

Waxphaltenes - when waxes become asphaltenes; wax model compounds and how they influence the fractionation of bitumen.

Michalina Makowska¹, Hilde Soenen², Jeroen Besamusca³, Xiaohu Lu⁴

¹Aalto University, ²Nynas NV, ³Kuwait Petroleum Research & Technology, ⁴Nynas AB

Abstract

In the bitumen and petroleum industry, fractionation or component separation is a common tool to describe the chemical nature of materials. From all components, the asphaltenes are definitely the most studied material in bitumen. Operationally, asphaltenes are defined as the material insoluble in n-heptane or n-pentane and soluble in toluene. Chemically, this fraction is associated to large conjugated polyaromatic compounds, and is also regarded as the most polar fraction present in bitumen. Other material classes including saturates, aromatics and resins have also been defined. The aim of this study is to investigate the validity and the risks of assigning chemical classes to fractions predominantly determined by solubility. In this study the authors investigated specifically if and under what conditions, a fully saturated hydrocarbon may become part of the asphaltene fraction. Fully saturated hydrocarbons would chemically be associated to the saturate fraction. For this purpose, several n-alkane substances were added to a wax-free naphthenic bitumen. In a first step, infra-red spectroscopy and calorimetry were used to assure a full blending between the n-alkanes and the bitumen, when preparing the blends at elevated temperature. Fractionation tests were conducted according to two common procedures: the Iatroscan method (IP 469) and the asphaltene separation method denoted as IP 143. Calorimetric data clearly show a melting point depression when adding n-alkanes to bitumen, as well as an increase in melting enthalpies with higher n-alkane percentages. The data also demonstrate that a recrystallization upon heating can take place, especially for the low molecular weight n-alkanes. The fractionation tests show further that low molecular weight n-alkanes are as expected part of the saturates or the maltene fraction, but for larger n-alkanes this is not always valid. The findings and its consequences are discussed in detail in the paper.

1. INTRODUCTION

Bitumen consists of a very large number of molecules, mainly containing hydrogen and carbon. But they vary widely in molecular structure, molecular size and polarity [1]. The chemical characterization of bitumen often starts with a separation into the classes of compounds based on their solubility. A large number of standard procedures is available to do so, such as the ASTM D 2007 [2], ASTM D 4124 [3], and IP 469 [4]. The differences between the methods originate among other things in the type of the bitumen dispersing solvent, type of solid phase during chromatography or filtration, as well as in the choice of solvents for the separation (also known as eluents). Consequently, the so obtained fractions are also named differently, depending on the method, as one can expect differences in the chemical nature of the fractions. Nowadays, the naming Saturates, Aromatics, Resins and Asphaltenes, or abbreviated SARA fractions has become very popular [5-9]. As a consequence, also fractions obtained with other methods and/or solvents, have been given the same naming's, although chemically they are probably different.

As a solubility class of hydrocarbon components, asphaltenes are typically defined to be the n-heptane insoluble and toluene soluble components of petroleum materials [10, 11]. For a very long time, a lot of research has been focused on understanding the chemistry and structure of asphaltenes in bitumen, as well as their mechanical and rheological impacts [12-19]. Commonly, asphaltenes are considered to consist of molecules of high molecular weight and high polarity. A classic model describing asphaltenes in bitumen is a colloidal dispersion of asphaltene micelles in an oil phase [12, 13]. The colloidal model, with asphaltenes as key components, has been used to explain rheological differences in bitumen, for example Newtonian and non-Newtonian behaviour. More recent studies have shown that the average molecular weight of asphaltenes is not that high, roughly 750 g/mole, within a range of 300 to 1400 g/mol [18, 20]. Regarding molecular structures, dominantly there is one polycyclic aromatic hydrocarbon (PAH) core per asphaltene molecule, and asphaltene PAHs have 4 to 10 fused rings [20]. The basic chemical and structural properties of asphaltenes have been used in the Yen-Mullins model for crude oils, in which there are three distinct structures, namely asphaltene molecules, asphaltene nanoaggregates, and clusters of nanoaggregates [17, 19]. The chemical and structural characteristics described above may also be valid for bitumen asphaltenes.

Another specific fraction in bitumen that has also been investigated for a long time is wax. Wax is characterized by its ability to crystallize or to form a solid liquid equilibrium at lower temperatures. In general, two fundamental types of petroleum wax can be found in bitumen, namely paraffinic and microcrystalline [21-23]. Paraffin wax refers to the group of normal alkanes with few or no branches. Waxes belong chemically to the saturate compounds, but at the same time, by definition, they can be a part of the asphaltene fraction, when they are large enough to be precipitated by n-heptane. The molecular size for such precipitation was observed to be around C40 by Iatroscan [23].

As already described, asphaltenes are defined as a solubility class rather than a chemical component class. The materials are still very heterogeneous, and slight variations in the separation procedure, or the separation conditions such as temperature and humidity, may create differences in the composition of this fraction. As demonstrated already during the introduction of IP 469 method, the compound class of asphaltenes determined by IP 469 is not identical to the asphaltenes as defined in ASTM D 3279 [10] or IP 143/ASTM D 6560 [11]. Ray et al. suggested the naming of the 3rd and 4th eluted fraction determined by the IP 469 technique to be Resin A and Resin B [24]. The asphaltenes obtained with the IP 143 procedure and analysed with IP 469 procedure contributed to two peaks. On the other hand, the IP 143 maltenes (asphaltene free fraction), contributed to all four peaks in IP 469. Currently, the suggested names for the fractions determined according to IP 469 are saturates, aromatics, polar I and polar II [4].

In literature, there is still a controversy between asphaltenes and waxes. A nice example is related to the explanations for the bee structures in bitumen. Bee structures can form on the surface of bitumen, it is a pattern of lower and higher phases, which have been evaluated mainly by atomic force microscopy. A number of studies relate these to the crystallization of natural wax in bitumen, while a number of other studies relate these to the presence of asphaltenes. The first group has demonstrated that bee structures appear when adding a commercial wax to a wax-free binder [25], while the second group demonstrated that bee structures, which were present in the original binder, were absent when removing the asphaltenes [26]. When adding the asphaltene fraction to the maltene fraction the bee-structure appeared again. Both investigations have proven their conclusions with their data and arguments. The controversy between asphaltenes and waxes was in fact the direct motivation for the investigations, presented further on in this paper.

The main objective of the study is to evaluate if waxes can become part of the asphaltenes fraction, and under which conditions this may happen. To increase the awareness about the differences in fractional composition as a result of the laboratory procedure, some of the methods for separating asphaltenes from bitumen have been re-evaluated and compared with each other. In order to demonstrate the behaviour of waxes in these procedures, well-defined n-alkanes of various chain lengths were analysed in their pure form, as well as when added to a wax-free binder. In the end, it was evaluated if, and under which conditions n-alkanes were found in the asphaltene fraction.

2. EXPERIMENTAL

2.1. Materials

An unmodified, wax-free bitumen was used, grade 160/220, with a penetration of 187 0.1mm at 25°C and a ring and ball softening point of 40°C. N-alkanes of four different chain lengths, respectively C18, C24, C40 and C44 were acquired from TCI EUROPE NV. The physical characteristics of these n-alkanes are listed in table 1. Blends of bitumen and the n-alkanes were prepared as follows: the bitumen was heated to 140°C, an amount of binder was taken, left to cool to room temperature, and the desired amount of the respective n-alkane was added, afterwards this blend was reheated to 140°C for a short period, typically 15 minutes, and homogenized manually by stirring the hot sample. DSC measurements were conducted to assure the homogeneity of the blends.

Table 1. Physical characteristics of the n-alkanes used in this study

Chain length Nr. C-atoms	Tm (melting temperature), °C	Tb (boiling temperature), °C	Purity (reported by TCI)
C18	29	317	> 98%
C24	52	391.3	> 99.0%
C40	84	523.9	> 97.0%
C44	86	547.5	> 97.0%

2.2. Characterization methods

DSC measurements were conducted with a Mettler Toledo DSC1. After heating the samples for a short time, a small amount (7-10 mg) was taken and sealed in an aluminium sample pan. The measurements started with a cooling scan, from +140 to -60 °C followed by a heating scan in the same temperature region. Scanning rates were 10 °C/min. High-Temperature Gas Chromatography (HTGC) was performed with an Agilent 7890 equipped with a flame ionization detector. The column used was 5 m long, 0.53 mm in diameter, and with 0.09 mm film thickness. Two percent (w/w) solutions of sample were prepared in CS₂, and 1 ml of sample solution was injected to the column using an autoinjector. Tests were performed under a helium flow rate of 15 cm³/min and a temperature program of 40-430 °C at 10 °C/min.

2.3. Fractionation methods

Fractionation tests were conducted in three laboratories: The applied methods and the investigated samples are given in Table 2 for each laboratory. In addition, a very detailed method description is included for the procedures followed in Lab 1 and Lab 2.

Table 2. Overview of samples and separation tests performed by 3 laboratories

Samples	Lab 1 IP 469	Lab 2 IP 143	Lab 3 IP 143 (qualitatively)
Ref sample, C24 and C44	X	X	X
Ref. + 2.5% C24	X		X
Ref. + 5% C24	X	X	
Ref. + 2.5% C44	X		
Ref. + 5% C44	X	X	
Ref. + 5% C40			X

Detailed test procedure Lab 1:

In this laboratory samples were fractionated according to IP 469, with some modifications, as explained further. A solution of the sample in toluene with a concentration of approximately 20mg/ml was prepared. On each rod, used in the investigation, 1 µl of this solution is applied in the origin region, resulting in an approximate sample size of 20 µg per rod. The first elution is performed in n-heptane for a period of 30 minutes (solvent front at 95-100 mm), the second one in toluene : n-heptane (80:20 vol./vol.) for 9 minutes and 7 seconds (50±5 mm), and the third one in dichloromethane : methanol (95:5 vol./vol.) for 2 minutes and 10 seconds (20±2 mm). These times were kept constant for all series. The elution tanks are filled with 70 ml of eluents. All used solvents were HPLC grade. The laboratory temperature is kept between 22-24°C, but the humidity is uncontrolled for.

Five deviations from IP 469 were made:

1. Instead of dichloromethane for the sample solution, toluene was used. This may influence the spot shape at the origin, and effectively to the reading related to polar II fraction. The switch is due to two aspects: the fact of

insolubility of some waxes in dichloromethane, the definition of asphaltenes as those soluble in toluene according to IP 143 to which the IP 469 was compared to, and the definition of bitumen being a material 99% soluble in toluene. Because a test of the references and samples in a similar procedure was desired, toluene as a dispersing solvent was used for all samples. However, as reported in the literature, the choice of dispersing solvent may significantly influence the repeatability of the results when compared with DCM [27]. The experience of this project suggests that the alteration of the solvent and a few other parameters (see following deviations number 2-4) results in values within the repeatability limits provided in the IP 469 instruction.

2. The toluene-based solution was warmed up in a water bath to approximately 50°C for 5 minutes before applying it on the rods. The application syringe, on the other hand was kept at room temperature.

3. The drying of the rods in between the different elutions was performed in nitrogen for a period of 10 minutes, instead of 2 minutes in air, to prevent oxidation. The nitrogen drying was suggested already by Ray et al. [24], drying is conducted to remove the solvent from the rods sufficiently, before applying a new solvent.

4. Both the silica rods and the equipment were of a more modern grade than described in the IP 469, namely Chromarod SV and Iatroskan MK6-S.

5. The separation of components is dependent on the amount of the sample. Therefore, when testing the two reference samples, C24 and C44, the concentration of the starting solution was lowered, and the n-alkanes were tested at masses similar to those in which they can be anticipated in the bitumen blends. This is needed to avoid overloading the origin with the wax fraction, possibly blocking the pores and hindering the mobility of solvents through the origin [28]. A solution of 4 mg/ml of C24 in toluene and 2mg/ml solution of C44 in toluene was prepared, which corresponds to 20 and 10% of the respective waxes in comparison to the concentration in the bitumen blends. The C24 dissolved fully at room temperature, while flakes of C44 remained visible in the solution. The solutions were warmed up to approximately 50 °C in a water bath. It was observed that C44 dissolved in warm toluene. Afterwards 1µl of each solution was applied onto at least four rods at the origin spot, and the rods were eluted according to the procedure described above for the bituminous samples [4].

Due to the fact that at any given time only 10 rods can be analysed, 4 analytical series of each 10 rods, were performed: 1- reference bitumen, 2 - C24 modified blends, 3 - C44 modified blends, 4 – reference waxes. The slight differences between series may be due to humidity or temperature [28].

The repeatability range for the distillation residues are given by the formulae:

$$0.5510 x_1^{0.4} \text{ for saturates, (1), } 0.6832 x_2^{0.5} \text{ for aromatics, (2),} \\ 0.6088 x_3^{0.7} \text{ for polar I, (3), } 0.7650 x_4^{0.5} \text{ for polar II, (4)}$$

where x_1 , x_2 , x_3 and x_4 are hereby constituting the average result from the reference bitumen of saturates, aromatics, polar I and polar II, respectively. A minimum of 3 rods/sample is suggested for analysis, 4 rods/sample are considered typical. In hereby study 5 rods were used per sample.

Detailed test procedure Lab. 2:

The ASTM D6560 / IP 143 is based on the removal of wax-free organic material insoluble in heptane, but soluble in toluene of the bitumen used. Depending on the expected amount of asphaltene IP 143 describes test portion and heptane volume.

The bitumen used in this investigation consists of approximately 10% asphaltene and therefore a 150 ml flask (A) was filled with 2 ± 1 g bitumen and 60 ± 30 ml heptane. After bitumen fully dispersed in heptane, the mixture was refluxed for 60 ± 5 minutes. Then the flask A was cooled, closed and stored in the dark for 90 – 150 min. A paper filter was folded, attached with forceps and put in a filter funnel on a clean 150 ml flask (B). Using forceps prevents the contamination of the filter and its contents. The stored material was used without agitation so the liquid was decanted directly on to the filter. Hot heptane was used to rinse the precipitated residue as much as possible onto the filter. Then the flask A was put to a side with the addition of 30 to 60 ml toluene. The filter paper was removed (by handling with the forceps) from the funnel into the reflux extractor. The collected heptane was used to reflux the filter with a rate between 2 and 4 drops/s for at least 60 min until a drop on a clean filter showed no discoloration. Then the toluene flask (B) was placed under the extractor. All organic material left on the filter was extracted with toluene until a drop on a clean filter showed no discoloration. The toluene solution was transferred to a tarred evaporation dish with small amount of extra toluene, not exceeding 30 ml. Toluene was evaporated under nitrogen on a heating plate. The dish was dried in the oven at 100° - 110°C for 30 min. After cooling for 30 to 60 min the dish was re-weighed and asphaltene content calculated.

In this investigation the IP 143 was used with two adaptations. In step 2 of the method, the suggestion is to remove the waxy substances by washing with hot heptane in an extractor. The specific heptane boiling temperature of 98°C was used. In addition, in the last steps of the procedure, where the final weight of asphaltene must be determined within one hour after evaporation of toluene in the oven, the waiting time was adapted. During the calibration of the test it was noted that the asphaltene fraction did not reach a proper equilibrium in weight within the described test period. Therefore, a 2nd measurement was performed after 18 hours. This resulted in a stable weight measurement, but always lower than the 1st measurement. Headspace GC analyses, confirmed the presence of toluene in the samples measured according the procedure of IP 143. So, prolonging this time is a suggestion to improve the procedure. The

repeatability of the asphaltene fraction was 1.4 % for the approximately 12 % (m/m) asphaltene content of the bitumen.

Detailed test procedure of Lab.3:

In this lab, a qualitative separation was conducted; according to DIN 51595, which is technically identical to IP 143, but the norm was modified in this way that the asphaltene fraction was washed with cold n-heptane. Afterwards warm heptane, at a temperature of approximately 55°C was applied onto the sample as well. The separated asphaltenes were investigated further by HTGC, before and after washing with warm n-heptane. As this separation test was performed using larger amounts, the long chain alkane used here was C40 instead of C44 due to high pricing of C44.

3. RESULTS

3.1. Blending of n-alkanes in the bitumen and the related phase diagrams

DSC measurements allow defining the first order transitions (like solid-liquid phase separations) and second order transitions such as a glass transition. In Figure 1, heating scans are presented for various concentrations of C24 in the reference binder. The data show that when adding this n-alkane to bitumen, there is a melting point depression, this indicates that there is an interaction between both compounds. The data also show a broadening of the melting region, which is also expected in a two-component blend. In addition, for the lowest concentrations of C24, especially for the 2.5% C24, the DSC heating curve shows a recrystallization, when heating through the glass transition. This has often been observed in waxy binders. In this study, this behaviour was only observed for the shorter n-alkanes, C18 and C24. Interestingly, in case of n-C40 and n-C44, the effect at low concentrations was missing.

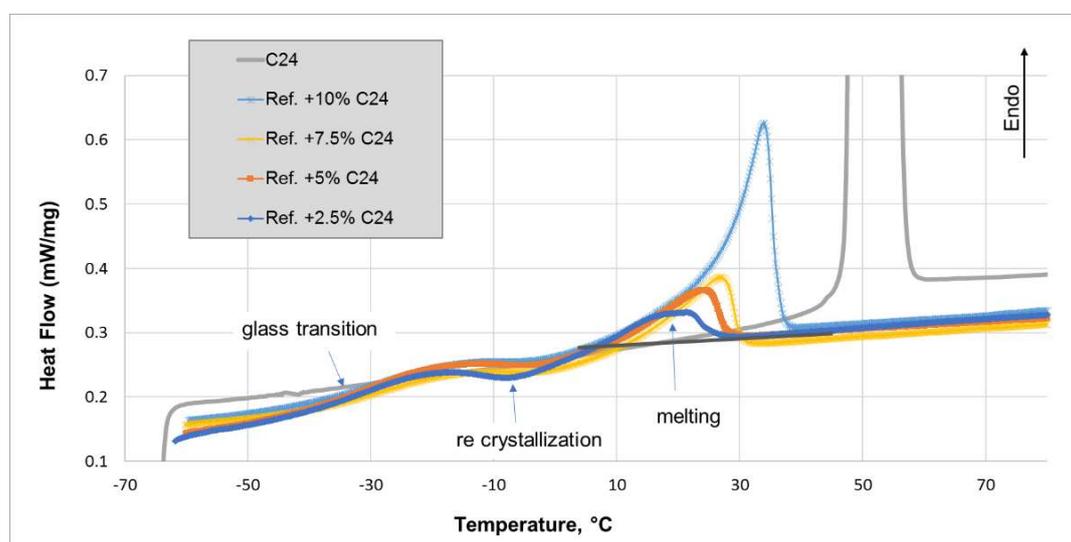


Figure 1: DSC heating scans of various bitumen and C24 blends

Aerts and Berghmans [29] demonstrate for a two component blend the melting point depression and the broadening of the melting signal. In [29], the both components of the blend having a melting behaviour, form an eutectic melting upon blending. Similarly, for bitumen and C24 only the C24 is crystalline, so in this blend, the melting point depression will continue up to low concentrations of C24, in fact until it reaches the glass transition region of the blend. Based on the DSC measurements a phase diagram for bitumen, with the various n-alkanes was constructed, represented in Figure 2. In this figure, only the peak temperatures are reported. It allows deriving the melting temperatures for the various alkanes at various concentrations in the bituminous blends.

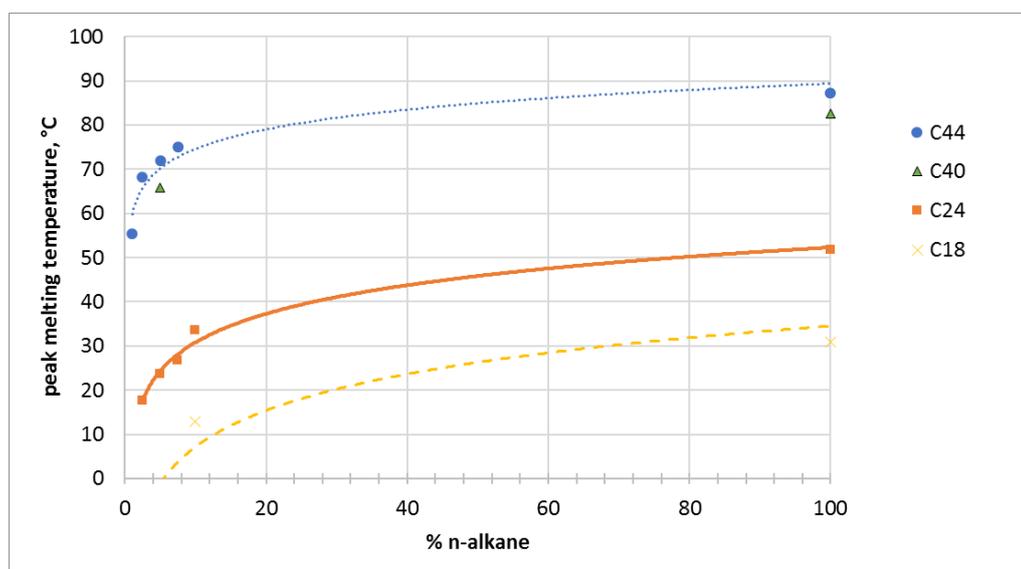


Figure 2: Phase diagrams of bitumen and n-alkanes

3.2. Fractionation results of Lab 1

The results after a mathematical integration processing, as described in IP 469 [4], are presented in Figure 3. The measured data, indicate that with increasing addition of C24 wax, the content of saturates is increasing in the blend. This is in fact as expected. Yet, with increasing addition of C44 the content of saturates is decreasing, suggesting that C44 is not contributing to this fraction. In addition, also the aromatics and Polar II fractions are decreasing, suggesting that C44 is contributing to the Polar I fraction. The increase in the Polar I fraction, and decrease in the aromatic fraction, is observed for all the samples containing alkanes. Therefore, possibly there may also be an effect of one extra heating step for the samples containing alkanes, as the mixing of the bitumen with the n-alkanes was not conducted on the reference sample. Although this mixing period was rather short, about 15 minutes.

The measured increase in saturates, is for the C24 samples not as high as expected under the assumption of identical contribution to the saturate fraction of bitumen from the pure n-alkanes substances and bituminous saturates. Nevertheless, the results are hereby evaluated based on the repeatability ranges provided in the IP 469 procedure description. Using these criteria, the only significant influence onto the saturate fraction was observed in the blends with C24 at 5%wt. This indicates that in case of IP 469, only the alkanes of certain length will contribute to this fraction. The long chain alkanes may remain invisible for the methodology of fractionation (e.g. C44 not fully dispersing in the cold toluene or dichloromethane). The other possibility is for them to contribute to polar I and polar II fractions due to the hindered solubility in the first eluent at room temperature (i.e. n-heptane).

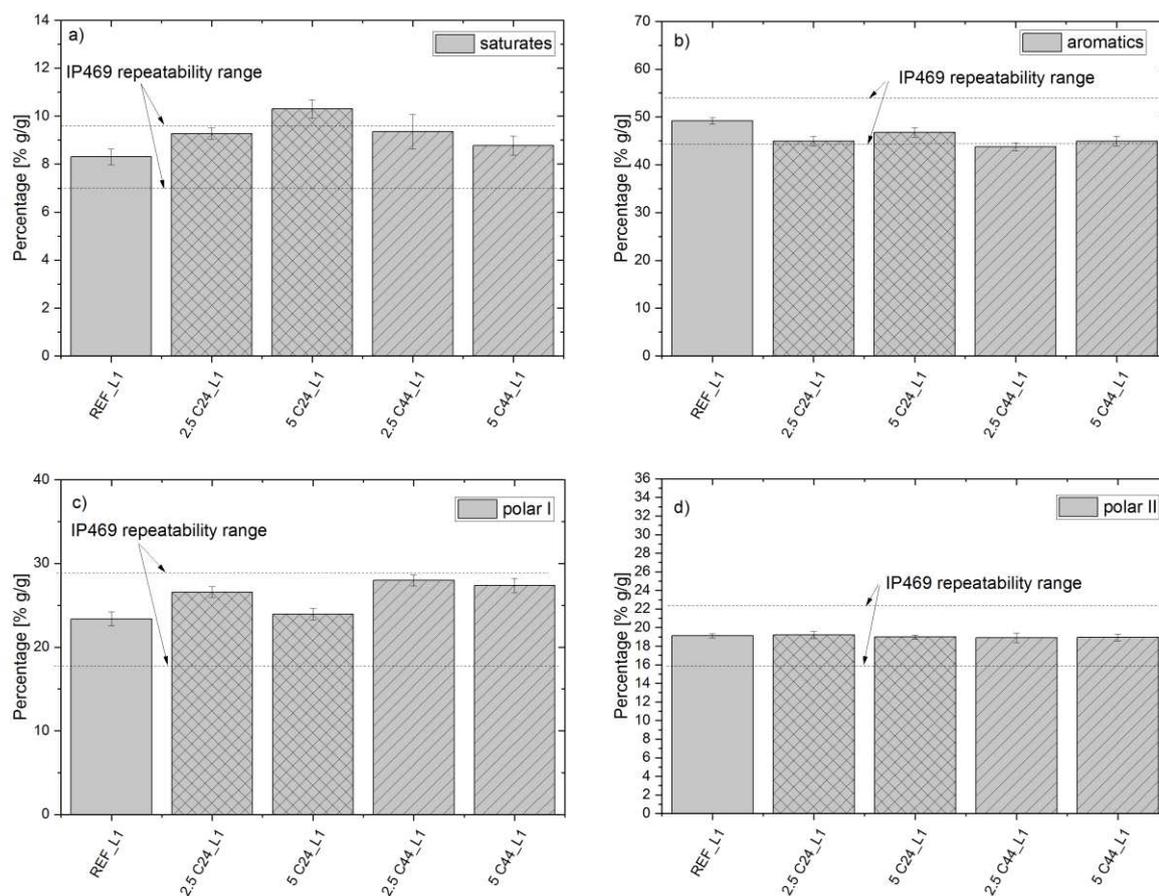


Figure 3: The average results of IP 469 fractionation for the Ref. and alkane modified samples, where error bars represent standard deviation (n=5) within each sample. The dotted lines of repeatability range defined in IP 469 are calculated using the average value for each fraction in Ref. sample (eq. 1-4).

To better understand the effect of n-alkanes in the Iatroscan method, the pure alkanes were tested, this is presented in Figure 4 together with the Ref. bitumen. Figure 3 demonstrates that wax C24 is eluting in the first bath in n-heptane to the region of saturates, while wax C44 remains in the region of Polar II (referred to often colloquially as asphaltenes). The analysis of C24 is more consistent and repeatable, while the analysis of C44 is challenging. Every consecutive rod produces a lower signal. The last two of the C44 solution stained rods did not give any signal at all. Most likely, this is related to the procedure to spot samples on the rods. More specifically, a precipitation of C44 on the walls of the (non-heated) application syringe was observed, which causes suspicion that not all of the sample is transferred to the rod. Therefore, the temperature of the toluene solution, and the syringe could be parameters needing better control in case of waxy or wax modified bitumens.

To sum up, the tests show that long chain waxes, like n-C44, do not contribute to the saturate peak in IP 469. One possible explanation was related to the insolubility of C44 wax in cold dichloromethane and toluene. As a result, this type of wax is most likely not a part of the analysed sample in normal IP 469 conditions. If transferred to the rod, it is most likely to become a part of polar II fraction, but a possibility of it contributing to polar I fraction when in blend is high, based on the collected chromatographs (Figure 3). For the short chain wax, n-C24, the sample contributed to the saturates part both as a pure substance and when in blend.

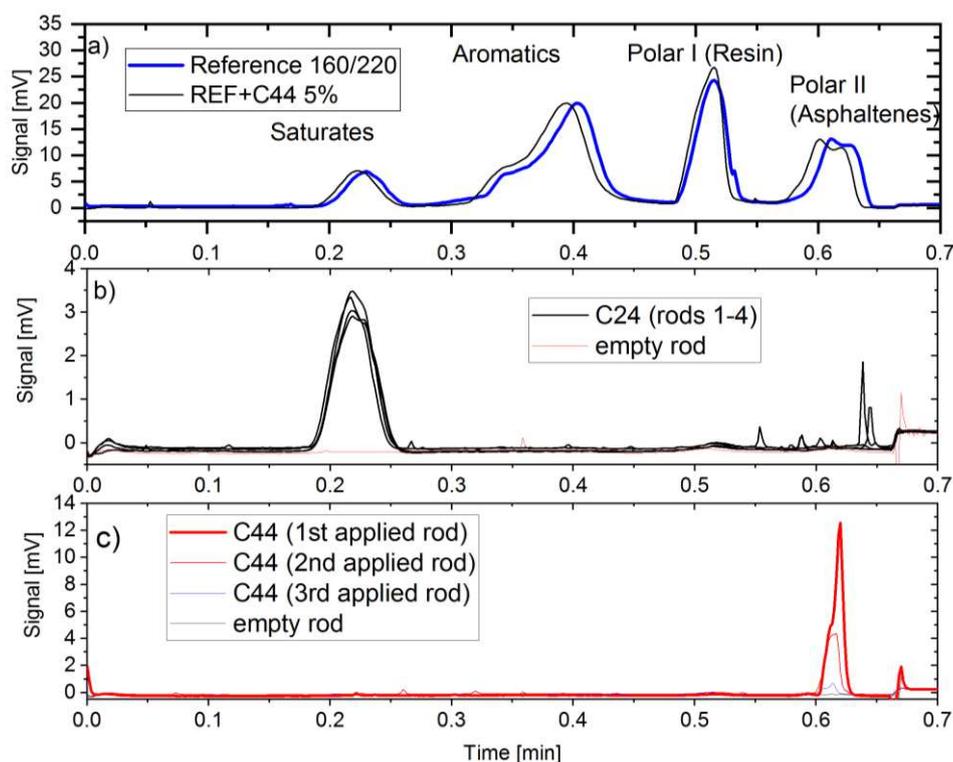


Figure 4: A typical chromatogram of reference bitumen (a), the chromatogram from four rods stained with C24 reference solution (b) and C44 reference solution (c). The scaling of the Y-axis is different in each graph.

3.3. Results of Lab 2

The results from Lab. 2 are presented in Table 5. From Lab. 2, data indicate that the n-alkanes were both not collected in the asphaltene fraction. So, using this method, and following it exactly will provide wax-free asphaltenes, at least as far as C44 n-alkanes are concerned. Nevertheless, the mass percentage of asphaltenes determined in the procedure IP 143, was not equal to the mass percentage of polar II fraction determined in the procedure IP 469 in Lab. 1. Using the term asphaltenes interchangeably for both procedures is not recommended.

Table 5. Results of Lab. 2.

Sample	Lab. 2:
	Asphaltenes (IP 143)
Ref. binder	11.6 ±1.4
Ref. +5% C24	12.1
Ref. + 5% C44	11.4

3.4. Results of Lab 3

In this laboratory a qualitative separation of asphaltenes was performed, according to IP 143, except for the last step, filtrating off the precipitated fraction in n-heptane being performed in cold n-heptane. For the three samples, the asphaltene fraction was analysed by HTGC. This is represented in Figure 4. The data show that for the asphaltenes from the Ref. sample, Fig. 4a, there is only a gradual curve, without discontinuing boiling signals, this is of course expected as this binder does not contain any waxes, so the asphaltenes should also not contain any wax fraction. The asphaltenes from Ref. binder +5% C24 (not shown) contained a very similar signal as the Ref. sample, indicating the lack of the wax presence. For the asphaltenes from the third sample, Ref. binder +5% C40, figure 4b, a clear high boiling peak is observed, which was identified as C40 by a calibration with standards. Its amount was estimated from the recovered masses to be around 15%.

In a next step, the 'IP 143 asphaltene' fraction of Ref. binder +5% C40 was tested after washing it with warm n-heptane at a temperature of 55°C. The results of this test are presented in Figure 4c. The data show that the amount of C40 has now decreased (scaling of the graph is different) and this time it is estimated to be around 5%. So, this shows that the temperature of the n-heptane is a crucial parameter governing the transfer of waxes into asphaltene

fraction. The postulate is that the controversy [30] on the subject of waxphaltenes, or asphaltenic waxes, should be rather turned into the discussion about the precision on reporting the parameters used during fractionation.

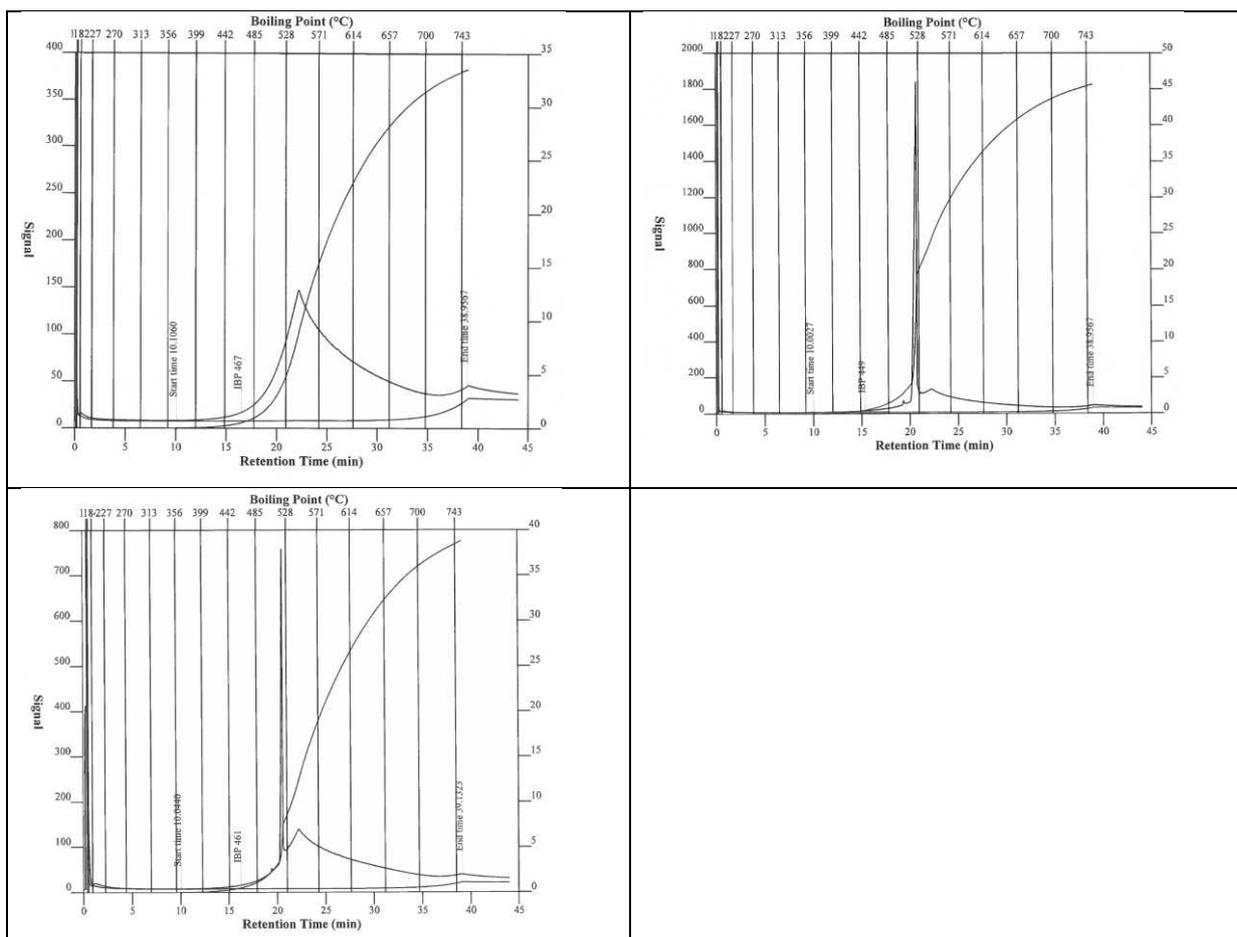


Figure 4: HTGC results of asphaltenes, (a) asphaltenes separated from ref. bitumen, (b) asphaltenes separated from ref. +5% C40 before washing with hot n-heptane (c) same as sample b after washing with n-heptane at 55°C.

3.5. Solubility tests

In order to visually demonstrate the differences in solubility of waxes, some solubility tests on C24 and C40 in n-heptane were conducted. A 10 %wt. solutions were prepared, and the solubility was followed visually. This is shown in Figure 5. The left part of the figure was taken at room temperature, and it is visible that the C24 readily dissolves (forms a transparent solution) while the C40 only dissolves fully after heating to 60°C. It is worth mentioning that solubility is both concentration and temperature dependant.

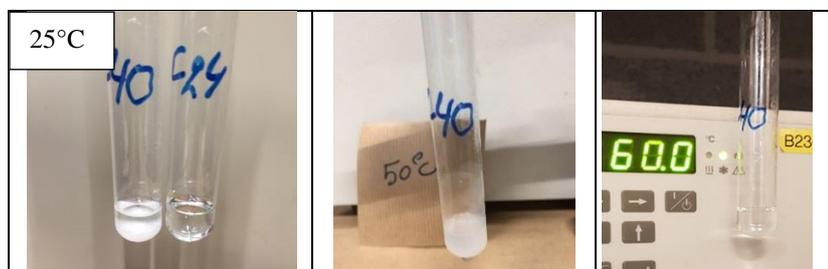


Figure 5: Solubility tests of C24 and C40 in n-heptane, 10w % solution, at different temperatures

4. CONCLUSIONS

The primary objective of this study was to identify if n-alkanes can become part of the asphaltenes, and the answer to this is positive.

In the IP 469, long n-alkanes, in this case C44 can fall into the polar II fraction, often referred to as asphaltenes. On the other hand, due to the physical phenomenon of hindered solubility of long chain alkanes in dispersing solvent, they may be even outside of the scope of this analytical procedure, thus invisible in the fractionation results.

In the case of IP 143, it was observed that the crucial parameter for the n-alkanes to be either asphaltene or saturate fraction is related to the temperature at which solutions are prepared, dissolved, filtrated and washed. If these temperatures are above the melting range of the n-alkanes they will dissolve and not stay in the asphaltene part. For the IP 143 method, provided that the method is correctly followed, n-alkanes, at least for chains \leq C44, will not stay in the asphaltenes and in fact as the norm states “wax-free” asphaltenes can be obtained.

Nevertheless, the “waxphaltenes” exist. Two compounds (C24 and C44), which by definition belong to the same chemical class of compounds, because of the difference in their physical properties (e.g. melting point, solubility) contributed to two different fractions, potentially creating a misunderstanding in respect of their chemical properties. In addition, specific conclusions can be made, for the test methods used in this paper.

It was observed, in case of the DSC analysis, that when adding well defined n-alkanes of a specific lengths to bitumen, the melting temperatures decrease and the signals broaden. It was observed that the recrystallization upon heating, often observed in bitumen and referred to as cold crystallization, is related to the presence of shorter alkane molecules, C18 and C24. The C40 and C44 did not show such a recrystallization.

In terms of IP 469, the temperature of the dispersing solution and the temperature of the syringe are postulated to affect the results and repeatability, especially in the wax rich bitumens.

Finally, the evaluation of IP 143 revealed that the drying time of the asphaltenes after filtration requires prolonging to assure full evaporation of toluene.

Importantly, comparison of numerical values between test procedures of IP 143 and IP 469, in terms of fraction content is not advised. The use of the word “asphaltene” for the 4th fraction obtained in IP 469 is misleading and is recommended to be abandoned, as is suggested by literature review, procedure instruction and hereby presented data. As a recommendation, when applying “asphaltene” term, one should always state the method of obtaining, specifying as many parameters as possible.

Finally, if n-alkanes can fall into the asphaltenes (IP 143) or polar II fractions (IP 469), this means that in some cases effects associated to asphaltenes could also be related to n-alkanes or wax molecules. This may possibly merge some of the different views and conclusions in literature, obtained after separating asphaltenes or adding n-alkanes to bitumen.

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