standard analytical techniques measuring PAHs of four different laboratories on a broad range of samples. ‘Path 2’ follows PAHs through the crude oil distillation process and ‘Path 3’ assesses the effect of oxidation and airrectification. PAH analysis for Path 2 and 3 were done at one laboratory (A) to exclude variation by different analytical methods.

3.1.1 ‘Path 1’ results

This Path 1 investigated approximately 25 samples that were sent to four different laboratories. This involved a range of materials –crude oils, intermediates, final products. Three products were measured in all four laboratories: one 160/220 penetration grade bitumen and two oxidised 100/25 and 95/40 industrial grade bitumen. Figure 2 gives the profile of the 95/40 and Figure 3 gives the profile of the 160/220.

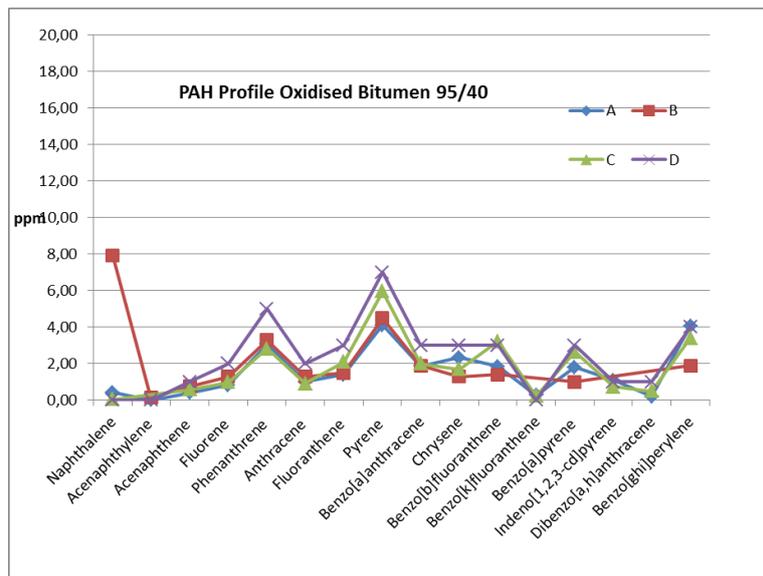


Figure 2: Profile of industrial oxidised bitumen 95/40

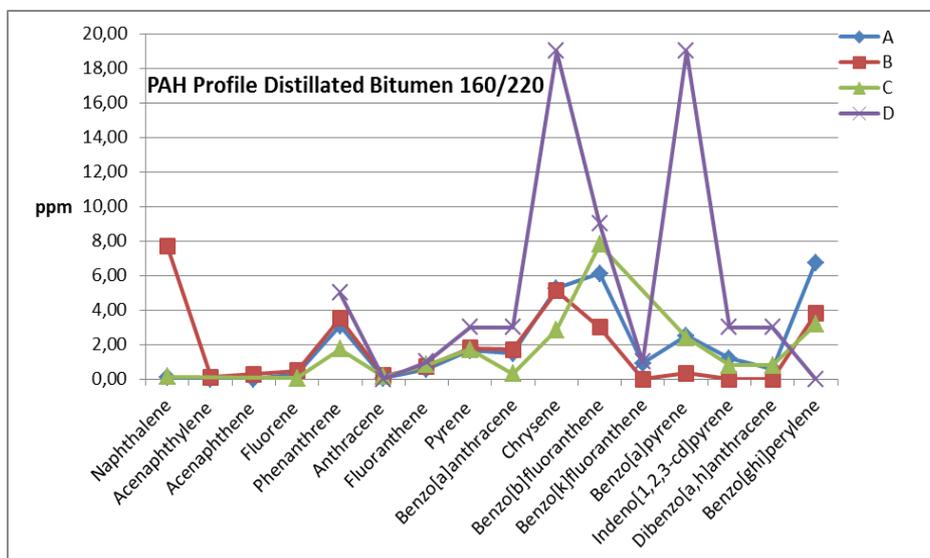


Figure 3: Profile of straight run 160/220 bitumen

The Σ 16 EPA PAH of duplicate samples that were measured in three laboratories are presented in Table 6 together with the variance of the mean in %. The laboratories did not know these same samples were included twice.

Table 6: Σ 16 EPA PAH in ppm, duplicate samples and their variance (%) in three laboratories

Sample/Lab	A		B		C	
160/220	29.7	1.5 %	41.7	18 %	37.3	7.4 %
	30.6		28.7		22.7	
100/25	30.6	1.7 %	40.1	34 %	39.1	8.2 %
	29.6		81.0		22.7	
95/40	28.7	7.4 %	44.6	22 %	30.4	1.3 %
	24.8		28.2		27.9	

3.1.2 'Path 1' discussion

The 16 EPA PAH profile of a 160/220 penetration grade bitumen is given in Figure 3 measured in four different laboratories. Globally the profiles look identical apart from a few noteworthy differences. The individual PAH content

is below 10ppm while the total Σ 16EPA PAH range from 11 to 42 ppm. The total Σ 16EPA PAH is generally below 70ppm in all final bitumen products analysed excluding crude oils, intermediate and distillates products which are not considered to be bitumen. For some bitumen products the total Σ 16EPA PAH is even below 1 ppm. These values are in line with those reported in literature [2, 5, 6, 7, 10, 11, 12, 13].

Comparing the values of individual PAH in the lower ppm range shows there can be large (up to a factor 8) difference between laboratories. This can be seen graphically in Figure 2 and 3. Rather large differences of individual PAHs such as Naphthalene or Benzo(a)Pyrene up to a factor of 100 are found. How do these differences arise?

All laboratories use gaschromatography methods, see Table 2. This analytical method, as well as the detection technique mass-spectroscopy are the base for published norms such as ISO 18287:2006 for PAH in contaminated soil [8] and the ZEK 01.4-08 that is used in the hazard assessment and classification of plastics, rubbers and varnish/resins [9]. For bitumen and/or bitumen-containing materials an equivalent standard method has not been developed suitable that would be suitable for setting limits satisfactorily. Published methods, such as Grimmer or Kriech seem to have been developed further into various 'in house' methods with the aim to improve precision. However, potential sources of error can be introduced due to a variety of causes: differences in sample preparation, use of different solvents and/or with different grades of purity, cleaning of GC columns, use of different (calibration and reference) standards (from 4 to 12), different detection techniques and associated detection limits or different data-processing software. Repeatability in one laboratory also raises some concern. For example, not all laboratories are below 10% repeatability for the total of 16 EPA PAH.

3.2.1 'Path 2' results

Table 3 gives the individual 16 EPA PAH in ppm as well as the sum of 2,3,4,5 and the total PAH content of crude CX and its distillation product and of crude CY and all its distillation products. Where relevant the standard bitumen properties, penetration at 25°C in 1/10mm EN 1426 and softening point in °C EN 1427, are included. It is noteworthy to see the significant difference between the measured data for the two crude oils when processed under similar conditions. In this example, a 100/150 penetration grade bitumen is obtained at an AET of approximately 400°C for crude CX while this grade is obtained at approximately 495°C for crude CY. This is indicative of differences found between crude oils from different sources.

Figure 4 gives the relative content of the 2-,3-,4- and 5+ ring PAH in the distillation product (residue and distillates) as a function of distillation temperature. The concentration is given relative to the content of that PAH in the original crude. The relative PAH content in the distillates increases as a function of distillation temperature. The lower boiling point PAHs (2 rings) show up at lower distillates temperatures, followed by 3,4 and finally the 5+ ring PAHs above 495°C. The reverse occurs in the residue fractions except there is an initial increase in the relative PAH content of 3,4,5+ rings at lower temperatures. This is explained by the fact that the high boiling point PAHs will accumulate in the residue so long as the distillation temperature is below the boiling point of the PAH. Above 500°C the content of 2,3, and 4 rings PAH is practically zero in the residue and the 5+ ring PAH well below 0.1 (i.e less than 10% of the amount in the original crude oil).

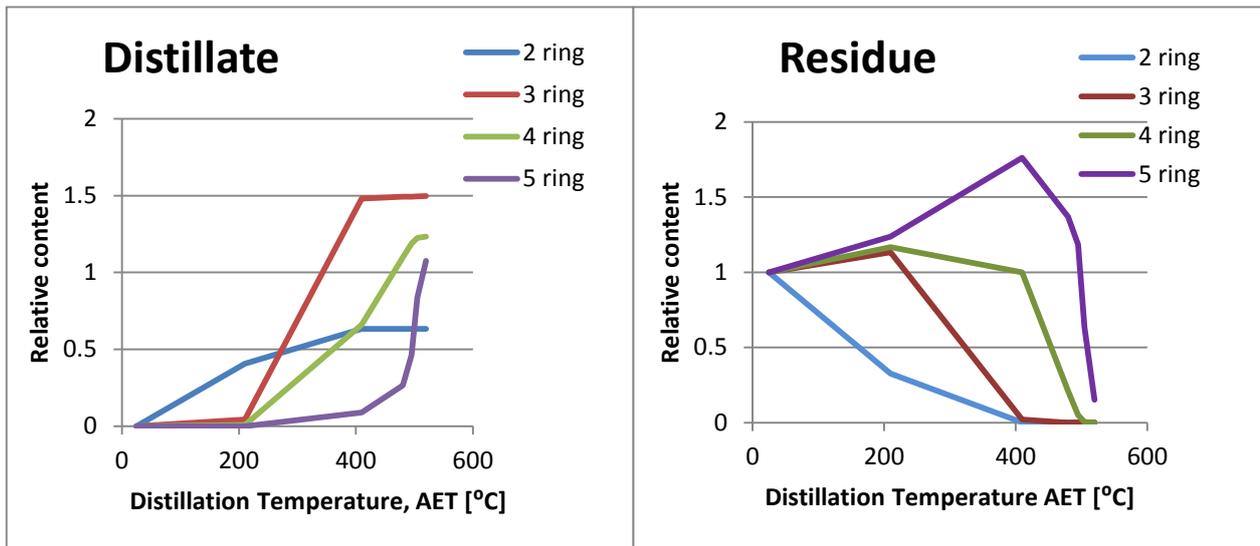


Figure 4: PAH content (relative to original crude oil) in distillates and residues as a function of distillation temperature (AET).

3.2.2 'Path 2' discussion

Distillation is a technique that separates mixtures using difference in boiling points. This is the principle refining technique for bitumen. The 16 EPA PAH, present in crude oil, have boiling points ranging from approximately 200 to 540°C. It is therefore evident that these are removed from crude oil and end up in the 'lighter' low boiling point distillate fractions and not in the 'heavier' high boiling point vacuum residues which are the base components of bitumen.

This is very nicely demonstrated in Figure 4. The heavier, higher boiling point PAH 4-, 5+ ring concentrate initially in the atmospheric and vacuum residue at lower AET (an increase relative to crude oil) but at distillation temperatures above 480°C a decrease is observed. The reverse is seen for the concentration of these PAH in the distillate fractions. The concentration of lighter, low boiling point PAH, i.e. 2- and 3- ring decrease in the residue already at lower distillation temperatures.

Harder grades of bitumen are produced by distilling at higher temperatures. For the same crude oil, a harder grade of bitumen will therefore have lower PAH content. The vacuum residues of crude oils CX and CY have very different standard bitumen properties (penetration and softening point) at the same distillation temperature around 400°C. To achieve the same grade of bitumen from both crude oils the distillation temperatures will need to be different. This results in different PAH contents. The inherent variability of crude oils and difference in distillation temperatures will result in variations in the PAH content when comparing bitumen from different refineries. However, if the distillation temperatures are sufficiently high the PAH contents will always be low. In the case of crude oil CX (producing a 100/150 penetration grade bitumen at 400°C) it would not be advisable to produce bitumen from this crude alone due to the low distillation temperature to achieve a 100/150 grade bitumen. In most cases such a crude oil would be blended and co-processed with a 'lighter' crude oil in order to raise the final distillation temperature to achieve the same penetration grade bitumen.

3.3.1 'Path 3' results

Table 4 and 5 give the individual 16 EPA PAH in ppm as well as the sum of 2,3,4,5 and total PAH content of the airrectified bitumen and oxidised bitumen and their corresponding raw materials (blowing unit feedstocks).

3.3.2 'Path 3' discussion

Airrectification and oxidation do not alter the PAH content of bitumen. The PAH profile of airrectified bitumen is similar to that of straight run bitumen. Only small differences may occur which can be explained by the process conditions during airrectification and/or oxidation. For example, 160/220 has relatively more 4-,5-ring than the 95/40 even though the latter is manufactured from the same 160/220. The relative shift towards 2-,3- ring PAH in the 95/40 may be explained by the use of a flux which is relatively richer in 2-,3-ring PAH and has more total 16 EPA PAH

(~100ppm). The overall PAH content of the 95/40 is therefore slightly higher and shifted toward smaller PAH when compared to the 160/220. The oxidation does not change the total PAH content of the input raw materials i.e. the bitumen and flux mixture. When comparing the composition of the blowing unit feed with the final product there even appears to be a trend that PAH content is lowered, in particular the 2- and 3- ring PAHs. This is very likely due to the high processing temperature, up to 280°C, during blowing which removes some of the more volatile, lower boiling point PAHs. Nevertheless using blowing feedstock materials, especially fluxes and distillates with low PAH content, will logically result in lower final PAH content of the final oxidised bitumen product.

4. CONCLUSIONS

4.1 'Path 1'

Ten years ago it was impossible to detect all the substances on the current EPA PAH list accurately at such low concentration as they are today. For example, until year 2000 Benzo(a)pyrene was used as a typical indicator to distinguish coal tar products from bitumen. In bitumen, Benzo(a)pyrene was hardly ever detected because the detection sensitivity was no better than around 5 ppm. Since then detection sensitivity has increased several orders of magnitude to the ppb range rather than ppm. This testifies the development in analytical capabilities, but it also shows in which extremely low concentrations we are searching and measuring materials on regulators' lists of hazardous chemicals today.

However, in order to compare results from different laboratories, it is absolutely essential to standardize the analytical methods. Our study has shown that large differences may be found well above the detection sensitivity of today. Furthermore, it has to be kept in mind that for concentrations around 5 ppm a deviation of only 1 ppm means a 20% impact. The sample preparation and every additional step in the analytical procedure may impact the outcome significantly and therefore influence comparisons between institutes and/or comparison with regulatory limits. No doubt the chemical complexity of a material like bitumen will play an important role. Independent from the differences observed on the same material between laboratories in this study, all the results demonstrate how extremely low the quantities of the PAHs are in bitumen.

4.2 'Paths 2&3'

During distillation of crude oil the majority of EPA PAHs present in crude oil are separated out due to their lower boiling points from the vacuum residue resulting in only small amounts of PAHs that remain in the final bitumen produced. In addition, refinery units are not perfect so that the distillation may be imperfect and some PAH remain. However, the $\sum 16$ EPA PAHs is well below 75 ppm for all bitumen materials we have included in this study. The PAH content of some bitumen products was even below 1ppm depending on process conditions (high AETs) and type of crude oils. In the example shown here, above 520°C the PAH content was below 1 ppm with the original crude oil having more than 300ppm of the $\sum 16$ EPA PAHs.

Our data confirms that *airrectification* (i.e mild oxidation) does not increase the PAH content. Normal airrectification process conditions (<300°C) do not lead to creating these type of compounds in bitumen out of the complex mixture of substances present.

During *oxidation* (i.e. severe oxidation) to produce industrial grade 'oxidised' bitumen the amount of PAH is determined by the amount of PAH in the raw materials used as blowing feedstock. Our data shows that the amount of PAH in the final product is directly related to the PAH content of the feed of the oxidation unit. The severe oxidation process, similar to the airrectification process, does not create any additional PAHs [14]. The higher PAH content of the oxidised bitumens in this paper is attributed to the flux used together with the vacuum residue in the blowing process. Logically, it is therefore advisable to use fluxes/distillates with as low/limited PAH content as possible in order to limit the PAH content of the final product.

Please note, even though small amount of PAHs may be found in all bitumen substances, this does not translate into any health risk. In its normal end use, bitumen is a solid material and the PAHs present do not become 'bio available' preventing occurrence of exposure of the general public. It has also been shown that at these low levels the PAHs do not leach into the environment [15]. When bitumen is applied, i.e. in an occupational setting, it is usually handled at elevated temperatures. In such a cases, trace amounts of PAHs may occur in the hot bitumen fume. However, bitumen

suppliers recommend product applications temperatures that are far below the boiling points of the 16 EPA PAH in order to limit exposure to these PAHs. In Europe, most bitumen manufacturers recommend a *maximum* paving application temperature of 200°C and a *maximum* application temperature of 230°C for industrial applications of oxidised bitumen. This ensures that concentrations of PAHs in bitumen fume are also very low.

5. SUMMARY

- Analytical methods are available to determine PAH in materials with great accuracy but applied to bitumen it seems further standardisation is required in order to be able to quantitatively compare values from different laboratories.
- The primary bitumen refining process ‘distillation’ is designed to remove PAH from bitumen. This results in very low concentrations of PAH in the final product bitumen.
- Secondary refining processes, ‘airrectification and oxidation’, do not increase the content of PAH in bitumen. The PAH content of the final product is therefore determined only by the content of the raw materials used.

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