

Rapid and Simple Method for Measuring Petroleum Asphaltenes by the Centrifugation Technique

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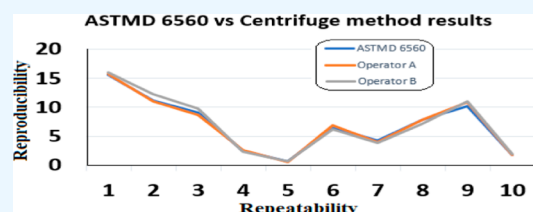
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ABSTRACT: Asphaltenes are heavy constituents of crude oil which affect the flow and viscosity of crude oil. They also stabilize water-in-oil emulsions which makes the separation process of water from oil during the primary treatment processes for crude oils more difficult and costly. Measuring asphaltenes has great importance, especially for crude oil production companies. Gravimetric and spectroscopic measurement methods are the basic techniques used by international references such as ASTM and IP. A new methodology has been introduced as a modification of ASTM D6560 gravimetric methodology by using the centrifugation technique in the separation of asphaltenes for different oil samples with the API gravity change from 17.4 (oil S1) to 39.8 (oil S5). The new methodology has the advantages of consuming little time, and multiple sample processing and can be done in the field and also in the lab. Moreover, it has good repeatability, reproducibility, and working range values compared to the reference gravimetric ASTM and IP methods. The repeatability of the new method was found to be 8.0% at its maximum value (S1, has a low asphaltene content), while the minimum value was found to be 3.75% (S10, has the highest asphaltene content). It was found that the maximum reproducibility value was 17.0% for the S1 sample and the minimum was 0.0% for S9 and S10 samples.



1. INTRODUCTION

Crude oil is a naturally occurring hydrocarbon mixture, generally in a liquid state, which may also include compounds of sulfur, nitrogen, oxygen, metals, and other elements.¹ It is difficult to know its detailed elemental composition, but it contains mainly the following groups of compounds: saturated hydrocarbons (paraffin and naphthenic), unsaturated hydrocarbons (olefins), and aromatic hydrocarbons.²

Asphaltenes are aromatic polycyclic compounds with a high molecular weight and low hydrogen/carbon ratio; actually, they are the heaviest components of crude oil. They contain most of the heteroatoms (O, N, and S) in their structure that are present in crude oil. They also contain traces of metals (nickel and vanadium).³

The “asphalting” name was initiated by Boussingault in 1837 when he found that the residue of some bitumen distillation had asphalt-like properties.⁴

They have been recently defined as the insoluble fraction of crude oil in low-molecular-weight alkanes (e.g., hexane and heptane) and are soluble in low-molecular-weight aromatic solvents (e.g., benzene and toluene).⁵ Because of their high molecular weight and relatively high polarity, they are solids at room temperature with relatively high melting points. They are present in a colloidal form in crude oil due to their incomplete solubility in the crude oil mixture that is because of their complicated macromolecule structure. Therefore, they increase

the viscosity of the crude oil. They also attract emulsified water and stabilize water/oil emulsions due to their strong polarity, which makes the first-stage treatment of crude oil challenging and time- and money-intensive. Asphaltenes also have a critical effect on crude oil transportation, storage, and refining processes.^{6,7} A lot of methods have been developed to quantify asphaltenes in crude oil: gravimetric methods (ASTM D6560 and IP143),^{5,8} optical spectroscopy on microfluidic films (ASTMD 7996: 2015),⁹ and on-column precipitation and redissolution.¹⁰ The viscosity of crude oils is increased by asphaltenes.

The ASTM D6560/IP143 gravimetric procedures, which are currently used to assess asphaltene content, require a lot of solvents and take a long time to complete.¹¹ These approaches also suffer from relatively high error rates, which is likely a result of the intensive sample modification. For instance, the standard test ASTM D6560 has a repeatability and reproducibility of 10 and 20%, respectively.⁵

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Table 1. Samples' General Properties

crude oil samples	properties						
	API	specific gravity	water (v/v %)	sulfur (wt/wt %)	kinematic viscosity (CSt)	pour point (°F)	asphaltenes (wt/wt %)
	ASTMD5002	ASTMD5002	ASTMD4006	ASTMD4294	ASTMD443	ASTMD5853	ASTMD6560
S1 (Behar field)	39.8	0.826	0.1	0.2	0.9	55	0.6
S2 (Behar-Shukair sample)	37.2	0.8388	0.2	0.6	3.2	50	1.8
S3 (Shukair sample)	33.7	0.8565	0.3	2.2	6.5	45	2.5
S4 (Yusr sample)	28.9	0.8822	0.1	1.4	14.6	40	4.2
S5 (Ghareb sample)	24.9	0.9047	0.3	1.8	75	40	6.5
S6 (Hamd sample)	22.7	0.9176	0.7	2.7	86.8	40	7.8
S7 (Bakr-Ghareb)	21.1	0.9273	0.3	3.5	89	40	9.1
S8 (North Bakr sample)	19.4	0.9377	0.6	3.3	188	40	10.2
S9 (Bakr field)	18.5	0.9433	0.6	3.7	302	45	11.2
S10 (South Bakr field)	17.4	0.9503	1.2	4.2	830	45	15.6

There are several methods for quantifying the asphaltene content in crude oil.⁸ The international reference methods are ASTM D6560 and IP143; they are the most widely used methods. These methods are classified as gravimetric methods which depend on the separation of asphaltenes from crude oil by precipitating them using heptane and refluxing the sample dissolved in heptane for a suitable time. The sample is then filtered through specified filter paper, and then the precipitated asphaltenes are weighed. The gravimetric method covers the quantification range of 0.5–30% asphaltenes, but it is time-consuming, cannot be done in the field, and consumes a relatively large sample quantity.

The spectroscopy method was another method recently developed by ASTM (ASTMD 7996-2016) as a sensitive method to collect the visible spectrum of asphaltenes in crude oils and petroleum products containing residual material using a microfluidic technique for asphaltene quantification. The oil sample is dissolved in heptane to precipitate asphaltenes. The precipitated asphaltenes are removed using a filter paper. The change in the visible spectrum of the sample before and after precipitation is due to the removal of asphaltenes. The visible spectrum of asphaltenes obtained using this technique is proportional to the concentration of the precipitated asphaltenes.⁹ The test is intended for samples with an asphaltene content less than 15% by mass, which need a UV–visible spectrophotometer and a microfluidic mixer, and cannot be done in the field with portable instruments.

Schabron and Rovani¹⁰ developed a new automated separation method that allows the quantification of asphaltenes using on-column precipitation and redissolution of asphaltenes. The on-column separation of asphaltenes was first developed by Boduszynski et al.¹² Heptane, pyridine, and toluene were used to dissolve and extract coal liquids deposited onto an inert column packing. Later, a similar technique of sequential extraction fractionation was applied to separate petroleum residues into different solubility fractions.¹³ These early attempts at the use of the technique pointed out that the packing material and the detection technique were two key aspects in the development of a more practical and faster methodology. In particular, it was important to use a packing material able to retain the asphaltenes based on a filtration process and not by adsorption.

An improved high-performance liquid chromatography (HPLC) analytical method for the measurement of asphaltene content in crude oils and petroleum products was reported by Schabron in 2009.¹⁰ He used an on-column precipitation and

redissolution technique coupled with an evaporative light scattering detector. The method requires a small amount of sample, takes few minutes, and has a minimum quantification limit of about 120 ppm with a relatively low error.

HPLC methods generally have the main disadvantage of the requirement of a sophisticated HPLC system and experienced operators, and they cannot be done in the field with portable instruments.

In the present work, a simple method was developed to make the determination of asphaltenes less time-consuming, available to do in the field portably, and have acceptable repeatability and reproducibility compared to the reference ASTM gravimetric method with no sophisticated instruments.

2. RESULTS AND DISCUSSION

2.1. Result Comparison. Crude oil samples from different wells listed in Table 1 were tested for asphaltenes (wt/wt %) using ASTM D6560 procedures. The samples were also tested using the new method according to the mentioned procedures in Section 4.3. The results were calculated according to eq 1 in Section 4.3 (u).

The results, repeatability, and reproducibility of the two methods were compared to each other as shown in Table 2 and Figure 1. With the maximum difference in the results between the two methods remarked in S5 which have the lowest asphaltene content, the ASTM method result was 0.6%,

Table 2. Comparison of Asphaltene Results with ASTM vs the Centrifuge Method

sample	results (wt/wt %)						
	ASTM D6560	centrifuge method					
		operator A			operator B		
	avg		avg		avg		avg
S1	0.6	0.64	0.6	0.6	0.74	0.66	0.7
S2	1.8	1.7	1.8	1.8	1.86	1.93	1.9
S3	2.5	2.7	2.5	2.65	2.45	2.17	2.3
S4	4.2	3.9	4.1	4	3.98	3.7	3.8
S5	6.5	6.8	7	6.9	6.07	6.32	6.2
S6	7.8	8	7.6	7.8	7.37	6.85	7.1
S7	9.1	8.5	8.9	8.7	9.6	10.0	9.8
S8	10.2	11	10.7	10.9	10.8	11.2	11
S9	11.2	11.3	10.8	11.05	12.5	11.9	12.2
S10	15.2	16	15.4	15.7	16.2	15.8	16

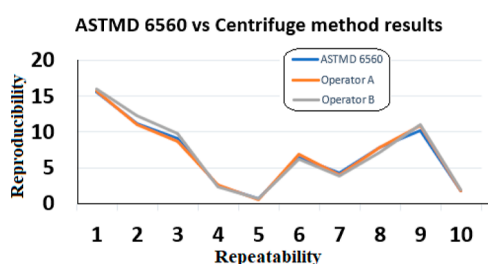


Figure 1. ASTMD 6560 results compared to centrifuge results.

while the operator B result was 0.7% which means that the difference is about 16.7% of the ASTM method result and this difference is still inside the ASTM D6560 reproducibility limits (20%).

The repeatability of the new method was calculated and found to be 8.0% at its maximum value (sample S1, which has a low asphaltene content), while the minimum value was found to be 3.75% (sample S10, which has the highest asphaltene content) as shown in Table 3.

Table 3. Summarized Repeatability and Reproducibility Values

method	max repeatability	max reproducibility
ASTMD 6560	10%	20%
centrifuge method	8.0%	17.0%

Also, the reproducibility of the new method was calculated by comparing operator B results with the operator A results; it was found that the maximum reproducibility value is 17.0% in the sample with the low asphaltenes (S1), and the minimum was 0.0% within the samples with high asphaltene content (S9, S10).

The comparison clarified that the usage of the centrifuge technique is acceptable. Although the new method shows that repeatability and reproducibility are getting higher with lower asphaltene content, they are still acceptable compared to the ASTM method. This increase in error with decreasing asphaltenes is basically due to weight errors on balance that increase with decreasing the weight of materials weighed on the balance.

2.2. Procedure Comparison. **2.2.1. Sample Quantity.** According to the ASTMD6560 method, a 100 mL sample of the crude oil needs to be distilled to 260 °C, and samples of 0.5–10 g (according to expected asphaltene wt %) of the residue of this distillation need to be refluxed in heptane. Note that this sample actually represents a larger sample of crude oil. According to the new method, there is no need to concentrate the asphaltenes by the crude oil distillation step, so there is no need to consume 100 mL of crude oil as a sample. Only 0.5–5 g (according to expected asphaltene wt %) of the crude oil needed to be centrifuged in heptane.

These grams of the sample that will be centrifuged represent itself, not like ASTM D6560 in which the grams of samples needed to be refluxed represent more quantity of the original sample (before distillation). Actually, ASTM D 6560 repeatability and reproducibility can be reached within the results with much smaller sample quantities by this method.

2.2.2. Steps and Apparatuses Needed. According to the ASTM method, the crude oil sample needed to be distilled (first step) to 260 °C to concentrate the asphaltenes in the

sample; then, sampling (second step) of a suitable quantity of the distillation residue must be done. The residue sample is then refluxed (third step) in heptane for 60 min and repeated at least two times. The solution after refluxing must be put in the dark until cool (fourth step) for about 60–90 min. Then, filtration (fifth step) of the solution is performed, followed by refluxing again in toluene, and then filtration through a filter paper. The mentioned steps were for only separating asphaltenes from the crude oil.

The new method steps are only for the sampling (first step) of suitable crude oil quantity to be centrifuged (second step) in heptane for about 10 min at least two times, and then decanting the clear heptane may be done without the need for filtration due to the adherence of asphaltenes as one big aggregate at the bottom of the centrifuge tube. The sample was centrifuged again with toluene, and then the toluene solution was decanted. Only these two steps were needed to separate asphaltenes from the crude oil in this method.

ASTM D6560 needs a sophisticated atmospheric distillation instrument and reflux glass apparatus. ASTM D7996 uses a UV–vis spectrophotometer. This method only uses ordinary benchtops or portable centrifuge instruments and glass tubes.

2.2.3. Method Time Comparison. The centrifugal force applied is sufficient to precipitate and separate heptane insoluble (asphaltenes + inorganic impurities), but some heptane soluble fractions may be trapped in the precipitate layer by the action of powerful centrifugation. To solve this problem, the sample must be refilled with clean heptane and recentrifuged until the decanted heptane is clean; this is a sign that there are no heptane soluble fractions.

According to the ASTM method, after refluxing the sample in heptane for about 60 min, the sample should be left for 90 to 150 min in the dark before filtration. This period of time is required to accumulate the asphaltenes to be in the form of big particles to not pass through filter paper, but the sample must be kept in the dark because both the high temperature of the sample and the long exposure to ultraviolet light may break some asphaltenes to smaller molecules which can dissolve in heptane and go through the filter paper, causing error in the results. The asphaltene percentage measured will be lower than the actual percentage in that case. In the centrifuge method, there is no need to wait for the sample because the powerful centrifuge precipitates asphaltenes as big aggregates which are often stuck at the bottom of the centrifuge tube, and the separation process of asphaltenes is done inside the instrument (in the dark), so no asphaltene losses by UV cracking are expected.

The ASTM D6560 method requires 330–450 min to test one sample (distillation, reflux, cooling, filtration, drying, and weighing) using the same apparatus, while this method requires about 50–70 min to test four samples (centrifuging, drying, and weighing) simultaneously using an ordinary four-sided centrifuge instrument, and this results in the average time required to test one sample using the centrifuge method being only 15 min. This time is about 20–28 times shorter than the ASTM test time (3.5–5% of the ASTM test time).

2.2.4. Method Range. According to ASTMD7996, the limit of asphaltenes is 15% by mass. According to ASTMD6560 and IP143, the limit of asphaltenes is 30% by mass. According to this work, the limit of asphaltenes is 30% by mass.

3. CONCLUSIONS

This new method requires a smaller quantity of samples and fewer procedures and consumes less time and resources compared to ASTM D6560 to quantify asphaltenes in crude oil samples. While ASTM D6560 and ASTM D7996 require sophisticated apparatus and cannot be done in the field portably, the centrifugation method can be done in a lab or field with few simple apparatuses. The results, repeatability, reproducibility, and working range of the centrifugation method are the same or even better than those of the ASTM D6560 method.

4. EXPERIMENTAL SECTION

4.1. Sample Preparation and Characterization. Different oil samples representing different reservoirs were collected according to ASTM D5854 from oilfields in the Ghrareb area, Egypt. The samples were decanted for 10 min to separate any nonemulsified water accompanying the oil. The emulsified water was measured using the ASTM D4006¹¹ distillation method. Only samples with emulsified water $\leq 1\%$ were accepted to be studied for physical and chemical properties.

Less than 1% were denoted as “dehydrated oils”. These dehydrated oils were characterized according to the standard methods used for the following physicochemical properties: water content (ASTM D4006), API gravity at 15.5 °C (ASTM D5002),¹⁵ kinematic viscosity at 100 °F (ASTM D443),¹⁶ pour point (ASTM D5853),¹⁷ total sulfur content (ASTM D4294),¹⁸ and asphaltene content (ASTM D6560).⁵ The properties of the five oils studied are presented in Table 1, which illustrates the API gravity change from 17.4 (oil S1, classified as heavy oil) to 39.8 (oil S5, classified as light oil). The water content was lower than 1.0% v/v for all samples. The samples were tested for asphaltene content according to the procedures in Section 4.3.

4.2. Reagents and Apparatus. The solvents used in this method are toluene and heptane (analytical grade). The used centrifuge (ORTO Alresa digtor 21C) is capable of spinning two or more filled cone-shaped, 203 mm (8 in.) centrifuge tubes at a speed that can be controlled to give a relative centrifugal force (rcf) of a minimum of 600 at the tip of the tubes.

The used centrifuge tubes are glass tubes with suitable volumes, calibrated for volume, and clearly graduated. See ASTM D4007 for centrifuge tube specifications.¹⁴

4.3. Procedure.

- Dry a clean centrifuge tube and weigh it to nearly 1 mg.
- Weigh 0.4 to 5.0 g of the prepared sample of crude oil (according to expected asphaltene content) into the tube and fill it to the 100 mL mark with heptane.
- Stopper the tube and shake until the mixture is homogeneous as shown in Figure 2.
- Remove the stopper, and using a wash bottle having a fine jet, wash all insoluble materials from the stopper into the centrifuge tube with a minimum of heptane.
- Balance the weights of each pair of filled centrifuge tubes, and place them in the centrifuge on opposite sides of the head.
- Centrifuge for 10 ± 1 min at a rate sufficient to produce a rcf between 600 and 700 at the tips of the whirling tubes.
- Carefully decant the supernatant liquid through a filter paper without disturbing or dispersing the precipitate,

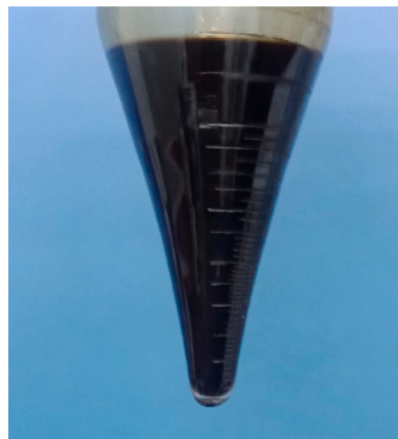


Figure 2. Crude oil sample dissolved in heptane.

leaving not more than 3 mL of liquid in the centrifuge tube as shown in Figure 3.



Figure 3. Decanting heptane after the first centrifuge run.

- Add 10 ± 1 mL of heptane to the tube through a filter paper. Dislodge and break the insoluble particles from the bottom of the tube by means of a clean stiff wire.
- Wash all insoluble particles adhering to the wire back into the tube with heptane as shown in Figure 4.
- Fill the tube to the 50 mL mark. Stopper the tube and shake until the mixture is homogeneous. Then, remove and wash the stopper as shown in Figure 5.
- Centrifuge for 10 ± 1 min.



Figure 4. Heptane after the first centrifuge run.

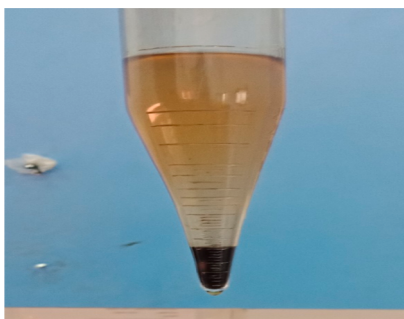


Figure 5. Clear heptane after the second centrifuge run indicates no more maltenes in the tube.

- (l) Pour the supernatant liquid from the centrifuge tube through a filter paper with care to avoid disturbing the cake of insoluble particles at the bottom of the tube as shown in Figure 6.



Figure 6. Asphaltene residue after the second centrifuge run with heptane.

- (m) Make a colorimetric comparison between the resultant heptane after each run and the pure heptane as shown in Figure 7; if decanted heptane shows a clear appearance

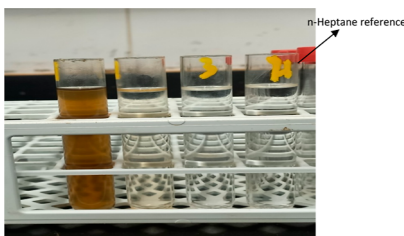


Figure 7. Colorimetric test for decanted heptane from the first run to the third (left to right) ascertains asphaltene purity; the heptane decanted from the third run is as clear as the reference heptane, so it leaves 100% pure asphaltene in the bottom of the tube.

as the pure reagent (which means that there are no more heptane soluble fractions and only asphaltenes with nearly a 100% purity at the tube bottom), continue to the next step; if it shows a darker appearance than the pure heptane, repeat the centrifugation steps of the sample with heptane.

- (n) Add 50 ± 1 mL of toluene. Break and dislodge all of the insoluble particles from the bottom of the centrifuge tube by means of a clean, stiff wire.

- (o) Wash any insoluble particles adhering to the wire back into the tube with toluene using a sufficient amount of this solvent to fill the tube to the 50 mL mark.
- (p) Stopper the tube and shake until the mixture is homogeneous.
- (q) Centrifuge until no visible insoluble particles remain in suspension in the solvent; 5.0 to 10 min is usually sufficient.
- (r) Decant the solution in a clean dish (through a filter paper), taking care not to disturb the precipitate.
- (s) Remove the toluene by evaporation.
- (t) Dry the dish and contents in an oven at 100 to 110 °C for 20 min. Cool them in a cooling vessel for 10 to 20 min and reweigh them by tare against the dish used previously for this purpose, which has been subjected to the same heating and cooling procedure as the dish containing asphaltenes.
- (u) Calculate the asphaltene content, A , in % m/m, of crude petroleum as follows

$$A = (w_1 - w_2) \times 100/m \quad (1)$$

where A is the asphaltene content %, m is the sample weight, W_1 is the dish weight with asphaltenes, and W_2 is the clean dish weight.

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Notes

The authors declare no competing financial interest.

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