AN IMPROVED SCALABLE METHOD OF ISOLATING ASPHALTENES.

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ABSTRACT

A new, improved and scalable procedure of asphaltene fraction isolation is presented and compared to standard test methods. The new procedure uses 1:40 feedstock to solvent (n-heptane) ratio (g/mL), filtration through a cellulosic thimble and extensive washing in a Soxhlet type extractor. The group type composition and purity of the asphaltene fractions have been examined using thin-layer chromatography with flame-ionization detection. This study revealed that the new procedure provides a higher purity of asphaltene fraction resulting in a more accurate determination of its content in bitumens when comparing to the standard test method. Moreover, an attempt of evaluation of the scale-up possibility of the proposed and standard test methods was made, revealing that new procedure is more scalable than standard test methods. It is possible to obtain large quantities of a high purity asphaltene fraction even on a process scale. This feature is crucial for technical analytics, for researchers studying asphaltenes characteristic as well as for other novel applications of asphaltenes such as its use as sorbents in separation techniques.

1. Introduction

Asphaltenes are the most aromatic group of chemical compounds present in the crude oil and the heaviest products of its processing; they quantitatively remain in a residue from vacuum distillation. Due to their complex composition, asphaltenes are a class of compounds defined on the basis of solubility (Linton, 1894; Marcusson, 1911; Parr et al., 1909) rather than molecular structure. They are insoluble in n-alkanes *e.g.* n-heptane, and soluble in toluene or benzene (Ferris et al., 1967; Hubbard and Stanfield, 1948; Kleinschmidt, 1955; Mitchell and Speight, 1973; O'Donnell et al., 1951; Strieter, 1941). In terms of molecular structure, asphaltenes are polycyclic aromatic compounds (PACs) comprised of 4-10 fused aromatic rings, peripherally attached alkyl chains and polar functional groups *e.g.* carboxylic acids, phenol, and pyridines (Groenzin and Mullins, 2000; Mullins, 2011, 2010). They consist mostly of hydrogen and carbon, with H:C ratio of about 1-1.2, and additionally heteroatoms such as oxygen, sulfur, nitrogen and trace amounts of vanadium and nickel can be found in their backbone (Leyva et al., 2013; Trejo et al., 2004). Typical asphaltene molecules have an average molecular weight of 750 g/mole (Badre et al., 2006; Groenzin and Mullins, 2000; Pomerantz et al., 2015) and are arranged into planar type structures with a tendency to form nanoaggregates (about six asphaltene molecules) and clusters (about eight nanoaggregates) (Mullins, 2010; Pomerantz et al., 2015; Schuler et al., 2015).

Asphaltenes exhibit wide range of interactions *e.g.* van der Waals, Coulombic, hydrogen bonding, and π-π stacking (Murgich, 2002). Because of their physicochemical similarity to resins, asphaltenes exhibit strong sorption interactions with them. In solution, asphaltene-resin interactions can be favoured over asphaltene-asphaltene interactions (Speight, 2004). Resins can adsorb in the form of multilayers on the surface of the asphaltenes and penetrate their microporous structure (León et al., 2002; Liao et al., 2005). This is beneficial when considering stability of refinery process streams, as resins stabilize asphaltenes in colloidal form (Aguiar and Mansur, 2015; Andersen and Speight, 2001; Koots and Speight, 1975), but can be a drawback if the purpose is to isolate pure asphaltenes.

Asphaltenes are of crucial importance in the petroleum industry, mainly due to the several technological issues created by them in crude oil processing *i.e.* formation of emulsions, fouling, well-bore and pipelines clogging, coke formation, and catalyst deactivation in conversion processes (Akbarzadeh et al., 2007; Almehaideb, 2004; Idris and Okoro, 2013; Kokal and Sayegh, 1995; Ramirez-Jaramillo et al., 2006). Currently, asphaltenes are utilized only in the production of bitumens, bitumen mixtures and mineral rubber (Rostler and Sternberg, 1949). Their content in bitumen is increased by oxidation (air blowing process) (Moschopedis and Speight, 1975) for upgrading of primary properties of vacuum residue, measured by penetration, softening point and breaking point parameters. They describe the stiffness and behavior of bitumen in high and low temperatures of its usage.

Recently, Boczkaj et. al. (2016) showed that asphaltenes present the possibility of being applied as a sorbent in separation techniques. Their unique selectivity, high thermal stability and low production cost makes it an interesting material for stationary phases for gas chromatography, as well as for preparative and process separations (Boczkaj et al., 2016, 2015). However, current methods of isolation are not sufficient for providing large scale quantities of this material. Therefore a new method is required.

Traditionally, asphaltenes are isolated by means of precipitation with saturated hydrocarbons, such as *n*-pentane and *n*-heptane (ASTM D2007, 2003; ASTM D3279, 2001; ASTM D4124, 2001; ASTM D6560, 2000). Precipitation conditions *i.e.* type of solvent type, solvent to feedstock ratio, standing time and temperature have a significant impact on the yield of obtained asphaltenes and co-precipitated resins (Andersen and Birdi, 1990; H. Alboudwarej et al., 2002; Mitchell and Speight, 1973; Speight et al., 1984). Thus, asphaltene fractions isolated under different conditions are not identical and consequently have different properties. Although some groups indicate that the mechanism of precipitation is independent of the isolation method, but rather that the quantity of isolated asphaltenes is of the same magnitude, their characteristic should also be the same (Andersen and Birdi, 1990).

The type of solvent and its amount have the most evident effect on the precipitate. The yield of asphaltenes increases with increasing number of carbons in an n-alkane and reaches a plateau using n-heptane. The usage of n-heptane as a solvent is favoured when asphaltenes are the subject of research, because their properties are virtually stable for n-alkanes above n-hexane (Andersen and Birdi, 1990; H. Alboudwarej et al., 2002; Mitchell and Speight, 1973; Speight et al., 1984). Studies revealed that to provide efficient separation of asphaltenes, at least 30mL of solvent to each gram of feedstock is necessary (H. Alboudwarej et al., 2002; Speight et al., 1984). Although settling time can have a significant impact on the obtained asphaltene fraction purity, it varies considerably in standard test methods; from 30 minutes (ASTM D2007, 2003) up to 16 hours (ASTM D4124, 2001). Studies revealed that to ensure stable yields of asphaltenes, standing time of about 8-10h is needed. Extending this time above 16h may lead to the adsorption of resins from the liquid on the asphaltenes surface (Speight et al., 1984).

A number of studies investigated the effect of temperature on asphaltenes precipitation. However in this case, conflicting information emerges, with some report a decrease in asphaltenes yield with increasing temperature (Ali and Al-Ghannam, 1981; Mitchell and Speight, 1973) and the possibility of enhanced co-precipitation of resins (Speight et al., 1984), while others indicate increased yield in higher temperatures (Andersen, 1994; Andersen and Birdi, 1990; Hu and Guo, 2001). Andersen and Birdi (1990) observed an increased yield of precipitate followed by decrease after reaching maximum at 25 °C. He ascribed it to enhanced adsorption of smaller molecules and further rupture of those interactions (desorption of molecules) as the temperature increases further. However, the most recent studies seem to confirm a decrease in yield of asphaltenes with increasing temperature (Andersen, 1995, 1994, Andersen et al., 1998, 1997; Andersen and Stenby, 1996; Hu and Guo, 2001; Maqbool et al., 2011) and a lower content of resins when precipitation is carried out at higher temperatures (Pineda et al., 2007). UV fluorescence studies revealed that when temperature decreases more compounds with smaller fused rings precipitate. Conversely, when the precipitation temperature increases, the isolated fraction is dominated by larger aromatic structures (Andersen and Birdi, 1990). This result is supported by molecular weight studies, as molecular mass increase when asphaltenes are precipitated at elevated temperatures. Another consequence of increased precipitation temperature is higher aromaticity (*i.e.* lower H/C ratio) and polarity of isolated fraction (Andersen, 1995, 1994; Andersen et al., 1997; Pineda et al., 2007). In the scope of the definition and up-to-date structural information about asphaltenes, as well as being insoluble in n-alkanes and consisting of aromatic core of 4-10 fused rings, the variation of temperature affects the precipitate yield due to the co-precipitation of smaller molecules (e.g. resins). Although, one need to remember that there is no distinct border between asphaltenes and resins.

The last step of almost all precipitation procedures include washing of the isolated asphaltenes, is to remove adsorbed resins as well as other components of the primary material (ASTM D2007, 2003; ASTM D3279, 2001; ASTM D4124, 2001; ASTM D6560, 2000). If asphaltenes-resins interactions are adsorptive, then it should be possible to remove resins with re-precipitations and/or intensive washing with the correct solvent. The second phenomenon that can hinder the isolation of pure asphaltenes is to block access of the solvent by occlusion, thus retaining resins (or generally other than asphaltene fractions) by asphaltenes (Derakhshesh et al., 2013; Liao et al., 2006, 2005; Strausz et al., 2006). Although, the importance of the washing step is recognised intuitively, it is the most imprecise and ambiguous step. Usually it is performed on a filter with the solvent used for the precipitation. A common criterion is to continue washing until the effluent is colourless (ASTM D4124, 2001). This implies arbitrariness and leads to different extents of washing. Another popular method of washing is to use a reflux extractor (ASTM D6560, 2000). Results presented in (H. Alboudwarej et al., 2002) revealed that using Soxhlet’s extractor led to removal of 22% w/w of maltenes from filter-washed asphaltenes.

As we have shown, a number of methods and refinements exist to isolate asphaltenes, but none allow for large scale production of a consistently pure product.

Therefore, the aim of this paper was to propose simplified, reproducible, easy to scale – up procedure of asphaltenes isolation, which will give at least similar results as the standard test method. It would be of great importance, not only for studies in our research group (Boczkaj et al., 2016), but for researchers studying asphaltenes characteristic and technical analysis of petroleum products as well. Usually asphaltenes are characterized by their average properties *e.g.* elemental composition and molar mass. In this paper, thin-layer chromatography with flame ionization detection (TLC-FID) was used to compare group type composition of asphaltene fractions obtained by studied methods. Moreover operation effectiveness, scale-up possibility as well as economic aspects of this methods were evaluated.

2. Experimental

2.1. Materials

Bitumen 20/30 SDA (Lotos Group, Gdansk, Poland) and n-heptane EMPLURA® (Merck, Germany) were used to isolate the asphaltene fraction. Depending on the isolation method used, mixture was filtered through a 0.45μm PTFE membrane filter (Achrom, Belgium) or a standard single thickness 33x100mm cellulose thimble (VWR, United States). During hydrocarbon group type analysis of the isolated fractions, the following analytical grade chemicals were used: dichloromethane (POCH, Poland), methanol (POCH, Poland), toluene (POCH, Poland) and hexane (Merck, Germany). To filter samples prior to analysis, 0.45μm PTFE syringe filters (Achrom, Belgium) were used.

2.2. Apparatus

To perform filtration a vacuum glass set (Glassco, India) was used. Isolated samples were washed in a Soxhlet type extractor. Weight measurements were performed with a WLC 6/A2 (readability 0.1g) and WPA 180/C (readability 0.1mg) balances (RADWAG, Poland).

To analyze the group type composition of the isolated fractions by means of TLC-FID technique an Iatroscan Mk.V (Iatron Lab., Japan), silica gel Chromarods S5 (Iatron Lab., Japan), 3200/IS-01 semiautomatic sampler (SES, Germany), 7102KH 2μL syringe (Hamilton, USA), TLC TK-8 Chromarods dryer (Iatron Lab., Japan), chromatographic chambers, AD converter, and corresponding software (Chomik, Poland) were used.

2.3. Procedures

2.3.1. Asphaltene fractions isolation

2.3.1.1. Procedure ASTM D4124

The reference samples of asphaltene fraction were isolated using the conditions described in ASTM D4124 (ASTM D4124, 2001). As a reference standard method of isolation ASTM D4124 was selected, because it exploits high solvent to feedstock ratio (100mL : 1g), long contact time (ca.16h) and extensive washing of isolated asphaltenes (till effluent is colorless). This should ensure high purity (low content of resins) of the asphaltene fraction. Bitumen was heated in an oven at 70^{o}C for 1h and 6g (weighed to the nearest 0.1g) were placed in 1L flask, which was gently heated to disperse bitumen on the bottom and lower sides of the flask. Next, the n-heptane was added in the ratio of 100mL per 1g of bitumen. The mixture was heated to boiling and refluxed for 1h with occasionally stirring. After the mixture was allowed to cool for 16h, it was filtered through 0.45μm PTFE membrane filter under the vacuum. The precipitate was washed with hot n-heptane until a colorless filtrate was obtained. The filtrate was consequently washed with 80mL of fresh n-heptane, and heated for 30min with occasional stirring and filtered again through a fresh tared PTFE membrane filter. The asphaltene cake was washed with hot n-heptane till the filtrate was colorless, dried (1h at 100°C) and weighed.

2.3.1.2. Procedure B1 and B16

The novel procedure of isolation proposed and tested in this paper is as follows: bitumen is heated in an oven at 70^{o}C for 1h and 15g of it is placed in 1L round-bottom flask. The flask is gently heated to disperse bitumen on the bottom and lower sides of the flask. Next, the n-heptane is added in the ratio of 40mL per 1g of the bitumen. The mixture is brought to a boil and refluxed for 1h with occasional stirring. Then it is set aside for 1h (procedure B1) and 16h (procedure B16) to cool and the content of the flask is filtered through a tared cellulose thimble. In procedure B1 the filtration started at temperature of the mixture being 55 °C, and in B16 procedure at 20 °C. The thimble is placed in a Soxhlet extractor and washed with n-heptane for 24h. Next, it is dried at 100^{o}C for 1h and weighed.

Figure 1 and 2 present steps of standard and proposed procedures for isolation of asphaltene fraction and experimental glassware setup, respectively.

2.3.2. Hydrocarbon group type analysis of isolated fractions.

The group type composition of bitumen and the isolated fractions was investigated by TLC-FID technique which allows a relatively fast analysis. A normal phase separation mechanism is used, resulting in a so-called SARA (Saturates, Aromatics, Resins, Asphaltenes) analysis. In this conditions asphaltenes are defined as a group of compounds having the highest retention.

Samples were prepared by dissolving the samples in dichloromethane to yield concentration of 2 mg/mL. This prevents overloading of the stationary phase and leads to a better separation of asphaltenes and resins. To remove any undissolved particles, the samples were filtered through 0.45μm PTFE syringe filters. Before spotting the samples, the Chromarods were activated in the flame of FID detector: once in time of 35s and twice in 50s. Then, they were placed in desiccator for 10min to cool down.

1μL of the samples were spotted in a small aliquots on the three Chromarods each, to obtain quantitative results. Next, the Chromarods with the spotted samples were placed in the dryer (set to 70°C) for 3min. A three-step elution sequence was used, with eluents in the following order:

1. dichloromethane:methanol (95:5 v/v) elution up to 45% of a stationary phase height
2. toluene elution up to 80% of a stationary phase height
3. n-hexane (95% water saturated) elution up to 100% of a stationary phase height

The set of solvents used in this work is a typical set used for hydrocarbons group type analysis of petroleum heavy fractions using TLC-FID technique (Sharma et al., 1998).

However, atypical is the sequence of the elution, which is contrary to what can be typically found in literature (Jiang et al., 2008; Sharma et al., 1998). In our work we developed the Chromarods beginning with the solvent ensuring the elution of asphaltene fraction. It follows from the high amount of asphaltene in the sample which are not solubilized and eluted by n-hexane (which is used as the first solvent in typical procedures). In our opinion fractions other than asphaltenes (i.e. saturates and aromatics) can be trapped under asphaltenes and shielded/covered by them, hence not eluted by the n-hexane used as first solvent. First solvent (dichloromethane:methanol) eluted all components of the spotted sample and increased accessibility of two other solvents to the whole amount of the sample. This approach was validated in our lab during a series of quality control analysis of bitumen, performed for a local refinery in Gdansk.

Each TLC chamber was lined with chromatographic paper, filled with eluent and left for saturation for 15min. The Chromarods were placed in the chamber and eluted accordingly. Before elution with toluene and n-hexane the frame with rods was held in headspace of eluent for 5 min to saturate the stationary phase with vapors of the eluent. After each elution step the rods were dried for 3min (or longer if a scent of a solvent was noticeable) and left in desiccator for 10 min to cool down.

Detection was carried out in a TLC-FID analyzer. Rod scanning time was set to 35s, hydrogen and air flow were 150mL/min and 1800mL/min respectively. Chromatograms were integrated with a normalization method. Obtained results were used comparatively for evaluation of purity of asphaltene fraction obtained by means of studied in this paper methods of isolation.

2.4. Quality assurance of data.

The average results for isolation of asphaltene fraction, by each procedure, are the mean values of three separate isolations. The average yield is a mass ratio of asphaltene fraction and feedstock (bitumen). For TLC-FID analysis, each sample was spotted on three rods to provide quantitative data. The average of asphaltenes content was calculated as a mean of the means for individual samples isolated with given procedure. The relative standard deviation (RSD%), which expresses the precision and repeatability was calculated as a ratio of standard deviation to the mean value of asphaltenes content, multiplied by one hundred.

To compare the accuracy of investigated procedures, mean results (which were obtained by the same analyst) were evaluated by means of F-Snedecor test, to confirm the homogeneity of variances and next with t-Student test. t-Student test is used for determining whether the observed difference between obtained means is statistically significant or not. F-Snedecor test is performed to check whether the variances of the two samples are equal and if t-Student test without correction can be used.

3. Results and discussion

Figure 3 shows exemplary TLC-FID chromatograms (SARA analysis) of analyzed sample isolated by B1 (B) procedure and feedstock bitumen (A). A baseline separation between resins and asphaltenes is obtained, allowing to control the precipitation.

Table 1 presents results of TLC-FID analysis of obtained asphaltene fractions. Table 2 presents differences between values of parameters given in Table 1 for the tested procedures.

Isolated asphaltene fractions were dark brown, black mat solids. Quantitative analysis revealed some differences which are consistent with obtained yields of asphaltene fractions. It is clear from data in Table 1 that ASTM standard test method has a false positive error i.e. it reports higher content of asphaltenes in bitumen due to the presence of impurities of resins fraction co-precipitating or adsorbing on asphaltenes. The studied alternative procedures exhibit an improved purity of obtained asphaltene fraction. It is possible, that in the case of bitumens having lower content of asphaltenes and higher of resins, this error for ASTM methods would be higher.

The average result of asphaltene fraction yield was 10.14 % w/w from the ASTM D4124 procedure and 8.79 % w/w from the new B1 procedure. This difference is mainly the result of lower resins content when proposed B1 procedure is used. These conclusions are supported by the TLC-FID data, which revealed that the asphaltenes content in isolated fraction is higher by 1.59% for B1 procedure.

The lowest yield of asphaltene fraction was obtained for our procedure with B1 contact time. At the same time this procedure gave the highest purity of asphaltenes. This indicates that B1 procedure, involving the washing in the Soxhlet, washed out more maltenes than the ASTM D4124, in which washing of the filter cake is performed manually. Additionally, the developed procedures have improved reproducibility, as the RSD% value is lower, comparing with ASTM method.

The second variant of the procedure, in which contact time was the same as in ASTM D4124 method, gave the results between standard and B1 procedures. The yield of asphaltene fraction was higher and purity of asphaltenes lower than in B1 procedure. Probably, it is due to a lower temperature of a mixture at the beginning of filtration and resulting higher adsorption of resins in B16 procedure. Still, this method provided higher purity of asphaltenes than ASTM method. This result clearly indicates the problem of the presence of resins fractions in precipitated asphaltenes fraction, which is almost completely solved in the developed method for optimized conditions of settling the solution, filtration and Soxhlet extraction stages.

The precision and repeatability of each procedure was sufficient and comparable, as the RSD% value was below 5% (Table 1). Table 3 presents values of calculated and critical parameters for the t-Student and F-Snedecor test. The t-Student test revealed statistical difference between mean results for ASTM D4124 and proposed B1 procedure. No statistical difference was observed for B16 and ASTM D4124 method. Between B16 and B1 procedures difference in purity of asphaltene fraction was insignificant, while difference in yield of asphaltene fraction was slightly significant. Comparison of standard deviations revealed that both proposed methods were slightly more precise than the standard test method.

As abovementioned, the goal of this research was to develop simple, cost-effective and easy to scale-up procedure of asphaltenes isolation which will give at least similar results, in terms of asphaltene purity, as standard test method. This has been achieved by lowering the feedstock to solvent ratio from 1g per 100mL to 1g per 40mL (this ratio is reported in some of ASTM methods as allowable) along with modification of purification step. As shown in Table 4 solvent consumption in B1 procedure was calculated as three times lower than in ASTM D4124. For ASTM D4124 calculation has been made on the basis of the amount of the solvent used in abovementioned experiment, while for the other two standard test methods quantities of solvent and feedstock specified in standard test method were used.

The studies revealed, that washing step is crucial for final asphaltenes purity. Lower solvent consumption allowed the use of bigger quantities of feedstock without fall-off in asphaltene fraction purity (in fact, a higher purity was obtained). This may be not only important for process scale isolation, but also in terms of asphaltenes research. Due to the high complexity of petroleum and its subfractions, asphaltenes are still relatively unknown and poorly studied group of chemical compounds. One of the difficulties associated with the correct characterization of asphaltenes is the lack of one universal and standardized method of isolation. Different research teams isolate asphaltenes by means of different ASTM or other standard methods described in the literature or perform isolation by means of their own developed procedures. This affects strongly the purity of asphaltenes and reproducibility of results, thus making comparisons limited. Proposed simple, reproducible procedure giving high quantities of asphaltene fraction with very low resins content is an important contribution to this issue.

Table 4 compares selected parameters of investigated procedures and two additional standard test methods.

Time consumption

B1 procedure is the most time consuming but it is caused by the most extensive washing among compared procedures. This extended purification is a must to obtain pure asphaltenes fraction and accurate results of determination.

In the case of standard test methods the isolation procedure time can be extended by problems with filtration rate. When isolating asphaltene fraction according to ASTM D4124-01, 0.45µm PTFE filters were used and especially in the case of higher amounts of asphaltene fraction, the filters have tendency to clog, thus decreasing the rate of filtration and significantly increasing the time of the filtration stage. The same issue may be observed in ASTM D3297 and D6560 procedures which utilize glass filter pads and cellulose quantitative filters, respectively. In B1 procedure filtration under vacuum with sub micrometer filter was replaced with simple filtration through cellulose thimble, in which the washing step is carried out later. No issues with filtration were observed when filtering through thimble and filtrations were completed in time under 15 minutes. To check if no asphaltenes are going through thimble during filtration, effluent was filtered through 0.45µm PTFE membrane filter and no solid particles were retained.

Solvent consumption, washing and purity of asphaltene fraction

The B1 procedure has the lowest solvent consumption yet the most extensive washing of the isolated fraction, giving the highest purity of asphaltene fraction. ASTM D3279 procedure consumes almost three times more solvent than B1 procedure and washing step is very limited. Although there is no data available about purity of asphaltene fraction isolated with ASTM D3279, because it is similar to ASTM D4124, the purity probably will not exceed the one obtained with ASTM D4124.

ASTM D6560 uses similar amount of n-heptane but incorporates dissolution/re-precipitation with toluene. It also involves washing in reflux extractor. However, contrary to Soxhlet extractor used in B1 procedure, it is constructed in a way that the solvent is constantly drained from sample. In Soxhlet extractor a chamber is flooded with hot solvent and periodically emptied by siphon. This ensures longer contact time and in case of bigger sample the whole asphaltene fraction should be evenly washed. ASTM D6560 procedure is somewhat alike to B1 in terms of solvent consumption and washing and can yield asphaltene fractions of similar purity.

Arbitrariness and laboriousness

Filtration in thimble and further Soxhlet washing allowed to omit a part of ASTM D4124 test method in which filter cake is transferred to beaker for extra washing and avoid manual washing of filter cake, which lowered the labor consumption and reduced arbitrariness.

Washing of asphaltene fraction in Soxhlet for a fixed amount of time eliminates the necessity of setting arbitrary end time of washing. Arbitrariness was evaluated on the basis of the precision of end points. In case of B1 and ASTM D3279 procedures end points are quantitative whereas in ASTM D4124 it is qualitative (color of effluent). In ASTM D6560 the washing step end point is measured in hours, however it is not fixed and only minimal time of washing is given.

Scaling up/automation

Table 5 presents the results of scaling up possibility evaluation. To estimate scaling up difficulty, the isolation process was divided into three parts: precipitation, filtration and washing. To every stage two numbers were ascribed: one representing its significance (wage) and second one describing difficulty of scaling up this stage. Difficulty was multiplied by significance of considered step and sum of those multiplications was treated as scaling up possibility parameter. Table 6 presents scale which was used to determine overall scale up possibility of the procedure.

Precipitation step was considered as having the lowest significance for the differentiation of the procedures because in every procedure it is conducted in the same way and only volume of a solvent differs. This difference was used to determine difficulty of scaling up. The bigger the feedstock to solvent ratio the bigger the vessel needed for precipitation step.

When evaluating filtration step, time and power consumption were taken under consideration. In case of ASTM D4124 significant problems with filtration resulting in extended filtration time were discussed above. Additionally in ASTM D4124 and D3279 procedures vacuum is used for filtration which increases power consumption. Those remarks are also true for washing step.

Due to the availability of wide range of Soxhlet dimensions, proposed procedure can be easily scaled up, from laboratory scale to automated. Continuous washing with hot solvent is also easier to implement on a process scale, than filtration through sub micrometer filters. Moreover, in B1 procedure after filtration asphaltenes remain in thimble in which they are washed and it should be easy to make it “one-pot” process. Additionally in B1 procedure asphaltenes are not dissolved in toluene after washing with n-heptane as in ASTM D6560 and there is no need for evaporation to reprecipitate asphaltenes.

Safety

Conducting purification step in Soxhlet extractor reduces risk to safety and health. In ASTM D4124 procedure washing with hot solvent is done manually and redissolving of asphaltene fraction in hot n-heptane takes place in an open beaker. The lack of proper attention can lead to overheating of the mixture, which may result in bumping, thus representing a hazard.

4. Conclusion

The procedures of asphaltene fraction isolation developed and tested in this paper provided higher purity of isolated fractions (containing less resins) and are characterized by improved reproducibility and precision comparing to standard test method, which is corroborated by the RSD% values.

Implementation of filtration through cellulose thimble and washing off isolated fraction in Soxhlet extractor is less laborious, less arbitrariness and easy to scale-up. This simplicity makes the scale-up easier which in connection with smaller solvent consumption per 1g of feedstock can lead to obtaining higher quantities of asphaltene fraction, which may be especially interesting for researchers working on characterization of asphaltenes *e.g.* structural analysis and further if kilograms of asphaltenes are needed for different studies. In this field particularly important are studies on bitumen properties related to asphaltene content and their physico-chemical character.

As abovementioned, asphaltenes are currently under investigation in terms of their sorption properties and employing them in separation techniques (Boczkaj et al., 2016, 2015). Such sorbents can be used in process scale separations or as a stationary phase for gas chromatography. In this case further scaling-up will be needed and previously mentioned advantages of proposed procedures can be crucial for isolating large quantities of this material. Furthermore, in process scale isolation, washing step can be based on the same principle as in Soxhlet extractor (recirculation of the hot solvent) and in turn will result in cost reduction of this step.

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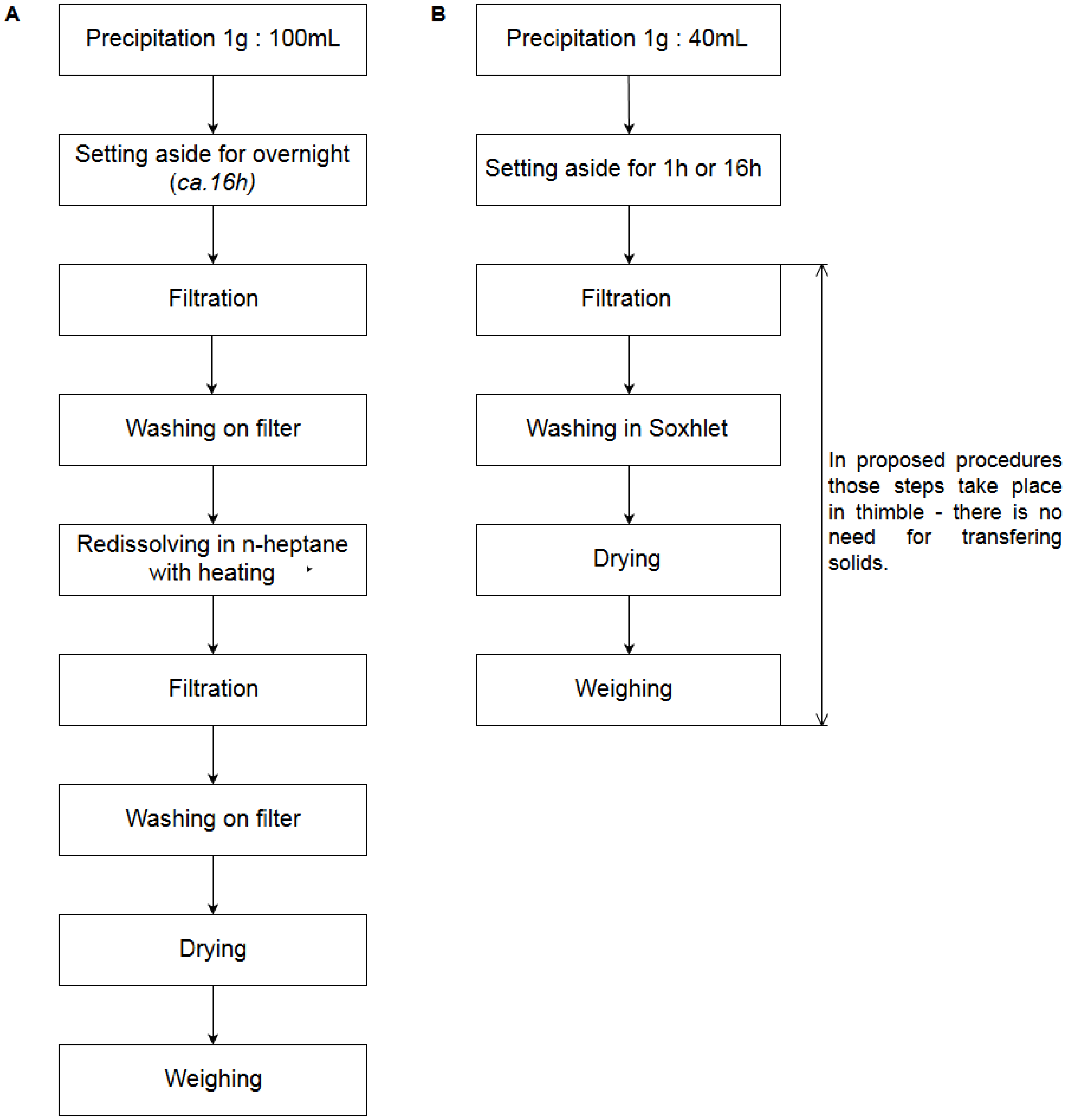

Figure 1. Scheme of studied procedures for isolation of asphaltene fraction. ***(SINGLE COLUMN)*** *A) standard test method ASTM D4124. B) Proposed procedures. For two tested variants B1 and B16 the scheme is the same, only time of setting aside changes (1h vs 16h).*

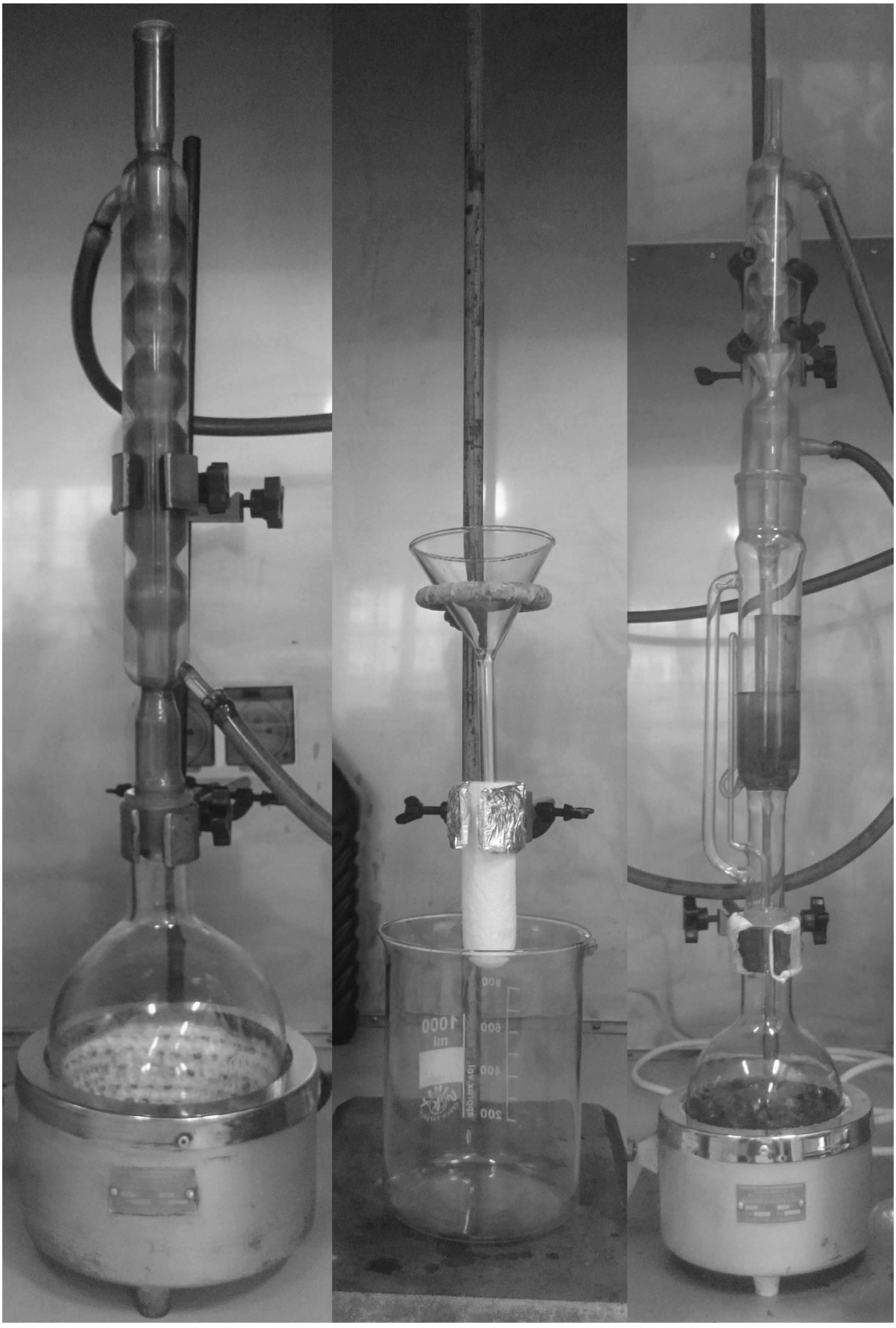

Figure 2. Experimental glassware setup. From left: precipitation set, filtration set, washing (Soxhlet) set. ***(SINGLE COLUMN)***

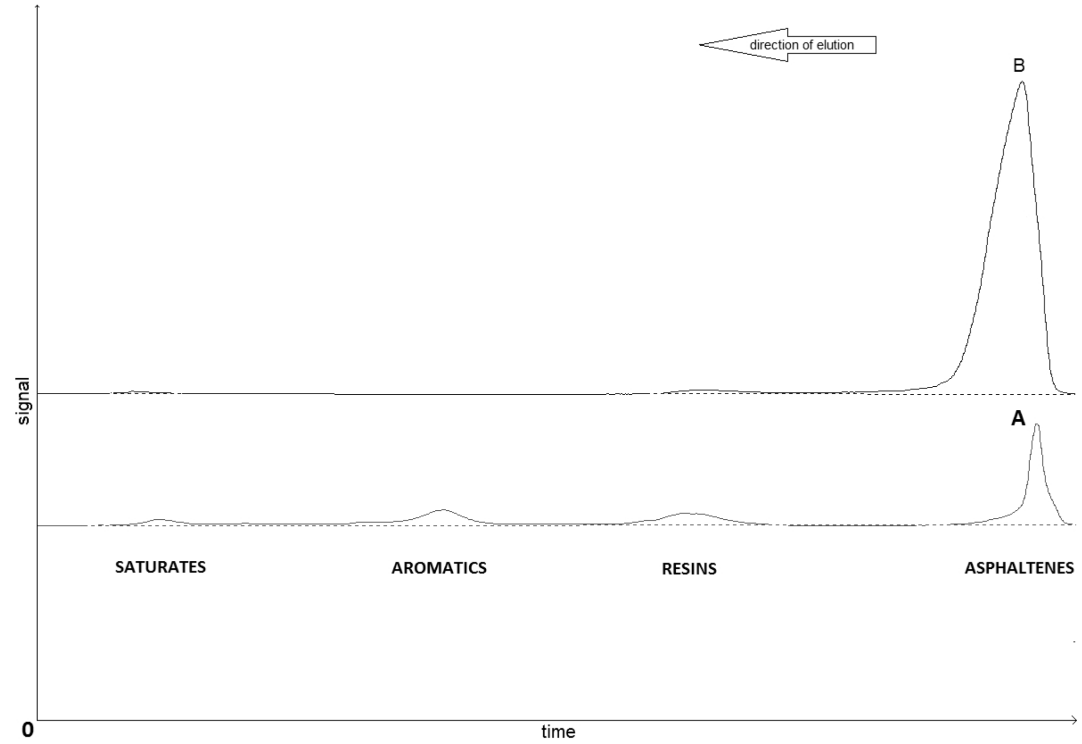

Figure 3. Exemplary TLC-FID chromatograms of SARA fractionation. ***(1.5-COLUMN)***
A) feedstock – bitumen 20/30 SDA and B) the asphaltene fraction isolated with tested B1 procedure.

*Table 1. Comparison of asphaltenes isolation results obtained with tested procedures.****(2-COLUMN)***

Method	**ASTM D4124**			**B16**			**B1**		
	Mean	**STD**	**RSD%**	**Mean**	**STD**	**RSD%**	**Mean**	**STD**	**RSD%**
Yield of asphaltene fraction [% m/m]	10.14	0.46	4.49	9.59	0.32	3.34	8.79	0.35	3.99
Asphaltene fraction purity[%]	95.80	0.30	0.31	96.49	0.47	0.49	97.39	0.76	0.78

Table 2. Differences between results for tested procedures. ***(1.5-COLUMN)***

	ASTM D4124 – B16	**ASTM D4124 – B1**	**B16 – B1**
Yield of asphaltene fraction [% m/m]	0.55 ± 0.14	1.35 ± 0.11	0.80 ± 0.03

Asphaltenes content [%]	0.69 ± 0.17	1.59 ± 0.46	0.90 ± 0.29

Table 3. Comparison of variances and means for two sets of results. ***(1.5-COLUMN)***

	ASTM D4124 – B16	**ASTM D4124 – B1**	**B16 – B1**
	F-Snedecor		
	F_{cr} ($\alpha=0.05$, $f_1=f_2=2$) = 19.00		
	F		
Yield of asphaltene fraction [% m/m]	2.07	1.73	1.20
Asphaltenes content [%]	2.45	6.42	2.61
	t-Student		
	t_{cr} ($\alpha=0.05$, $f=n_1+n_2-2=4$) = 2.776		
	t		
Yield of asphaltene fraction [% m/m]	1.70	4.04	2.92
Asphaltenes content [%]	2.14	3.37	1.74

Table 4. Comparison of procedures for isolation of asphaltene fraction. ***(2-COLUMN)***

	B1	**ASTM D4124-01**	**ASTM D3279-07**	**ASTM D6560-00 (IP 143/01)**
Time consumption	*ca.* 28h	*ca.* 20h	*ca.* 3h	*ca.* 10h
Solvent consumption	50 mL/g	*ca.* 150 mL/g	*ca.* 130 mL/g	*heptane: ca.* 50 mL/g toluene: *ca.* 10 mL/g
Washing	24h Soxhlet	on filter washing, until filtrate is colorless	on filter, 3 x 10mL	min. 1h reflux extractor
Laboriousness	+	-	+	- -
Purity of asphaltene fraction	97.39 ± 0.76	95.80 ± 0.30	NA	NA

Scaling up/automation	easy	difficult	moderate	moderate
Safety	safe	hazardous steps	safe	safe
Arbitrariness	++	-	++	+

Table 5. Collation of grades ascribed to isolation process stages describing its importance and difficulty of scaling up. ***(2-COLUMN)***

Stage	**Wage**	**B1**		**ASTM D4124-01**		**ASTM D3279-07**		**ASTM D6560-00**	
		Difficulty	**Mult.**	**Difficulty**	**Mult.**	**Difficulty**	**Mult.**	**Difficulty**	**Mult.**
Precipitation	1	2	2	4	4	4	4	2	2
Filtration	2	2	4	5	10	3	6	3	6
Washing	3	2	6	4	12	3	9	4	12
Scaling up parameter			12		26		19		20

Table 6. Scale used to determine the possibility of process scale up. ***(SINGLE COLUMN)***

Scaling up parameter	Scaling-up difficulty
≤ 15	easy
15-20	moderate
> 20	difficult