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Compatibility of Crude Oil Blends—Processing Issues Related to Asphaltene Precipitation, Methods of Instability Prediction—A Review

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ABSTRACT: Processing crude oil of variable composition, especially due to the need to process crude oil blends obtained from various sources, presents a tremendous process challenge. This is mainly due to the destabilization of the colloidal system manifested mostly by the precipitation of the asphaltene fraction. The precipitation of asphaltenes from crude oil is a serious problem during extraction, transport, and processing. In the latter case, engineers and scientists have spent a lot of time determining what mechanisms are conducive to the occurrence of this phenomenon. On the one hand, there was a scientific curiosity about the principles of the nanoworld (nanoscale) of asphaltene molecules that determine their stability, and on the other hand, the willingness of process engineers in refineries to maintain the equipment in the best condition and maximize plant profits. Over the years, many methods have been developed to assess the stability of asphaltenes in crude oils and their blends, starting with methodologies based on the separation of a complex mixture into basic groups of compounds with similar properties (SARA) to sophisticated numerical models on an increasingly better understanding of interactions between molecules under changing conditions. In the former case, the basic instruments available in every laboratory are used whereas in the latter case technically advanced measurement systems capable of reproducing the real conditions of crude oil processing are employed. This paper reviews the methods of determining the stability of crude oils and their blends along with a critical assessment of their effectiveness.

1. INTRODUCTION

With the current geopolitical dynamics, crude oil processing requires the maintenance of a sufficiently wide diversification of sources of supply of this raw material. An indispensable aspect of the diversification of crude oil sources is the compatibility of crude oil types with the technological configuration of a particular refinery. In simple terms, a refinery plant designed based on the assumption of the characteristics of the processed crude and the range of products obtained, may not be fully adapted to the effective processing of a crude oil blend with a completely different hydrocarbon composition. While refineries are capable of accurately assessing the mass product potential of crude oil blends, they encounter problems with the process aspect of their processing. Blending a few to a dozen or so types of crude oil to optimize yields causes destabilization of the internal equilibrium of each of them, and the side effect is often the precipitation of a solid asphaltene fraction. This problem affects in particular small and medium-sized recipients with limited possibilities of simultaneous processing of many types of crude oil.

As already mentioned, blending a few to a dozen or so types of crude oil (in a tank or online—in a pipe) results in

destabilization of the charge for the crude distillation unit (CDU). During storage, as well as during pumping and heating, of the charge, a solid asphaltene fraction precipitates. According to the Yen−Mullins model, single molecules combine into nanoaggregates which further form clusters (Figure 1). Flowing through the preheat train (PHT), the clusters stick to their interior, reducing the heat exchange surface and causing a decrease in heat exchange efficiency and the need to replenish it in the furnace (Figure 2).

Currently, two theories describing the mechanism of precipitation of the asphaltene fraction from crude oil under the influence of precipitating factors prevail.[1] The first one assumes the occurrence of asphaltenes as micelles with resins adsorbed on their surface. Micelles are stabilized in an environment rich in aromatic compounds.[2] The appearance of *n*-alkanes causes irreversible destabilization of the system,
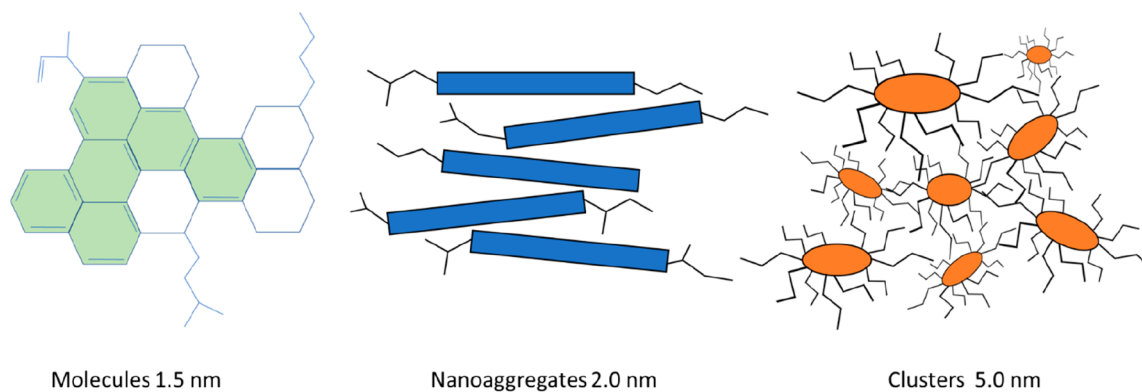
Figure 1. Asphaltene structures according to a modified Yen−Mullins model.
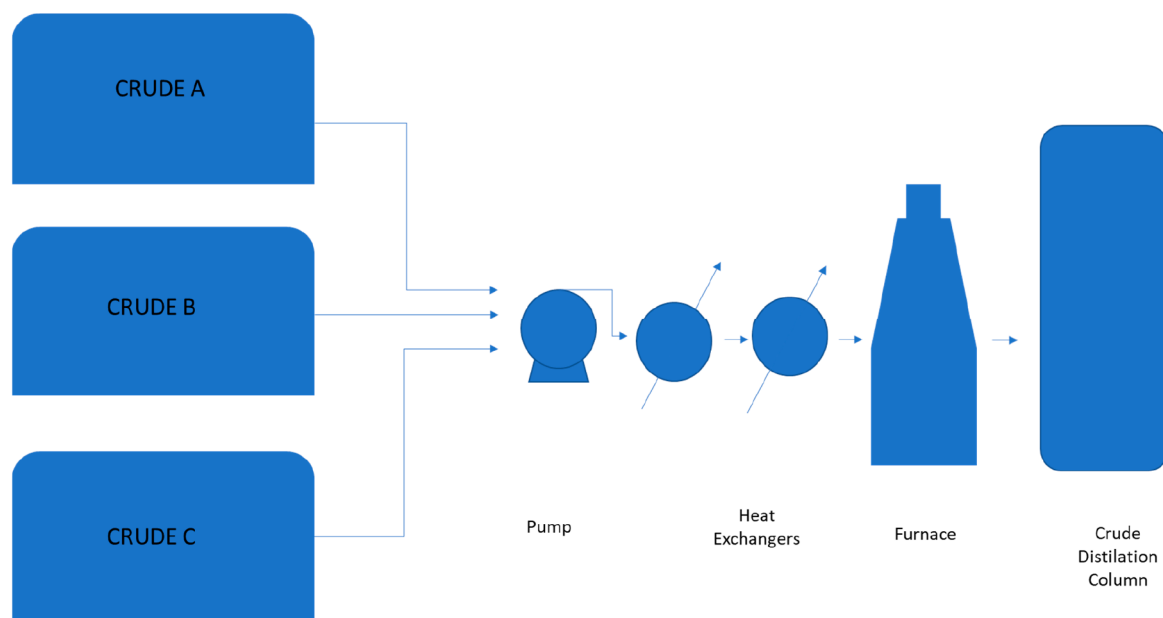

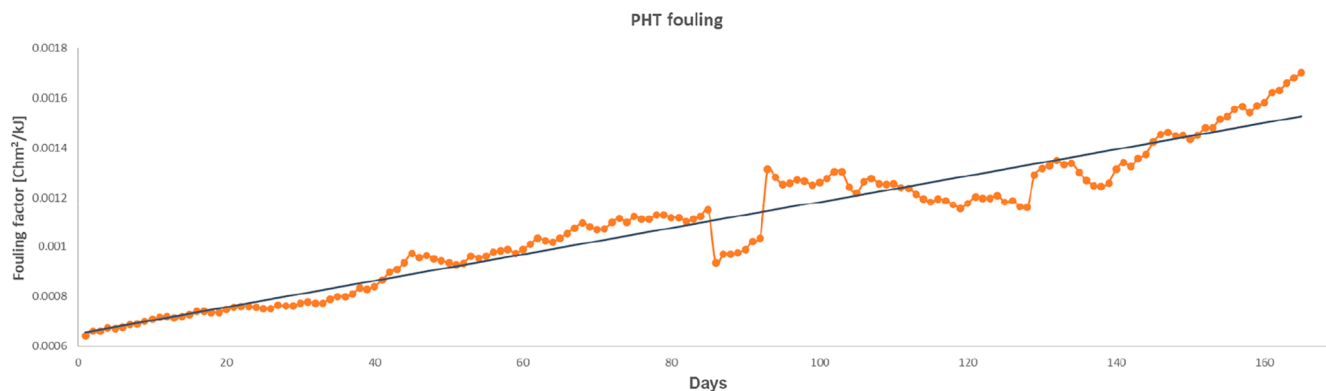**Figure 2.** Diagram of the supply of crude oil to the CDU.

Figure 3. Increase of the fouling factor based on reduced heat transfer efficiency in a heat exchanger (own study).

the disintegration of the resin shell, and precipitation of asphaltenes out of solution.[1,3,4] The second theory assumes that asphaltene coagulation is thermodynamically dependent and reversible. The asphaltenes remain dissolved in the solution until certain critical values are exceeded. The knowledge of the influence of temperature and pressure on the solubility of asphaltenes makes it possible to select the composition of the crude oil blend in terms of the stability of asphaltenes in the crude oil under the process conditions.[1,5]

As mentioned earlier, precipitation of the asphaltene fraction results in a decrease in the heat transfer efficiency in the preheat train (PHT) (Figure 3). This has a direct impact on
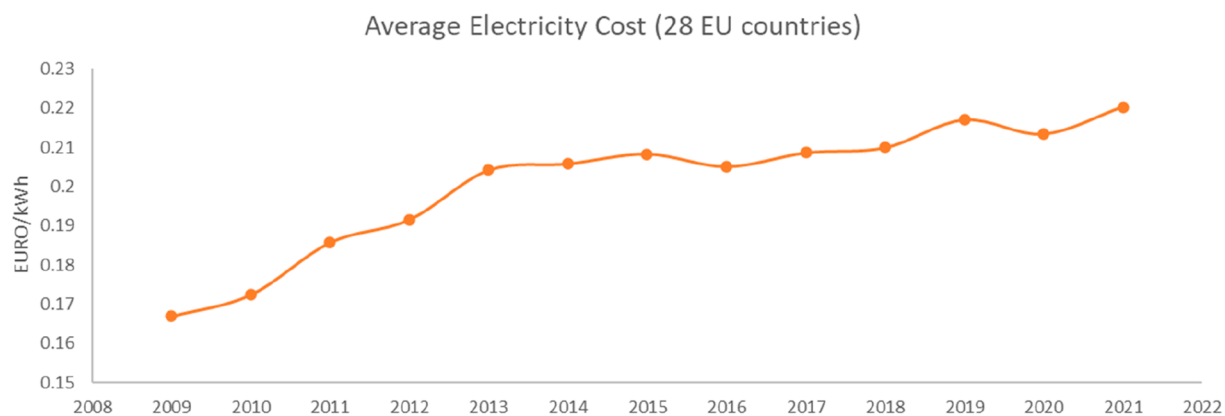
Figure 4. Electricity cost in the European Union [Euro/kWh].

the economics of the process and the profitability of processing a given blend.[6] In the EU, one of the key costs of crude oil processing is the cost of energy (Figure 4).[7]

The increase in fouling of exchangers during the processing of cost-effective crude oil can completely eliminate the profitability of processing. It should be remembered that as a result of high temperature, the asphaltene fraction, initially accumulated in the form of a loose layer of particles on the surface of the heat exchanger tubes, compacts into a tight structure and becomes more difficult to remove mechanically or by dissolving.[8] The above problems make knowledge about the behavior of various crude oils and their blends during processing a key factor for the production efficiency and economic success of the company. With the constant uncertainty of markets and changes in product margins, reducing downtimes and improving energy efficiency become the most important factors in the profitability of processing. The ability to quickly determine the compatibility of new crude oil offered on the market as a long-term contract or the so-called spot/opportunity crude may bring the company significant benefits and an advantage in the competitive refining market. It should also be remembered that many crude oil producers are switching to the production of finished fuels to improve their profit. This means that despite the increase in production and consumption, the supply of crude oil on the market may decline over time, and companies without their raw material resources will be closed or sold to large global concerns. Currently, the three largest crude oil producers in the world are the United States, Russia, and Saudi Arabia, and the main products of these suppliers are WTI (West Texas Intermediate), REBCO (Russian Export Blend Crude Oil), and Arab. In Europe, a lot of oil comes from the North Sea, where the main producers are Norway, Great Britain, Denmark, and Germany.[9]

Crude oil available on world markets is characterized in several ways.[10] The first is to determine the density and assign oil to one of three categories: light (up to about 830 g/dm^3), medium (from about 830 g/cm^3 to about 880 g/dm^3), or heavy (over 880 g/dm^3). The first category includes Polish Rozewie crude oil (815 g/dm^3), medium crude oil is REBCO (about 870 g/dm^3), and heavy crude oil includes the Venezuelan Orinoco, whose very high density and viscosity precludes pumping without previous dilution.

Another way to classify crude oil is by comparing its dominant chemical structure. This is how the oil is broken down into paraffinic, naphthenic, paraffinic−naphthenic, aromatic, paraffinic−naphthenic−aromatic, and paraffinic−aromatic.

Such a classification, based on the dominant groups of compounds, allows for quick determination of suitability for processing in a given plant due to the preferred structure of petroleum products. Paraffinic and paraffinic-naphthenic crudes yield more light distillates (LPG, gasoline, and kerosene). The increasing fraction of aromatic compounds and long paraffinic chains (medium- and high-paraffin crudes) results in a higher yield of middle distillates (aviation fuel, diesel fuel) and the products of processing of atmospheric residue (base oils, asphalts). Another important way to classify crude oil is with respect to its sulfur content. There are low-sulfur crudes (sweet; S content < 0.5 [wt %]) and high-sulfur crudes (sour; S content > 0.5 [wt %]). Due to the environmental protection regulations that are constantly tightened by world governments, this parameter has become one of the most important factors when assessing the quality of the raw material. There are only a few plants and outlets ready to process high-sulfur crudes, and their desulfurization is economically unprofitable for many customers.[11]

The above list does not cover all important parameters considered when deciding on the purchase of crude oil. Viscosity, acid number, metal content, and others are equally important, but the individual values of these parameters and their impact on the profitability of processing depend on the individual needs of the recipient.

The high dynamics of the crude oil market and the strategic importance of this raw material in global politics require greater flexibility in the processing of various types of crude oil and their blends. Good identification of the risks associated with the blending of crude oils with different characteristics can give a competitive advantage or constitute a serious disadvantage for an oil processing plant. It should be noted that many of the available types of crude oil (REBCO, Brent, etc.) come from blending (mixing) crude oil from different sources (different oil fields, often very distant from each other) in order to obtain a resultant product of the declared quality. Already at this stage, it is important to recognize the potential influence of the mixing process on the homogeneity of the final product.

2. CHARACTERISTICS OF ASPHALTENES

Asphaltenes are a hydrocarbon fraction defined as that part of crude oil that is soluble in aromatic compounds (toluene, benzene) and insoluble in paraffinic solvents (*n*-heptane, *n*-
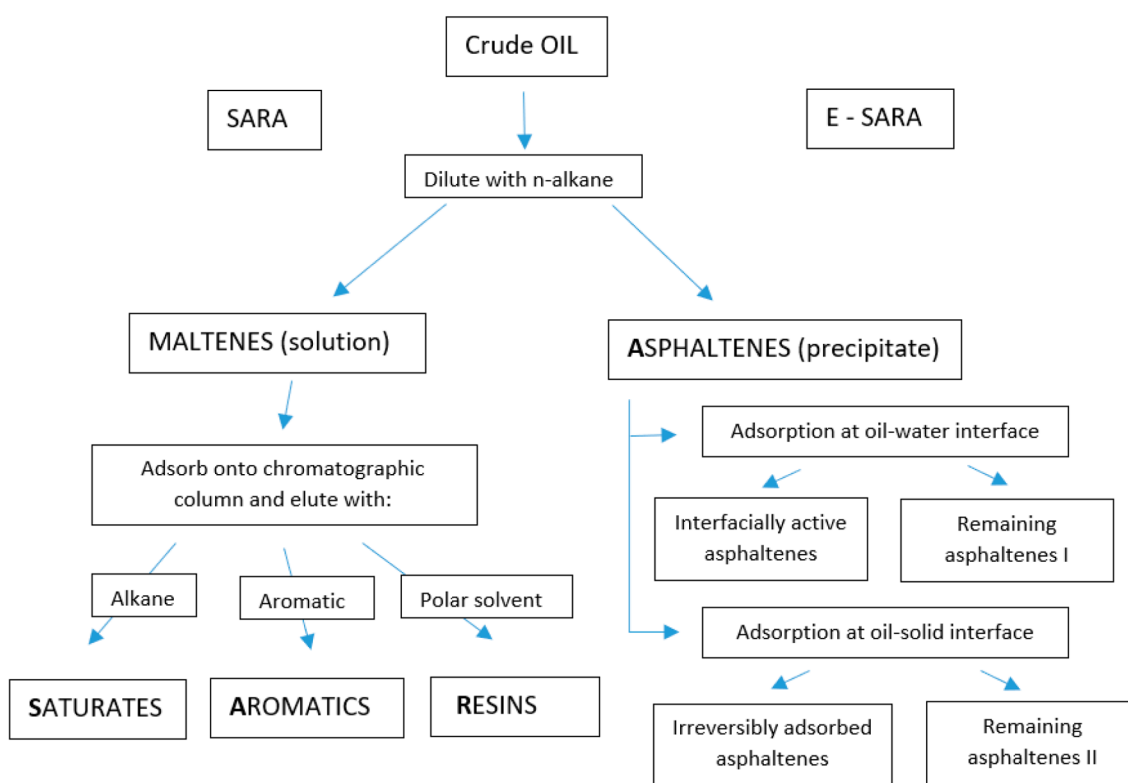
Figure 5. Comparison of standard SARA and e-SARA analyses.

pentane). It is composed of many (at least 100 000[3] to about a million[12]) different molecules containing numerous heteroatoms (N, O, S) and metals (Fe, Ni, V). They consist of aromatic and naphthenic cores (about 50%[12]) with numerous aliphatic moieties[13] reaching high molar masses and a boiling point of 650+ °C. Due to the complex structure and not fully clear mechanisms of interactions taking place in the asphaltene fraction, modeling their precipitation and fouling presents a serious challenge. There is no universal method of predicting the stability and solubility of asphaltenes in solutions, and the solutions to the problems that may occur must be adapted to the specific process conditions.[14]

3. METHODS OF DETERMINATION AND CHARACTERIZATION OF COMPATIBILITY

Over the years, many attempts have been made to determine the factors and procedures for estimating the compatibility of crude oils. The increasing volume of crude oil production from previously unavailable sources resulted in the growing interest in the issue of oil stability from the extraction stage to blending and processing. A compilation of the methods for determining the stability of crude oil and its blends available in the literature is presented below.

3.1. Methods Based on SARA Analysis. There is a group of factors and procedures for determining oil stability based on the SARA analysis (S, saturate; A, aromatic; R, resin; A, asphaltene). It is an analysis method that divides crude oil components according to their polarizability and polarity without determining individual components (a group-type separation).

In its basic version, the SARA analysis is based on solvent fractionation of a crude oil sample into the groups mentioned above using chromatographic techniques and gravimetric

determination of the content of each group after evaporation of the solvent. The first step is to precipitate the asphaltenes with a paraffinic (straight chain alkane) solvent followed by adsorption of the remaining three groups on the chromatographic column. By using suitable eluents, successive groups of compounds are eluted from the column followed by quantitative component analysis (Figure 5).[2,15,1,16]

Extended SARA (E-SARA) is an extension of the group composition analysis of crude oil with an additional division of the asphaltene fraction. This methodology allows for the separation of the subgroups of compounds based on adsorption at the oil−water and oil−solid interface and the determination of their chemical structure. E-SARA enables the separation from the asphaltene fraction of groups of compounds responsible for phenomena typically attributed to the entire asphaltene group, such as stabilization of water−oil emulsion, fouling, etc.[15]

The Thin Layer Chromatography Flame Ionization Detector (TLC-FID) technique enables efficient and relatively quick analysis. It involves placing a drop (1 μL) of a sample diluted with dichloromethane on a quartz rod (a so-called chromarods) coated with a layer of sorbent (silica gel). The tip of the rod is immersed vertically in successive eluents which elute successive SARA fractions up the rod. Elution order follows a mechanism of normal phase LC. Generally, a step elution using *n*-heptane, followed by toluene and finally dichloromethane-methanol (95−5 v/v) is used. Between each separation, the chromarods are placed in a dedicated oven to remove remaining eluent before following next step of the elution. The sample, thus separated on the rod, is placed in the apparatus and exposed to the flame of the FID detector, the output signal of which is recorded in the form of a chromatogram. Typically, one frame contain separately placed

10 chromarods, which allows to perform analysis of 3 samples (each in triplicate) and one blank analysis at the same time. Additional information on the development of SARA group composition methodologies and their advantages and disadvantages can be found in the literature.[17]

The literature describes several methods for determining and correlating the stability of asphaltenes in oil blends based on SARA analysis. The individual approaches are characterized below.

3.1.1. CII Colloidal Instability Index. In this approach, crude oil is treated as a colloidal system. The mathematical description results directly from the influence of individual components on the stability of the asphaltene layer. Asphaltenes and saturated compounds are treated as flocculants (destabilizing agents) while resins and aromatic hydrocarbons are components that stabilize the blend.[6,19,20] The lower the CII index, the higher the stability of the asphaltene layer. The CII is calculated using the equation:

$$CII = \frac{As[wt\%] + S[wt\%]}{R[wt\%] + A[wt\%]} \quad (1)$$

Asomning and Watkins[13] define the ranges of the CII index as CII ≥ 0.9, unstable asphaltene fraction; 0.7 ≤ CII < 0.9, stability uncertain; and CII < 0.7, stable asphaltene fraction

3.1.2. Colloidal Stability Index. The approach is analogous to CII, with additional consideration of the polarity of individual fraction to better represent the physicochemical properties of oil components. The main focus is aimed on relations between asphaltenes and resins because the interactions between these two groups of compounds have highest significance for the overall crude stability.[21] The parameter assumes a higher polarity of the asphaltene fraction in unstable crude oils and a lower polarity for stable types.[13,18]

It is calculated from the equation:[13]

$$CSI = \frac{\varepsilon^{As*}As[wt\%] + \varepsilon^{S*}S[wt\%]}{\varepsilon^{R*}R[wt\%] + \varepsilon^{A*}A[wt\%]} \quad (2)$$

where dielectric constant values for SARA fractions are the following: ε^{AS}=18.4 (unstable)/5.5 (stable), ε^{R} = 3.8(unstable/ 4.7 (stable), ε^{S} = 1.921, and ε^{A} = 2.379. If CSI < 0.95, the crude oil is stable.

3.1.3. Stability Index. The simple relationship of asphaltene and resin content (As/R) is used for fractions containing minimum (or no) volatiles.[13] The resins stabilize the asphaltenes and prevent them from aggregating into clusters and precipitating out of the solution. Being the two heaviest SARA fractions, the asphaltenes and resins can be precisely quantified which makes the analysis more dependable. If the A/R ratio is lower than 0.35, the crude oil is considered to be stable.[18]

3.1.4. Stankiewicz Plot (SP). Stankiewicz plot is a graphical method of presenting the dependence of crude oil stability on A/R and S/Ar ratios. The regions of stability and instability are arbitrarily assumed and marked on the plot (Figure 6).[13,18]

3.1.5. Sepulveda Stability Criterion (QQA: Qualitative– Quantitative Analysis). The analysis involves making graphs of the ratio of shares of individual fractions (R/A, S/A, Ar/A, Ar/(S/A), (R/A)/(S/Ar), S/(ArA)) based on SARA analysis.[13,18] The graph shows the stable, metastable, and unstable zones with respect to the ordinate values (0Y axis). To determine the limits for individual zones, the maximum value of the coefficient is divided by 2 (stable/metastable limit) and
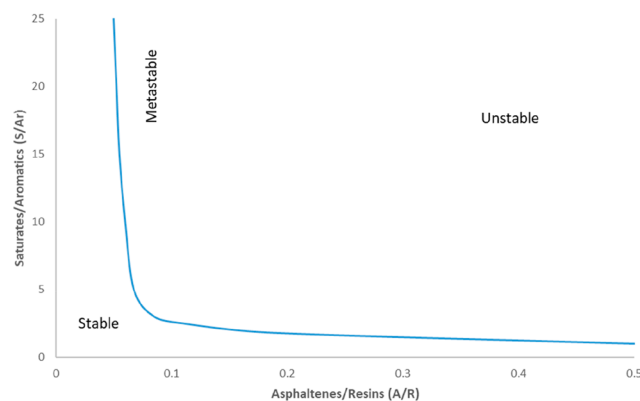

Figure 6. Stankiewicz plot with stability criterion marked.

by 4 (metastable/unstable limit). Each of the designated zones is assigned a numerical value of 10, 5, and 1. The crude oil to be characterized is assigned a numerical value corresponding to its zone (Figure 7).

A summation of values assigned to each zone (stable, metastable, or unstable) is performed for each relationship. By following this procedure for all relationships, a summation for each crude oil sample is done.

For $\sum \geq 30$, the crude oil is stable, for $30 > \sum \geq 15$ the crude oil is metastable, and for $\sum < 15$ it is unstable.[10]

3.1.6. Stability Cross Plot (SCP). The method is an extension of the QQA analysis and involves the simultaneous interpretation of four graphs with zones of stability marked based on SARA analysis (Figure 8): SCP1, Ar/A vs (R/A)/(S/ Ar); SCP2, R/A vs (R/A)/(S/Ar); SCP3, R/A vs S/(ArA); and SCP4, Ar/(S/A), (R/A)/(S/Ar).

The results of SARA analysis of the crude oil after superposition on the graphs allow determining the stability range of the analyzed sample. The use of four plots improves the accuracy of the stability analysis and allows for faster classification when the obtained parameters oscillate around the limiting values for individual zones (stable, metastable, unstable).[13,18]

3.2. Experimental Methods. In addition to methods based on group composition analysis, there are methods for determining crude oil compatibility using a wide range of analytical, numerical, and commercially available analyzers. These methods are described below.

3.2.1. Spot Test. The method, based on the ASTM D4740 standard, involves the visual assessment of the spot formed by placing a drop of the sample on a filter paper that has been kept in the oven at 100 °C for an hour[17] and assigning it to one of five categories as shown in Table 1.[13]

The analysis of the results is based on a visual assessment of the presence of a dark ring of asphaltenes precipitated from the sample. The clearer and darker the asphaltene ring is, the more unstable the sample is. The literature treats samples assigned to category 3 and higher as unstable.

The modification of the above-mentioned method is the so-called Shell Spot Test.[53] The change involves preliminary dilution of the sample with 10% v/v hexadecane (cetane). After conditioning (60 °C for 1 h), a drop of the solution is placed on a filter paper and the resulting spot is washed with heptane. After drying, the spot is inspected for the presence of a dark inner ring. The presence of the ring indicates that the blend is incompatible.
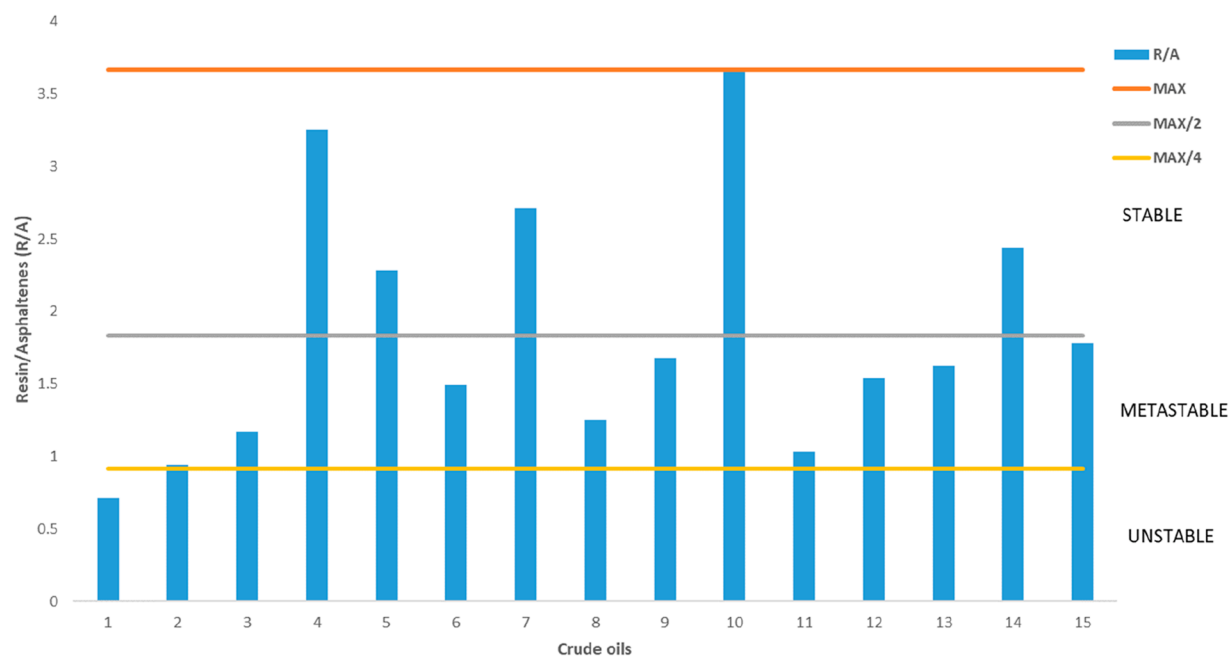
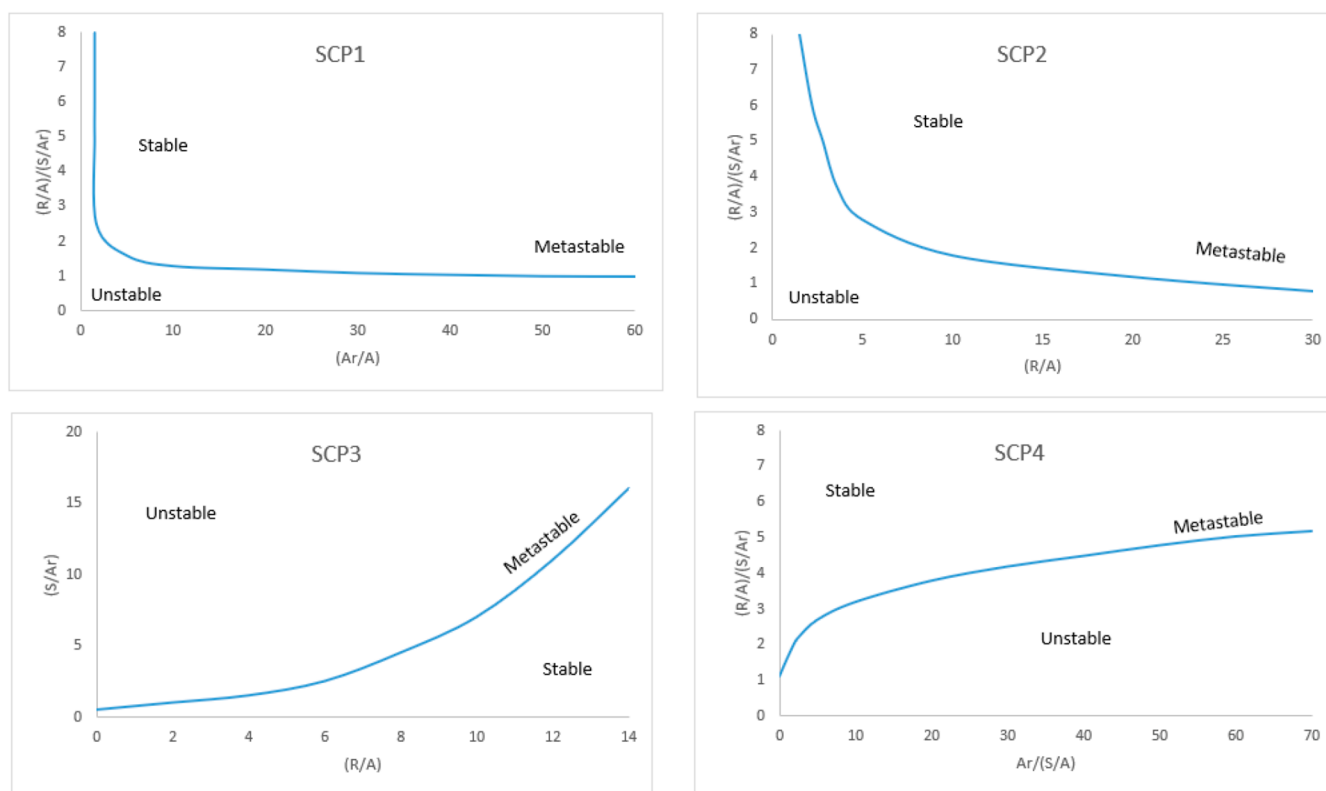**Figure 7.** Example of classification of stability zones for R/A.

Figure 8. Stability cross plots.

3.2.2. Heithaus Parameter (P Value). An experimental method based on the ASTM D-7112 standard involves the preparation of a series of solutions of crude oil in an aromatic solvent (*e.g.,* toluene), which are then titrated with a paraffinic solvent (*e.g.,* heptane) until asphaltene precipitation occurs.[13,18]

A flocculation ratio is then calculated from eq 3

$$FR = \frac{V_S}{V_S + V_T} \tag{3}$$

where V_S is the volume of aromatic solvent and V_T is the titrant volume.

The concentration of crude oil in the mixture of solvents at which asphaltene precipitation takes place is calculated as

**Table 1. List of Categories Characterizing Spots in the Spot Test**

categories	spot characteristics
1	homogeneus spot without inner ring
2	faint or poorly defined inner ring
3	well-defined thin inner ring, only slightly darker than the background
4	well-defined inner ring, thicker than the ring in reference spot N0; three and darker than the background
5	very dark solid or nearly solid area in the center; central area is darker than the background

$$C = \frac{W_A}{V_S + V_T} \tag{4}$$

where W_A is the mass of oil in the sample, V_S is the volume of aromatic solvent, and V_T is the titrant volume.

The titration is repeated at least four times with different concentrations of crude oil.

Values for FR and C at each concentration are plotted and a linear regression is done through the four points to give the intersection with FR and C axes (Figure 9). The intersection
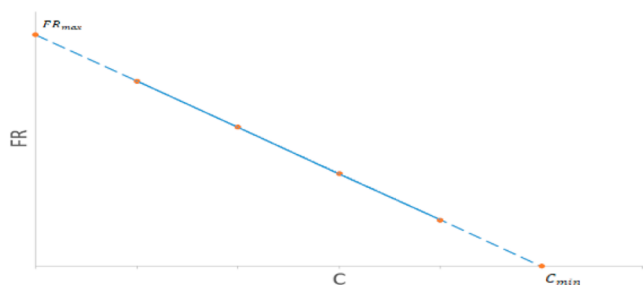
Figure 9. Plot illustrating determination of parameters FR_{MAX} and C_{MIN}.

with the FR axis is denoted as FR_{MAX}, which is the ratio of solvent to titrant at which the asphaltene fraction is soluble in all concentrations. The intersection with the C axis is denoted as C_{MIN}, which is the minimum amount of the paraffin solvent added to the crude oil sample to cause asphaltene precipitation without the addition of the aromatic solvent.

Afterward, other parameters are calculated, beginning with the solubility of asphaltenes in crude oil from eq 5.

$$P_a = 1 - FR_{max} \tag{5}$$

More insoluble asphaltene molecules are present in crude oil with low values of P_a. P_0 is the solubility power of maltenes in bitumen. The higher the P_0 value, the higher the solubility power.

$$P_0 = FR_{max} \times \left[\left(\frac{1}{C_{min}} \right) + 1 \right] \tag{6}$$

Finally, parameter P (Heithaus parameter) is calculated:

$$P = \frac{P_0}{(1 - P_a)} \tag{7}$$

When $P < 1$, crude oil is unstable. For higher values of P, the stability of crude oil increases.

3.2.3. Toluene Equivalence (TE). The test involves dissolving a sample of crude oil (2 g) in toluene−*n*-heptane mixture (10 mL) with a variable content of the first

component.[12,13,22] From a series of measurements, the minimum toluene content which stabilizes the solution preventing the precipitation of asphaltenes is determined[13]

$$TE = \frac{V_T}{V_T + V_H} \times 100\% \tag{8}$$

where V_T is the toluene volume and V_H is the hexane volume.

3.2.4. Heptane Dilution Test H_D. The test involves titrating a sample of crude oil (5 mL) with *n*-heptane.[12,22,24] It allows the determination of the maximum amount of asphaltene destabilizing agent in crude oil (*n*-heptane in ml) that can be added before precipitation occurs. The test is quick and can be used not only in the laboratory but also in the field.

3.2.5. Oil Compatibility Model (OCM). Stability is assessed based on two parameters: I_N (insolubility number), which represents the degree of asphaltenes insolubility, and S_{BN} (solubility blend number) related to the crude oil capacity for solubilizing asphaltenes in solutions of crude oil in *n*-heptane/toluene mixtures with variable mass fractions of both components (test liquid—volume V_{TL}).[2,13,22] I_N is a measure of the ability to dissolve a liquid in *n*-heptane. If there are no asphaltenes in the solution and it is completely soluble, the I_N value is 0. If the asphaltenes are barely soluble, the parameter is 100. S_{BN} is a measure of the liquid's similarity to *n*-heptane as a solvent. If crude oil is a weak solvent like *n*-pentane, the value of the S_{BN} parameter is zero. If crude oil dissolves asphaltenes as well as toluene, then the value of the parameter is 100.

For each volume ratio of oil (V_{OIL}) to test liquid (V_{TL}), the minimum volume of toluene to keep asphaltenes in solution is determined.

The results of the analysis are presented in the graph (Figure 10),[12,22] where the OY axis represents the ratio of the
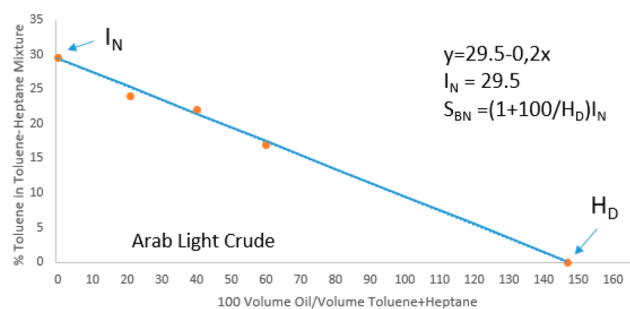
Figure 10. Graphical representation of the determination of I_N and S_{BN}.

minimum toluene content to V_{TL} (expressed as a percentage), and the OX axis is the ratio of V_{OIL}/V_{TL} multiplied by 100. The following linear equation is obtained (eq 9):

$$\frac{100 V_T}{V_{TL}} = I_N + \frac{100 V_{oil}}{V_{TL}} \times \left[\frac{I_N - S_{BN}}{100} \right] \tag{9}$$

where the *y*-axis intercept is equal to the insolubility number I_N, while the *x*-axis intercept is H_D. This term is used to calculate the solubility blend number S_{BN} as follows:

$$S_{BN} = I_N \times \left[1 + \frac{100}{H_D} \right] = I_N \times \left[1 + \frac{V_H}{V_{oil}} \right]_{V_T=0} \tag{10}$$

The S_{BN}/I_N ratio is used for predicting the pure oil stability by which a high value will correspond to more stable crude
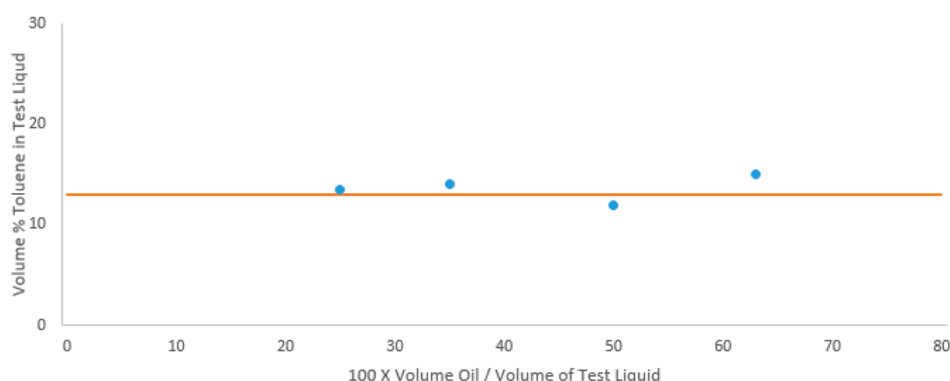
Figure 11. Graphical representation of self-incompatible oil Yme (North Sea) where $I_N = S_{BN}$.

oils.[12] To simplify and speed up the measurements, the S_{BN} and I_N parameters can also be calculated based on the results of the toluene equivalence test (TE) and heptane dilution test (HD) using eqs 11 and 12

$$I_N = \frac{TE}{1 - \frac{\nu_H}{25d}} \quad (11)$$

$$S_{BN} = I_N \left[1 + \frac{\nu_H}{5} \right] \quad (12)$$

where ν_H is maximum amount of *n*-heptane that can be added without precipitating asphaltenes and d is the oil density [g/mL].

For self-incompatible oils, *i.e.,* oils that contain insoluble asphaltenes (*e.g.,* Yme, Isthmus[12]), no *n*-heptane needs to be added to precipitate asphaltenes. For such oils $\nu_H = 0$ which means that their I_N and S_{BN} are equal (Figure 11).

Attempts were undertaken to determine the two parameters by methods other than the instrumental method using a large amount of hazardous solvents. The use of nuclear magnetic resonance (NMR) can serve as an example.[25]

Although OCM concerns the characteristics of individual crude oils, Irvin A. Wiehe proposed a criterion using I_N and S_{BN} to determine the limiting fractions of crude oils in a blend.[23,24] The criterion states that for compatibility the solubility blending number of the mixture of oils must be higher than the insolubility number of any oil in the mixture.[26]

$$(S_{BN})_{blend} > I_{N_{max}} \quad (13)$$

3.2.6. Asphaltene Stability Class Index (ASCI). This method assigns a sample containing asphaltenes to a grade based on the intrinsic stability of the asphaltenes and their susceptibility to precipitation. The analysis involves the preparation of 21 toluene/*n*-heptane solutions with a stepwise increasing (every 5% w/w) content of *n*-heptane creating 21 classes (class 0 is assigned to a solution with a zero *n*-heptane content, and class 20 with 100% *n*-heptane content). The same amount of sample should be added to each solution and stirred vigorously. Samples stored at 45 °C are evaluated after 48 h for asphaltene precipitation. The first sample (starting from class 0) in which the asphaltenes precipitated determines the ASCI class assigned to a given oil.[27,28]

3.2.7. Onset of Asphaltene Precipitation (OAP) in Crude Oils. By blending crude oils or adding precipitants, the internal stability of each is disturbed. By changing the proportions of individual components, using the trial and error method, the

proportions at which the asphaltenes are precipitated can be determined. There are several experimental methods to measure the onset of asphaltene precipitation:

- optical[29,30]
- viscosity measurement[29,31,32]
- refractive index measurement[29,33,19,34,32]
- gravimetric[29]
- interfacial tension (IFT) measurement[29]
- heat transfer technique[29]
- density measurement[29]
- acoustic resonance technique (ART)[29]
- light scattering technique (LST)[29]
- transmittance measurements in near-infrared (NIR) region (ASIT^{SM}, asphaltene stability index test, APDT, Asphaltene Precipitation Detection Test)[27,35−37]

3.2.8. S-Value. The test is based on the ASTM D-7157 standard method and involves automatic titration of three different samples of crude oil dissolved in variable amounts of an aromatic solvent (toluene) using *n*-heptane as titrant. An optical sensor is employed to detect the moment of flocculation by monitoring changes in light intensity.[13]

3.2.9. Turbiscan. A commercial method based on the standardized ASTM D-7061 method and involving measuring transmittance or light scattering of infrared radiation as a result of asphaltene flocculation. The measurement is carried out on a sample placed in a glass cylinder. To obtain high resolution, several scans are performed with steps of 40 μm.[13]

The analyzed samples are first destabilized by the addition of *n*-heptane to the solutions of crude oil and toluene in varying proportions. The obtained curves are a picture of transmittance and scattering intensity as a function of the cell height and time.

The average transmittance (x_i) for each measurement (n) is used to calculate the total average transmittance (x_T) of the sample, which in turn is used to find the separability number (S_N) as follows:

$$S_N = \sqrt{\frac{\sum_{i=1}^{n} \times (X_i - X_T)^2}{n - 1}} \quad (14)$$

If $0 < S_N < 5$, the oil is highly stable, if $5 < S_N < 10$, the oil stability is low, and for $S_N > 10$ the oil is unstable.

3.2.10. K-Model (Crude Oil Compatibility Parameter K). The model is based on the analysis of the effect of the physicochemical properties of crude oil (or oil blends) on its stability.[18]

The first step is to prepare graphs (Figure 12) illustrating the effect of varying the properties (or the ratio of properties) on
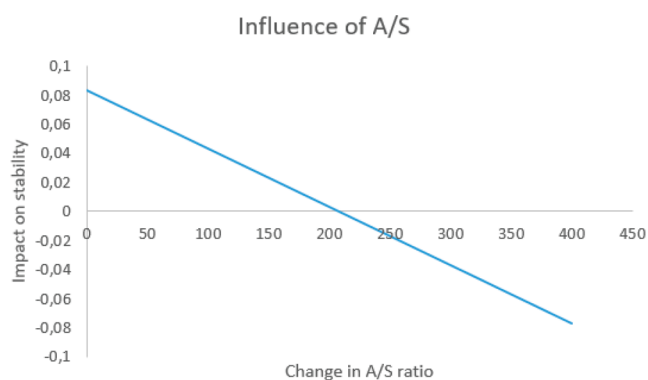
Figure 12. Example of the impact of A/S ratio (OX axis) on crude oil compatibility (OY axis).

the change in the compatibility of the oil (or oil blend). Compatibility of oil samples, calculated using the methods based on SARA analysis (CII, CSI, SP, QQA, SCP, OCM, parameter P) is the training set of the model. It is obligatorily taken as the value of the parameter K for a given oil sample. Changes in properties and the corresponding changes in the parameter K for all samples are used to perform a linear regression analysis, which yields the slope of the regression curve k, which is characteristic of a given property (or property ratio).

The mathematical model to determine the compatibility parameter K based on the parameter ratios is called the compatibility prediction model (or the K model) and it is given by eq 15 below:

$$K = k_1\left(\frac{1}{C}\right) + k_2\left(\frac{C}{A}\right) + k_3\left(\frac{C}{S}\right) + k_4\left(\frac{\log(S)}{C}\right) + k_5\left(\frac{A}{S}\right)$$
$$+ k_6\left(\frac{S}{V}\right) + k_7\left(\frac{V}{A}\right) + k_8\left(\frac{V}{C}\right) \tag{15}$$

where k_i are coefficients of regression read from the graph for a given ratio of parameters.

If the laboratory values of the physicochemical properties that were used to calibrate the model are known, the compatibility of new crude oil or blends of crude oil can be quickly determined and the batch optimized. If the K value is ≥ 0 then the crude oil (or blend of oils) is compatible. If $K < 0$, the oil or blend is incompatible.

The model allows the use of only those parameter ratios which significantly affect the compatibility. The publication describes an example of the application of the above-mentioned model.[18]

3.2.11. Crude Oils Solubility Profile, ΔPS Parameter. The asphaltene profile experimental method involves precipitation of the asphaltenes in a Teflon-packed column using *n*-heptane and then gradually and continuously modifying the mobile phase so that the asphaltenes eluted from the column at each time are related to the solvent power of the mobile phase (*n*-heptane, 9:1 methylene chloride/methanol, methanol). In this way, it is possible to produce a response that can be associated with the solubility distribution of asphaltenes.[14]

The solubility profiles are analyzed to obtain a ΔPS parameter, which represents the time taken for the elution of

the middle 50% area (between 25% and 75%) distribution of the solubility profile. A higher ΔPS parameter value (the broader the distribution) indicates higher instability of asphaltenes.

There are two distinct types of solubility profiles: unimodal and bimodal. The unimodal distribution indicates similar solubility behavior for all the asphaltene fractions. These fractions are characterized by higher stability. Bimodal distribution means that there are two different groups of molecules that are insoluble within one another. This apparent gap causes a greater instability of the asphaltene fraction

3.2.12. Ellipsometry. Ellipsometry is the method of measuring the change in polarization of the electromagnetic wave reflected from the sample. A linearly polarized wave after reflection becomes elliptically polarized, hence the name of the method.[14]

The oil blend being analyzed is centrifuged to produce a density profile in the sample. Portions of the centrifuged sample from different heights (and therefore of different densities) are analyzed in the apparatus, obtaining a polarization change profile with a change in density, and this is correlated with the refractive index. This profile is compared with calibration data obtained from analyses of samples of known compatibility analyzed by known and accepted methods (*e.g.*, OCM[14])

This method is proposed as a quick form of crude oil compatibility analysis and assessment under process conditions.

3.3. Thermodynamic Models. The next group is based on a mathematical description of interactions occurring in solutions at the molecular level. The objective is to create as simple an equation as possible to describe complex relationships, focusing on those whose influence on the final result is the greatest.

3.3.1. Regular Solution Model (RSM). The regular Solution Model is a method based on the assumption of a liquid−liquid equilibrium between an asphaltene (and resin) rich so-called heavy phase and a precipitant-rich light phase.[40]

The partition coefficient of each component is calculated from eq 16:

$$K_i^{hl} = \frac{x_i^h}{x_i^l}$$
$$= \exp\left\{\frac{\nu_i^h}{\nu_m^h} - \frac{\nu_i^l}{\nu_m^l} + \ln\left(\frac{\nu_i^l}{\nu_m^l}\right) - \ln\left(\frac{\nu_i^h}{\nu_m^h}\right)\right.$$
$$\left. + \frac{\nu_i^l}{RT}(\delta_i^l - \delta_m^l)^2 - \frac{\nu_i^h}{RT}(\delta_i^h - \delta_m^h)^2\right\} \tag{16}$$

where K_i^{hl} is the partition coefficient, x_i^h is the mole fraction of heavy phase, x_i^l is the mole fraction of light phase, R is the gas constant, T is the temperature [K], ν is the molar volume of component i, and δ is the solubility parameter of component i. Subscript m represents the properties of the mixture, and subscript i represents a given component.

Unlike the equations of state, the method is only applicable to the liquid−liquid equilibrium. Another limitation is the assumption that only resins and asphaltenes are present in the heavy liquid. Due to the nature of the data needed, the possibility of obtaining them for very high pressures and temperatures is limited.[41] The main advantage of the RSM

method over the equations of state is the simplicity of calculations due to the lack of binary interactions and a smaller number of parameters to be calculated and fitted.[40−43] Modeling of oil blend stability can be based either on SARA analysis or oil assay data. The practical application of the model along with the computational procedures has been described in several papers.[41−47]

3.3.2. Solubility Parameter δ. The Hildebrand solubility parameter is the square root of the cohesive energy density, and it is used in the RSM model (Hildebrand, Scatchard).[22] It is defined as

$$\delta = \sqrt{\frac{E_V}{V}} = \sqrt{\frac{\Delta H_V - RT}{V}} \qquad (17)$$

where E_V is the energy of vaporization to ideal gas, ΔH_v is the enthalpy of vaporization, R is the gas constant, T is the temperature, and V is the molar volume.

The solubility parameters readily available for crude oils and their blends allow for their classification as stabilizing or destabilizing. Numerous studies indicate the existence of a threshold value at which oil is destabilized upon the addition of precipitants.[37,48] This resulted in attempts to correlate the solubility parameter with other known parameters, such as I_N and S_{BN}, using the formulas 18 and 19:

$$I_N = 100 \frac{(\delta_f - \delta_H)}{(\delta_T - \delta_H)} \qquad (18)$$

$$S_{BN} = 100 \frac{(\delta_{oil} - \delta_H)}{(\delta_T - \delta_H)} \qquad (19)$$

where δ_{oil} is the solubility parameter of oil sample, δ_H is the solubility parameter of heptane, δ_T is the solubility parameter of toluene, and δ_f is flocculation solubility parameter, the threshold solubility parameter separating compounds (x) in which the sample dissolves ($\delta_x > \delta_f$) from those in which asphaltene precipitation occurs ($\delta_x < \delta_f$)

3.3.3. Perturbed Chain Statistical Associating Fluid Theory (PC-SAFT). The SAFT model in its original form describes the interaction of macromolecular systems in mixtures with a complex structure. It models molecules as a series of successive spherical sections forming long chains.[50,51] Based on this theory, Gross and Sadowski developed its extension using a model liquid as a reference.[52] This approach accurately predicts the phase behavior of high-molecular-mass fluids such as asphaltene fractions.

PC-SAFT equation of state is formulated with the definition of reduced Helmholtz free energy as described by the general formula 20:[49]

$$\tilde{a}^{res} = \tilde{a}^{hc} + \tilde{a}^{disp} + \tilde{a}^{assoc} \qquad (20)$$

where $\tilde{a}^{res}$ is the reduced Helmholtz free energy, $\tilde{a}^{hc}$ is the hard chain contribution to reduced Helmholtz free energy, $\tilde{a}^{disp}$ is the dispersion contribution to reduced Helmholtz free energy, and $\tilde{a}^{assoc}$ is the association contribution to reduced Helmholtz free energy.

The procedure for the application of the PC-SAFT model to crude oil and its blends was proposed by Ting.[53,54] The literature describes a number of practical approaches to the use of the PC-SAFT model.[51−54] To simplify its use for complex asphaltene molecules, attention is focused on the structure and interactions within the molecule to be characterized, which requires three parameters: the number of segments (spheres)

per molecule (m), segment diameter (∂), and segment dispersion energy (ε/k).

3.3.4. *Flory−Huggins Theory (FH).* The theory is based on Gibbs free energy and is described by a general eq 21:

$$\Delta G_m = RT[n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_1 \phi_2 \chi_{12}] \qquad (21)$$

where R is the gas constant, T is the temperature, n_i is the number of moles of solvent (subscript 1) or solute/polymer (subscript 2), ϕ_i is volume fraction of solvent (subscript 1) or solute/polymer (subscript 2), and $\chi_{12(FH)}$ is the Flory−Huggins interaction parameter.

$$\chi = \frac{V_m}{RT}(\delta_2 - \delta_1)^2 \qquad (22)$$

where V_m is the molar volume of mixture components other than asphaltenes and δ_i is the solubility parameter.

Models based on this theory assume that asphaltenes act as large polymer molecules and can be characterized by a pseudocomponent with averaged properties dissolved in the oil fraction. According to the theory, two assumptions can be made:[3]

(1) Asphaltenes precipitate completely and are the only component of precipitates, passing to the so-called heavy phase.

(2) The precipitates are a mixture of asphaltenes and components of the oil fraction.[44]

One of the first developed models describing the behavior of asphaltene fractions, the Hirschberg model,[3,44,56] is based on the first assumption that the mixture Gibbs free energy can be derived from eq 23[49]

$$\frac{\Delta G}{RT} = \frac{\varphi_1}{r_1}\ln \varphi_1 + \frac{\varphi_2}{r_2}\ln \varphi_2 + \chi_{FH}\varphi_1\varphi_2 \qquad (23)$$

where r_x is the relative molar volume, where $r_1 = 1$ and r_2 is obtained from expression 24

$$r_2 = \frac{v_2 MW_2}{v_1 MW_1} \qquad (24)$$

where $\nu_{1,2}$ is the specific volume of solvent (subscript 1) or solute/polymer (subscript 2) and $MW_{1,2}$ is molar mass of solvent (subscript 1) or solute/polymer (subscript 2).

Over the years, many models based on the F−H theory have been developed.[3,49,55,−57] One of the most recognizable is the Asphaltene Solubility Model (ASM).[44]

3.3.5. Yen−Mullins Model. The Yen−Mullins model describes the behavior of asphaltene molecules in solution and changes in the structure of these molecules with a change in concentration.[58] The model assumes the most probable molar mass at the level of approximately 750 g/mol with most of the population being between 500 and 1000 g/mol.[59] A single asphaltene molecule has the "island" molecular architecture with one aromatic ring per molecule and a number of peripheral aliphatic chains (Figure 1). As the concentration of molecules increases, asphaltenes begin to form nanoaggregates, which in turn form clusters. The model has been validated by numerous studies using increasingly sophisticated analytical methods,[31] such as nuclear magnetic resonance (NMR), time-resolved fluorescence depolarization (TRFD), small-angle X-ray scattering (SAXS), or small-angle neutron scattering (SANS).

The assumptions of the Yen−Mullins model allowed for the formulation of the first equation of state describing the
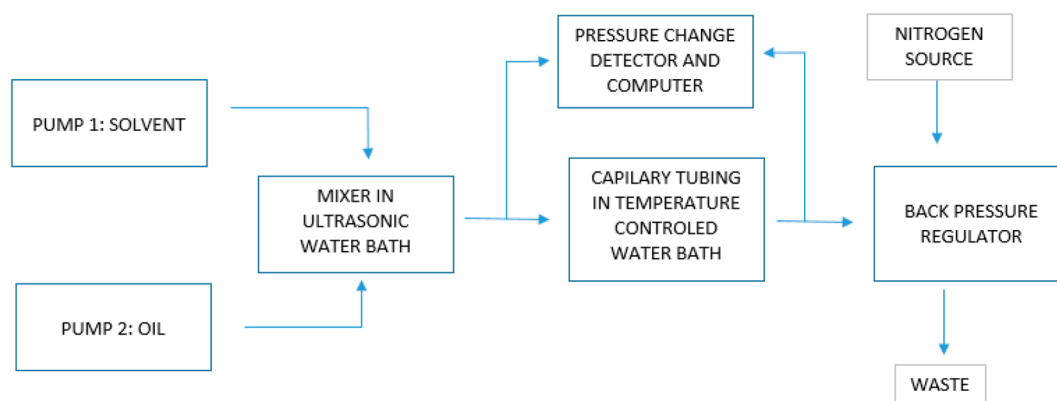
Figure 13. Experimental setup of Wang et al.

behavior of asphaltenes during extractions from deposits called the Flory−Huggins−Zuo equation of state (FHZ EoS).[57,59]

3.3.6. Cubic Plus Association Equation of State (CPA EoS). The model was developed by SHELL (Amsterdam branch), which at the turn of the 20th and 21st centuries was joined by other companies, such as Statoil, BP, or TOTAL. The project aimed to extend the applicability of standard equations of state to systems containing hydrogen bonds and polar interactions which are of interest to producers of crude oil and its products.[61,62] The CPA model is an equation of state that combines the Soave−Redlich−Kwong (SRK) equation of state and the association term from the Wertheim theory.[60,64] The association term takes into account the specific interaction due to hydrogen bonding between like and unlike molecules. Later, researchers modified the equation for both the term describing the physical properties (SRK) and the term responsible for intermolecular interactions, obtaining different versions of CPA EoS for specific types of intermolecular interactions.[62,63,65] The original equation based on SRK EoS and the association term described by Michelsen and Hendriks has the form[63]

$$P = \frac{RT}{V_m - b} - \frac{\alpha(T)}{V_m(V_m + b)} - \frac{1}{2}\left(\frac{RT}{V_m}\right)\left(1 + \frac{1\delta \ln g}{V_m \delta(1/V_m)}\right)$$
$$\sum_i X_i \sum_{A_i}(1 - X_A) \tag{25}$$

where V_m is the molar volume, X_A is mole fraction of A-sites of molecule i not bonded with other active sites, g is the radial distribution function, x_i is the mole fraction of component i, R is the universal gas constant, and T is the temperature.

Since its inception, CPA EoS has found increasing applicability both in its original and modified form.[62,63] It is a valuable tool providing very good results for modeling complex systems, which is confirmed by comparative studies with both PC SAFT and the Hirschberg method.[64,65]

3.4. Systems for Dynamic Testing of Compatibility of Crude Oils. The methods of testing asphaltene stability in the solution discussed above are based on laboratory measurements or assumptions regarding standard conditions that can be much different from the actual process conditions. Frequently, they focus on the microscale to predict the behavior of molecules in model solutions under standard pressure and temperature conditions. The practice of processing crude oil blends requires a more practical approach to provide a picture of macro-scale changes taking place in

actual installations. Many researchers adopted this point of view and proposed their setups for the dynamic study of the asphaltene behavior in crude oil blends (Figure 13), including[5] Wang, Broseta, Salimi, Alboudwarej, Peramanu, Alcor Hot Liquid Process Simulator (HLPS),[63,64,66,67] and others.[24,68,69]

The vast majority of these are loop systems consisting of a thermostated crude oil tank equipped with an agitator and the systems injecting both oil stabilizing and destabilizing solvents. Another element is a pump delivering the blend (crude oil and possibly stabilizers and destabilizers) to a heating system simulating a heat exchanger. The entire system is controlled by a computer control system.

The proposed measurement systems have the advantage that they enable dynamic modeling of the stability of crude oil blends both in terms of composition and processing parameters. By taking into account the effect of temperature and pressure variability, it is possible to model the composition and yields of individual fractions after distillation of crude oil and, thus, the economic effect of oil processing.

4. SUMMARY

The possibility of predicting the impact of crude oil on installations allows to accurately estimate the profitability of processing and to reduce the risk of situations requiring the reduction or even stoppage of production.

Professional and scientific literature provides many examples of methods for determining crude oil compatibility, which was discussed in this review. However, many of them are based on simplifications that differ from industrial practice and give only a general picture of behavior. So far, attempts have been made to design dynamic systems that try to accurately reproduce the crude oil processing and its long-term impact on the installation. However, it is impossible to design one model for all processing scenarios. The proposed methods remain only mathematical models, which each time must be adapted to the individual needs of the company.

The comparison of SARA-based methods with actual industrial data revealed large discrepancies in the correct determination of compatibility. Studies of crude oil samples from the Brazilian region[13] showed that the CII, CSI, SP, QAA, and SCP are 87% effective in the prediction of the stability of stable crude oil samples. The largest differences were for QAA and SCP. However, for incompatible samples, the prediction accuracy is only 25% with CII and SCI being the most effective. The prediction accuracy for crude oil from the Arabian region is different.[18] For CII, the accuracy of

prediction is only 8%, for QAA 30%, for CSI, SI, and SP around 80%, and 100% for SCP. Both Comparisons reveal that CII is better suited for indicating crude oil incompatibility. Also a Mexican region crude comparison revealed that CII and CSI, has much better accuracy of prediction.[70] The methods based on the comparison of several parameters, such as QAA and SCP, show the greatest number of correct predictions. Predictive methods based on the SARA analysis are characterized by simplicity, but as experience shows, each of them individually does not guarantee satisfactory results of compatibility prediction.[71] The approach suggested in the literature is to analyze all parameters simultaneously to obtain the dominant result.[13,18,20,70] The QQA, SCP, or K model based on this approach gives better results, which are still subject to uncertainty and must be further correlated with the behavior of the tested raw material to select the models that best fit the actual conditions of processing.[18]

Experimental methods present a wide spectrum of complexity, from a simple spot test, through a heptane dilution test or TE, to those requiring specialized equipment: S-value, P-value, or Turbiscan. These methods are in common commercial use. Each of them provides information that requires a long-term process of observation and comparison of results with actual process data or other analytical methods, e.g., OCM.[38] Building a database, although time-consuming, gives the best prediction results based on real process data. If the experiments described in this paper provide promising results, the authors emphasize the need for further analyses.[39] In this group, OCM is the most complete method of testing the stability and compatibility of crude oils and their blends.

Studies of emerging publications reveal that thermodynamic models are most likely to correctly estimate the compatibility of crude oils and their blends. Physicochemical relationships, despite numerous simplifications and assumptions, provide results that are more satisfactory and accurate compared to other discussed approaches.[3] Among the models available in the literature, the PC-SAFT and CPA are rated the highest.[49] They can reproduce laboratory data in the ranges they were calibrated with very high accuracy.[51−54] They also allow to simulate the reaction of the system under varying conditions of the environment, but with variable accuracy, which limits their use outside the calibration range. Despite many advantages, they require very complex calculations and analytical activities to obtain the required batch data. For these reasons, they cannot be considered simple methods. Furthermore, no description of predictive analyses under process conditions using these methods is available in the literature.

The application of the above-mentioned methods in industrial practice encountered numerous difficulties. The results obtained under laboratory conditions, even when compared with the process data, were unreliable when transferred to industrial practice. A need arose to fully reproduce the blending and processing of crude oils. Installations for dynamic compatibility testing proposed in the literature were the answer. They allow for precise reproduction of physicochemical parameters of oil processing and control of the duration of the experiment, which facilitates the implementation of the results of analysis into industrial practice. The biggest disadvantage of this approach is the cost of the measuring system.

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