

**DERIVATIVE UV-VIS SPECTROSCOPY OF CRUDE OIL AND ASPHALTENE SOLUTIONS FOR COMPOSITION DETERMINATION \*\***

**E. E. Banda-Cruz, N. V. Gallardo-Rivas\*, R. D. Martínez-Orozco,  
U. Páramo-García, A. M. Mendoza-Martínez**

*Centro de Investigación en Petroquímica at Tecnológico Nacional de México,  
Instituto Tecnológico de Cd. Madero, Altamira, Tamaulipas, Mexico;  
e-mail: nohvigari@itcm.edu.mx*

*The determination of the first and second derivatives in the UV spectra of crude oil and asphaltene solutions allows the identification of signals attributed to compounds in the crude oil that cannot be seen in the normal spectrum. This processing of the crude oil UV-Vis spectrum to determine first and second derivatives allowed the identification of five maxima. The maxima observed in the first derivative spectrum can be related to different types of compounds in crude oil: ~230 nm for benzene compounds, 259 nm for naphthalene compounds and their derivatives, 295 nm for pure phenanthrene, 328 nm for aromatic chromophores with three or four aromatic rings, and 401 nm for the Soret electronic absorption band of vanadyl porphyrins. The shape of the spectra was analyzed to predict the presence of colloids or particles in the solutions.*

**Keywords:** derivative UV-Vis spectroscopy, crude oil, asphaltenes.

**СПЕКТРОСКОПИЯ ПРОИЗВОДНЫХ В УФ-ВИДИМОЙ ОБЛАСТИ  
ДЛЯ ОПРЕДЕЛЕНИЯ СОСТАВА РАСТВОРОВ СЫРОЙ НЕФТИ И АСФАЛЬТЕНОВ**

**E. E. Banda-Cruz, N. V. Gallardo-Rivas\*, R. D. Martínez-Orozco,  
U. Páramo-García, A. M. Mendoza-Martínez**

УДК 543.42

*Центр нефтехимических исследований Национального технологического института Мексики,  
Альтамира, Тамаулипас, Мексика; e-mail: nohvigari@itcm.edu.mx*

*(Поступила 26 сентября 2019)*

*Определение первых и вторых производных УФ-спектров сырой нефти и растворов асфальтенов позволяет идентифицировать сигналы, относящиеся к соединениям в сырой нефти, которые нельзя увидеть в обычных спектрах. Обработка УФ-видимого спектра сырой нефти для определения первой и второй производных позволила идентифицировать пять максимумов. Максимумы в спектре первой производной могут быть связаны с различными типами соединений в сырой нефти: 230 нм для бензолных соединений, 259 нм для соединений нафталина и их производных, 295 нм для чистого фенантрена, 328 нм для ароматических хромофоров с тремя или четырьмя ароматическими кольцами и 401 нм для электронной полосы поглощения Соре ванадилпорфиринов. Форма спектров проанализирована с целью определения наличия коллоидов или частиц в растворах.*

**Ключевые слова:** спектроскопия производных в УФ-видимой области, сырая нефть, асфальтены.

**Introduction.** Crude oil is a complex mixture of thousands of components that are difficult to characterize in their entirety [1–4]. The vast number of components in crude oil has been compared to the number of genes in the genome, giving rise to the use of words such as petroleome and petroleomics [5]. Other authors [6] studied the results on quantitative and qualitative dissolution of HCO (heavy crude oil) using organic solvents (with and without ionic liquids). Quantitative studies on the dissolution of crude oil were carried out

\*\* Full text is published in JAS V. 87, No. 6 (<http://springer.com/journal/10812>) and in electronic version of ZhPS V. 87, No. 6 ([http://www.elibrary.ru/title\\_about.asp?id=7318](http://www.elibrary.ru/title_about.asp?id=7318); [sales@elibrary.ru](mailto:sales@elibrary.ru)).

with the use of a UV-Vis spectrophotometer, while qualitative studies on the dissolution of HCO were carried out using FTIR and  $^{13}\text{C}$  NMR techniques. In a recent investigation, prepared samples of crude oil and fractions isolated with acetonitrile were analyzed with UV-Vis spectroscopy from 190 to 1100 nm. For these analyses, all samples were diluted in DCM at a concentration of 2 mg/mL. The researchers observed a well-defined Soret band at 408 nm [7]. Other authors [8] used spectroscopic techniques such as attenuated total reflectance Fourier transform infrared (ATR-FTIR) absorption and synchronous ultraviolet fluorescence (SUUVF). In the analysis of the aromatic compounds present in crude and asphaltene solutions using UV spectroscopy, the part of the molecule that is involved in absorption processes is known as the chromophore. The spectral patterns that arise from different chromophores are the “fingerprints” that allow us to identify and quantify specific molecules. These fingerprints are the building blocks of the spectra and are associated with molecular structures and transitions between molecular orbitals. On the other hand, the simplest requirement in UV spectrum exploration is the visualization of signals. In 2007, Tomas et al. [9] reported qualitative methods for UV-Visible spectral processing. Classification was performed based on the number of spectra. For a spectrum, the use of derivatives allows better characterization since it provides information about the slope of the spectrum and enhances the points of inflection and shoulders. Detailed analysis of a UV-Vis spectrum provides valuable information on the composition of an analyte. In recent research, we reported the UV-Vis spectrum of heavy crude oil solutions using cyclohexane as a solvent [10]. This research mainly focused on the analysis of the UV-Vis spectra of crude oil solutions using first and second derivatives as analytical tools. Derivative spectroscopy can be used as a tool to detect signals that are not visible in the normal spectrum. Derivative spectroscopy refers to a spectral measurement technique in which the slope of the spectrum is measured. Slope can be understood as the rate of change in absorbance with the wavelength. Derivative 1 can be used to highlight small variations in the spectrum, and second derivative is the derivative of the first derivative spectrum. It is a measure of the curvature of the spectrum and has absorbance units of square nanometers.

**Materials and methods.** High-purity cyclohexane (99.9%) was supplied by Tedia and used as the solvent. UV-Vis spectroscopy was performed using a Cintra 303 spectrometer from GBC Scientific Equipment and an OHAUS Adventurer Pro analytical balance (model AV264C).

*Crude oil samples.* Solid asphaltenes were extracted from two samples of heavy crude oil according to ASTM-D2007-98 methodology. The analyzed crude oil samples were labeled C1-RC and C2-RM, and the asphaltene fractions were labeled AC1-RC and AC2-RM, respectively. Sample C1-RC corresponds to a crude oil of coastal origin (12.90°API; saturates, 20.83 wt.%; aromatics, 34.44%; resins, 29.32 wt.%; and asphaltenes, 15.39 wt.%), while sample C2-RM is of maritime origin (12.50°API; saturates, 24.36 wt.%; aromatics, 42.62 wt.%; resins, 7.51 wt.%; and asphaltenes, 24.80 wt.%).

*UV-Visible spectroscopic analysis of the crude oil-solvent and asphaltene-solvent solutions.* From standard solutions of 100 mg/L crude oil and asphaltenes in cyclohexane, solutions of 10 to 90 mg/L and 40 to 100 mg/L, respectively, were prepared. Successively and in triplicate, each solution was analyzed on a UV-Vis spectrophotometer in the range of 200–450 nm. Evolution of the different absorbance signals ( $A$ ) in the spectra were plotted with respect to wavelength ( $\lambda$ ). The accumulated data were plotted to obtain a curve showing variations in absorbance versus concentration. The equation of the line and the coefficient of determination ( $R^2$ ) were determined. For each concentration, the highest absorbance peak was sought, which was important for the calibration curves.

*Spectral analysis: first and second derivatives.* The first and second derivatives of the spectra were processed over the entire wavelength range from 200 to 450 nm to minimize the range of noise detected. Previously, the spectra were smoothed to obtain filtered signals and achieve a better resolution of those signals using the Savitzky–Golay method [11, 12].

**Results and discussion.** *UV-visible spectroscopy of crude oil solutions and asphaltene solutions.* Depending on the type of solvent used for analysis of the crude oil and its subfractions, the signals detected using UV spectroscopy change in terms of position (wavelength) and intensity. In 2005, Dixon et al. [13] reported the absorption of benzene and naphthalene in cyclohexane. Benzene in cyclohexane generates a noisy spectrum in the range of 226–265 nm, and naphthalene in cyclohexane generates a noisy spectrum at 240–293 nm. Figure 1 shows raw UV-Vis absorption spectra of both C1-RC and C2-RM samples of crude oil and their respective asphaltenes at concentrations of 10 to 100 mg/L in cyclohexane, which have been previously reported [14]. The absorption spectra showed three characteristic bands in the range of 200–450 nm for both crude oil and asphaltene solutions. The first absorption band, in the spectral region of 220 to 250 nm, corresponds to a single aromatic ring in benzene and its derivatives. The band observed be-

tween 255 and 280 nm is attributed to double-ring chromophores of naphthalene [13]. The absorption bands at approximately 410 nm are associated with electronic transitions of the Soret band of vanadyl porphyrins. It is further noted that with decreasing concentrations of crude oil in a cyclohexane solution, the intensity of the three signals is reduced by the effect of the concentration. Calibration curves were generated for all solutions and are presented in the supplementary material. For both spectra (Figs. 1a,b), the signal-to-noise ratio increased, mainly in the region corresponding to benzene compounds and their derivatives. The UV-Vis spectra of asphaltene solutions AC1-RC and AC2-RM in cyclohexane at concentrations ranging from 100 to 40 mg/L are shown in Fig. 1c,d. Both solutions of asphaltenes exhibit the three absorption bands previously described, similar to the spectra of the corresponding crude oil. However, it is observed that the spectra of asphaltene sample AC2-RM, at concentrations between 100 and 70 mg/L, show a greater amount of noise than the AC1-RC spectra in the same analyzed wavelength range from 200 to 350 nm, as well as a higher level of absorbance. This can be attributed to the fact that the structure of AC2-RM (12.5°API) contains a greater number of aromatic groups, while AC1-RC (12.9°API) has a lower content of aromatic groups.

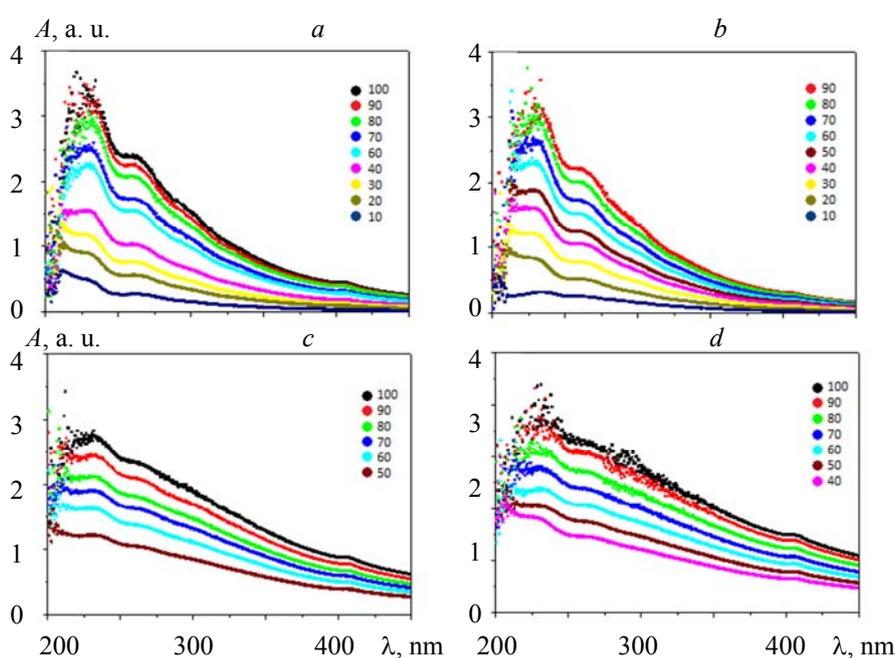


Fig. 1. UV spectra of (a) C1-RC, (b) C2-RM, (c) AC1-RC, and (d) AC2-RM at concentrations of 10–100 mg/L.

*Qualitative analysis of UV spectra. Form of the UV spectrum.* A direct comparison of the UV-Vis spectra of samples C1-RC and C2-RM at a concentration of 40 mg/L is shown in Fig. 2a, and a comparison of the spectra of the asphaltene solutions at the same concentration is displayed in Fig. 2b. As seen in the absorption spectra, the intensity of the absorption bands for C2-RM is greater than that for C1-RC, which can be attributed to a greater amount of asphaltenes in the composition of C2-RM (24.8%). On the other hand, Fig. 2b shows greater absorbance intensity of the three bands in the AC2-RM spectrum, indicating the presence of a greater number of aromatic compounds in the composition of this type of asphaltene. The UV-Vis absorption spectra of the C1-RC and C2-RM samples are uniform in shape, while those of the AC1-RC and AC2-RM samples have a flat shape. A flat spectrum shape suggests the presence of solid asphaltene particles suspended in cyclohexane [9].

*First and second derivatives.* Figures 3a,b show the first derivative spectra of C1-RC and C2-RM. For both C1-RC and C2-RM samples, four maximums were identified, which can be related to different types of compounds in the petroleum: ~230 nm for benzene compounds, 259 nm for naphthalene compounds and their derivatives, 295 nm for pure phenanthrene, 328 nm for aromatic chromophores with three or four aromatic rings, and 401 nm for the Soret electronic absorption band of vanadyl porphyrins [13, 15–17]. It is important to mention that these maxima could not be perceived with the naked eye in the raw spectra; however, with the use of first derivative, their determination was possible.

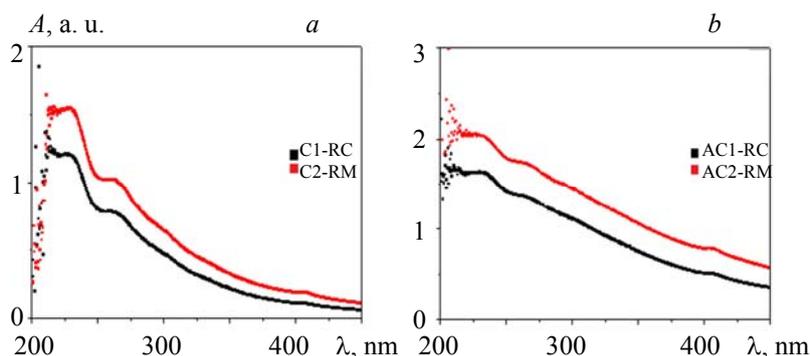


Fig. 2. UV spectra for crude oil (a) (C1-RC and C2-RM) and asphaltene (b) (AC1-RC and AC2-RM) solutions at a concentration of 40 mg/L.

Figures 3c,d present the second derivative spectra of C1-RC and C2-RM. For both crude oils in the range of concentrations measured, the second derivative spectra have maximum values at the same wavelength as the peaks in the first derivative spectra but in the negative direction. The second derivative spectra cross the  $X$  axis at the point of maximum slope of the first derivative spectra, generating a large absorbance band. In these curves, the inflection points of the absorption peaks coincide with the maxima of individual bands of all aromatic components. It is important to mention that due to the differentiation process, the position of the zero point in the first derivative spectra and the position of the minimum in the second derivative spectra can be displaced. This displacement is with respect to the position of the maximum absorption in the original spectrum [18]. To better observe the resulting signal, we analyzed the data at a concentration of 40 mg/L, for which it was possible to obtain the best individual derivative spectra for C1-RC (Figs. 4a,b) and C2-RM (Figs. 4c,d).

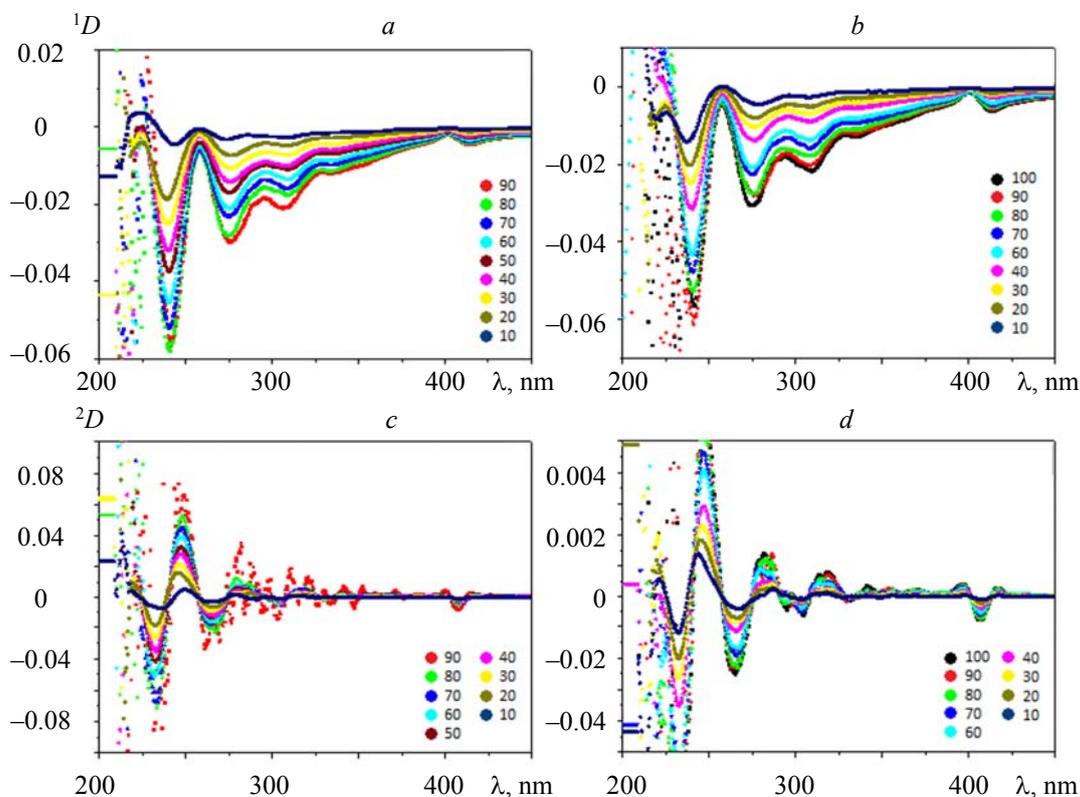


Fig. 3. First (a, b) and second (c, d) derivatives spectra of crude oil solutions C1-RC (a, c) and C2-RM, (c) second derivative of C1-RC, and (d) second derivative of C2-RM.

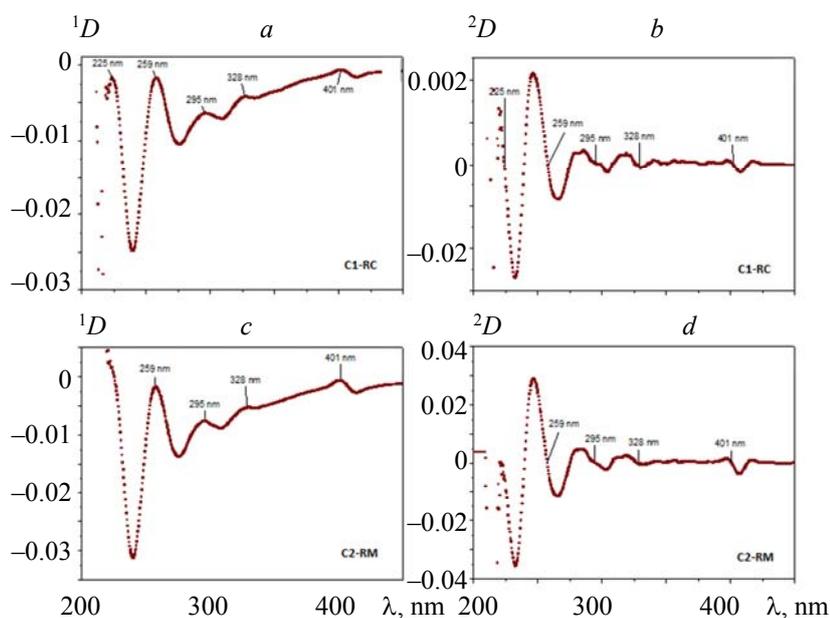


Fig. 4. First (a, c) and second (b, d) of crude oil solutions C1-RC 40 mg/L (a, b) and C2-RM 40 mg/L (c, d).

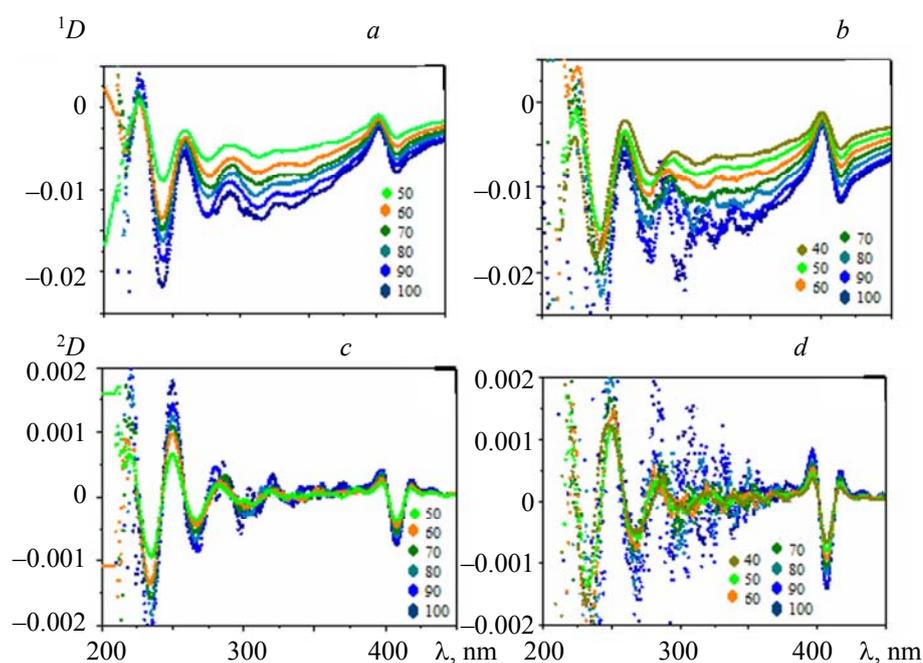


Fig. 5. Derivative spectra of asphaltene solutions. first derivative of AC1-RC (a) and AC2-RM (b), second derivative of AC1-RC (c) and AC2-RM (d).

Figures 5a,b present the plots of first derivative spectra of AC1-RC and AC2-RM at concentrations of 100 to 40 mg/L. The first derivative spectra show five maximum signals at approximately 230, 259, 295, 328, and 401 nm for both asphaltene solutions. Due to the low signal-to-noise ratio, in the first derivative spectra of AC1-RC and AC2-RM, it was not possible to identify the signals for all analyzed concentrations. By comparing the first derivative spectra of both asphaltene solutions, a greater amount of noise was observed for the AC2-RM sample than for the AC1-RC sample in the wavelength range of 275 to 375 nm, which can be attributed to the greater number of aromatic species present in the former type of asphaltene. Figures 5c and d also show the second derivative spectra of AC1-RC and AC2-RM. In the spectra, it can be

seen that the inflection points of the absorption peaks coincide with the maxima of individual bands of all aromatic components.

**Conclusions.** Crude oil and asphaltene quantification by UV-Vis spectroscopy is a viable, safe, and reliable method with no major difficulties. It can be carried out in a laboratory with available equipment, which helps reduce costs. The method proposed here is suitable for crude oil at low concentrations since there is no data dispersion. By means of UV-Vis spectroscopy, it is possible to visualize spectra with three bands for petroleum and asphaltene solutions. Processing of the crude oil and asphaltene spectra for the determination of derivative 1 and second derivative allowed the identification of five maxima at 230, 259, 295, 328, and 401 nm. The maxima determined can be related to different types of compounds in the crude oil and asphaltenes: ~230 nm for benzene compounds, 259 nm for naphthalene compounds and their derivatives, 295 nm for pure phenanthrene, 328 nm for aromatic chromophores with three or four aromatic rings, and 401 nm for the Soret electronic absorption band of vanadyl porphyrins. It is important to apply derivative spectroscopy as a tool in the identification of signals that cannot be detected in zero-order spectra, such as phenanthrene peak at 295 nm and the peak attributed to aromatic chromophores containing three or four aromatic rings at 328 nm. With increase in the degree of derivation, the spectra become more complex. On the other hand, analysis of the shape of the spectra with the naked eye indicates that the crude solutions gave rise to uniform spectra with marked shoulders, indicating the presence of the colloidal state of oil, while the flat spectra of the asphaltene solutions indicate the presence of particles in solution. By direct comparison of the C1-RC and C2-RM spectra and the AC1-RC and AC2-RM spectra for samples at the same concentration, it is possible to estimate the difference in the composition of aromatic species.

**Acknowledgments.** The authors thank Consejo Nacional de Ciencia y Tecnología (CONACYT) Projects of Scientific Development to Address National Problems (APN) for financial support of project No. 3676. Furthermore, we appreciate the funding provided by the TNM for project No. 5090.19P.

## REFERENCES

1. H. Alboudwarej, J. J. Felix, S. Taylor, R. Badry, Ch. Bremner, B. Brough, C. Skeates, A. Baker, D. Palmer, K. Pattison, et al., *Oilfield Rev.*, **18**, 34–53 (2016).
2. N. H. Abdurahman, Y. M. Rosli, N. H. Azhari, B. A. Hayder, *J. Pet. Sci. Eng.*, **90**, 139–144 (2012).
3. L. Xia, S. Lu, G. Cao, *J. Colloid Interface Sci.*, **271**, 504–506 (2004).
4. P. K. Kilpatrick, *Energy Fuels*, **26**, 4017–4026 (2012).
5. A. G. Marshall, R. P. Rodgers, *Chem. Underworld Proc. National Academy of Sciences*, **105**, N 47, 18090–18095 (2008).
6. S. Sakthivel, R. L. Gardas, J. S. Sangwai, *J. Mol. Liq.*, **221**, 323–332 (2016).
7. D. Giraldo, M. Chacón, J. S. Ramirez, C. Blanco, M. Y. Combariza, *Fuel*, **226**, 103–111 (2018).
8. O. Abbas, C. Rebufa, N. Dupuy, A. Permanyer, J. Kister, *Fuel*, **98**, 5–14 (2012).
9. M. F. Thomas, N. Azema, O. Thomas, In: *UV-Visible Spectrophotometry of Water and Wastewater*, Eds. O. Thomas, C. Burgess, Elsevier Science, 201–224 (2017).
10. E. E. Banda, S. I. Padrón, N. V. Gallardo, J. L. Rivera, U. Páramo, N. P. Díaz, A. M. Mendoza, *Pet. Sci. Technol.*, **24**, 732–738 (2016).
11. O. Thomas, V. Cerda, In: *Techniques and Instrumentation in Analytical Chemistry*, Eds. O. Thomas, C. Burgess, Elsevier Science, vol. 27, 21–45 (2007).
12. O. Thomas, J. Causse, In: *UV-Visible Spectrophotometry of Water and Wastewater*, Eds. O. Thomas, C. Burgess, Elsevier Science, 37–72 (2017).
13. J. M. Dixon, M. Taniguchi, J. S. Lindsey, *Open Acc. Photochem. CAD Spectra Database*, **81**, 212–213 (2005).
14. E. E. Banda, N. V. Rivas, U. Páramo, I. A. Estrada, D. Pozas, J. Reyes, *Pet. Sci. Technol.*, **34**, 1812–1817 (2016).
15. J. Lin, W. Hu, C. Cheng, X. Gu, W. Du, C. Quo, J. Zhang, *Fuel*, **218**, 213–217 (2018).
16. I. Evdokimov, A. Fesan, A. Losev, *Energy Fuels*, **31**, 3878–3884 (2017).
17. S. M. Rowland, W. K. Robbins, Y. E. Corilo, A. G. Marshall, R. P. Rodgers, *Energy Fuels*, **28**, 5043–5048 (2014).
18. M. L. Lopez, D. P. L. Lopez, *Educ. Quím.*, **4**, N 3, 160–170 (1993).