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Adaptation of Mathematical Models for the Determination of Crude Oil Blends Stability

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Abstract
Crude oil blend formulation has been topical in recent times with research focus on yield maximization by appropriate feedstock preparation. The present work developed a simple mathematical algorithm to predict with precision, asphaltene precipitation as measure of crude oil blend stability and compatibility. Crude oil Blend stability was measured in terms of Colloidal Insolubility Index (CII), Asphaltene to Resin (A/R), ratio and ration of the Solubility Blending Number (S_{BN}) and Insolubility Index (R). Results of the present work are in good agreement with plant data and simulation results of previous work for all parameters of blend stability determination. In each case, both studies gave stable blends as shown above. Main contribution of this work to the subject matter is in its unambiguous and precise nature, and its simplicity, both of formulation and application.

Keywords: ***Crude oil; Crude Oil blend, Mathematical models; Crude Oil Stability; Mathematical algorithm***

1.0 Introduction

Crude oil blending is a subject that has attracted more than considerable research attention (Aida et al., 2000, Eneckwe et al., 2012 and Naji et al., 2021). Ranging from development of blend recipes as analytical equations to linear and non – linear programming model, and even computer simulation solutions, blending of crude oils for various purposes, though mainly feed stock suitability has been substantial. The foregoing underscores importance of crude oil blending in the global energy value chain. Initial target of crude oil blending was to improve gasoline yield in refining, as it was the most predominant and sought – after product. While gasoline still remains the fossil fuel with highest global demand (Mohan Kelkar, 2024), different competing reasons now exist for crude blending. One such reasons is the reduction of crude oil sulphur content to increase the market price. Though, there are several classifications of crude oil, a major one is that based on its API gravity and sulphur content. Under this classification, crude oils can be divided into four major groups (Vignesh et Al., 2019):

- Light low sulphur (API 30 – 40°, S ≤ 0.5% mass)
- Light, moderate sulphur (API 30 – 40°, S = 0.5 – 1.5% mass)
- Heavy, high sulphur (API 1 – 30°, S = 1.5 – 3.1% mass)
- Extra heavy high sulphur (API = 15°, S ≥ 3% mass).

High sulphur crude oils have low commercial value than low sulphur crudes. To enhance profitability therefore, crude oils are blended to reduce their sulphur contents to acceptable limits. Different chemical treatment processes for sulphur reduction in crude oils include catalytic oxidation in presence of hydrogen peroxide (Cullen, 2004), Nitrogen oxide and sulphuric acid (Guth et al., 1975), etc. The chemical treatment methods for sulphur reduction are however more cumbersome to manage given the separation processes involved in the resulting mixture. Consequently, a better solution for the problem of sulphur reduction in crude oil is blending high sulphur (sour crude) with low sulphur (sweet crude) to have acceptable intermediate or moderate sulphur crude (Naji et al., 2021).

Crude oil produced in deep offshore and onshore wells are transported across long distances to their storage and processing facilities. Heavy crude oils cause fouling of pipelines and create flow obstruction and interruptions. Thus, as a necessary measure, heavy crude oils are blended with much lighter ones to reduce their viscosity and improve flow properties. Hasan et al. (2010) studied heavy crude oil viscosity reduction for easy pipeline transportation. The work was focused on possible blending alternatives that existed to reduce the viscosity and other rheological properties of heavy crude oils to enhance their flowability in pipelines. Hart (2013) carried out a comprehensive review of blending technologies for crude oil and bitumen transportation through pipeline, while Saniere et al. (2004) looked at blending and the strategic economic implications of pipeline transportation of heavy crude oils.

An important point to note in the transportation of heavy crude oils in pipelines is the phenomenon of fouling, where components of crude oil form deposits on the inner surface of the pipeline (Yousef Easa Al-Shamlan, 2019). Directly responsible for this phenomenon are crude oil components that tend to dissociate out of solution, whether during transportation or storage (Watkinson, 1995). In crude oil blending, mixing of crude oils with different API gravities sometimes result in non – homogenous mixtures with precipitation of crude oil components. These mixtures are generally referred to as “Unstable Blends” or “Non – compatible”, while the homogenous mixtures are referred to as “Stable Blends” or “Compatible” (Scott Sayles and D Mark Routt, 2011, George Mushrush and James G. Speight, 1996).

The chemical composition of crude oil is primarily divided into four hydrocarbon groups: Paraffins, Olefins, Naphthenes and Aromatics. This classification is not totally exclusive, as other classifications exist based on the purpose and use. For the purpose of determination of crude oil stability or compatibility of mixing, the classification of components is based on solubility and polarity (Evdokimov, 2010). These components are Saturates (non – solvent), Aromatics (solvent), Resins (dispersant), and Asphaltenes (solute). Asphaltenes are components of petroleum, whose behaviour and structure change with temperature, pressure and the composition of oil.

Asphaltenes have a high affinity towards aggregation and as a result, easily precipitate and form deposits in production and processing equipment (Bambinek, 2023). Asphaltenes are thus used as the basic standard in determination of crude oil and products blend stability (Asomaning, 2013). Mahmoud and Aboujadeed (2017) studied the compatibility of four Libyan crude oil prior to blending, to determine asphaltene precipitation for possible pipeline transportation using standard ASTM and IP methods.

2.0 Objectives of the Work

The present work developed a simple mathematical algorithm to predict with precision, asphaltene precipitation as measure of crude oil blend stability and compatibility. In this regard, the specific goals of the work included, but not limited to:

i. Determine individual SARA components in the different crude oils of S – M – N – A
ii. Develop mathematical models to describe the flocculation tendency of crude oil Blends based on the Case study in the work.
iii. Determine Blend stability in terms of Colloidal Insolubility Index (CII), Asphaltene to Resin (A/R), ratio and Blend stability in terms of Solubility Blending Number and Insolubility Index (R)

Suffice to note however, that the present work is only relevant and applicable in situations where the crude oil blend assay does not clearly define compositions of the individual crude oils from where the blend is produced. This is frequently the case as the primary assay from where blends are produced is often overlooked, especially for trading companies.

3.0 Crude Oil Blend Compatibility and Stability Criteria

As a measure of crude oil instability, Asomaning and Watkinson (2000) introduce the Colloidal Instability Index (CII) as given in (1). They concluded that blends with $CII > 2$ tend to be incompatible or unstable, and precipitate asphaltenes.

$$CII = \frac{(Saturates + Asphaltenes)}{Resins + Aromatics} \quad (1)$$

A second parameter for determination of the compatibility or incompatibility of oils and their blends is the ratio of *Solubility Blending Number (S_{BN})* to the *Insolubility Number (I_N),* given by the extent of solubility or otherwise of the oil in a solution of n – heptane and Toluene. This relationship gives the point of flocculation for oils as well as evidence of asphaltene precipitation. When $S_{BN(Mix)} > I_{N(Max)}$, then the crude oil blends are compatible and stable without Asphaltene precipitation, otherwise, the system is incompatible and unstable. It is mathematically expressed as ratio of (R) given in (2). When $R > 1$, blend is compatible, but incompatible when $R < 1$.

$$R = \frac{S_{BN(Mix)}}{I_{N(Max)}} \quad (2)$$

Where $S_{BN(Mix)}$ is given by (3) and S_{BN} by (4).

$$S_{BN(Mix)} = \frac{V_1 S_{BN1} + V_2 S_{BN2} + V_3 S_{BN3} \ldots\ldots V_n S_{BNn}}{V_1 + V_1 + V_1 \ldots\ldots . V_n} \quad (3)$$

$$S_{BN} = I_N \left(1 + \frac{100}{HD}\right) \quad (4)$$

$$HD = Volume\ of\ n - heptane$$

$$I_N = \%\ volume\ of\ Toluene\ in\ test\ Liquid$$

Similarly, a third empirical correlation for determination of blend stability is the Asphaltene to Resin ratio (A/R). The study determined $A/R > 0.35$ to be an unstable crude oil blend, and the contrary as stable.

4.0 Development of Mathematical Algorithm

To successfully develop a mathematical procedure or algorithm for the exact determination of blend stability based on the criteria set above, the composition of individual SARA components has to first and foremost be determined. Consequently, the mathematical formulation is based on four Libyan Crudes oils simply represented by the letters: S, M, N, A, in two blends as was given by Mahmoud and Aboujadeed (2017):

Blend 1: S – M – N

Blend 2: S – M – A

All properties of the four crude oils and the two blends above and their empirical data and correlations with respect to blend compatibility and stability are given in Table 1 – 3.

Table 1: Composition by Percentage Volume (% v) and Solubility Blending Number and Insolubility Index of Crude Oils

Crude Type	Blend – 1	Blend – 2	S_{BN}	I_N
S	55.0	55.0	40.50	25
M	30.0	22.5	39.44	34
N	15.0	-	34.56	27
A	-	22.5	39.68	31

Table 2: Crude Oil SARA Composition by Percent Weight

Composition	Blend-1 wt. %	Blend-2 wt. %
Saturates	64.40	65.70
Aromatics	10.10	11.30
Resins	24.91	22.30
Asphaltenes	0.70	0.59

Table 3: Colloid Instability Index for Crude Oil Blends

Name	Blend-1	Blend-2
CII	1.85	1.97
A/R	0.024	0.031
$S_{BN(Mix)}$	40.06	38.92
R	1.17	1.14

4.1 Determination of Individual SARA Components

Representing the SARA composition of any particular crude as w, x, y, z respectively, then compositions for the four different crude types can be given as in Table 4:

Table 4: SARA Composition of the Different Crudes S – M – N – A

Crudes	S	M	N	A
S	w_1	w_2	w_3	w_4
A	x_1	x_2	x_3	x_4
R	y_1	y_2	y_3	y_4
A	z_1	z_2	z_3	z_4

From Table 2 and 4, the SARA compositions for the two crude oil Blends can be expressed mathematically as:

Blend - 1

$$w_1 + w_2 + w_3 = 0.644 \quad (5a)$$
$$x_1 + x_2 + x_3 = 0.006 \quad (5b)$$
$$y_1 + y_2 + y_3 = 0.249 \quad (5c)$$
$$z_1 + z_2 + z_3 = 0.101 \quad (5d)$$

Blend - 2

$$w_1 + w_2 + w_4 = 0.657 \quad (6a)$$
$$x_1 + x_2 + x_4 = 0.007 \quad (6b)$$
$$y_1 + y_2 + y_4 = 0.223 \quad (6c)$$
$$z_1 + z_2 + z_4 = 0.113 \quad (6d)$$

Using the data in Tables 1 and 2, equations (5) and (6) can be further expressed in matrix algebra for the SARA components as follows:

Saturate (S):

$$S = \begin{pmatrix} 0.55 & 0.30 & 0.15 & 0 \\ 0.55 & 0.23 & 0 & 0.23 \end{pmatrix} \begin{pmatrix} w_1 \\ w_2 \\ w_3 \\ w_4 \end{pmatrix} = \begin{pmatrix} 0.644 \\ 0.657 \end{pmatrix} \quad (7)$$

Asphaltene (A_1):

$$A_1 = \begin{pmatrix} 0.55 & 0.30 & 0.15 & 0 \\ 0.55 & 0.23 & 0 & 0.23 \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \\ x_3 \\ x_4 \end{pmatrix} = \begin{pmatrix} 0.006 \\ 0.007 \end{pmatrix} \quad (8)$$

Resins (R):

$$R = \begin{pmatrix} 0.55 & 0.30 & 0.15 & 0 \\ 0.55 & 0.23 & 0 & 0.23 \end{pmatrix} \begin{pmatrix} y_1 \\ y_2 \\ y_3 \\ y_4 \end{pmatrix} = \begin{pmatrix} 0.249 \\ 0.223 \end{pmatrix} \quad (9)$$

Aromatics (A_2):

$$A_2 = \begin{pmatrix} 0.55 & 0.30 & 0.15 & 0 \\ 0.55 & 0.23 & 0 & 0.23 \end{pmatrix} \begin{pmatrix} z_1 \\ z_2 \\ z_3 \\ z_4 \end{pmatrix} = \begin{pmatrix} 0.101 \\ 0.113 \end{pmatrix} \quad (10)$$

4.2 Determination of CII

With data from section 4.1 on individual SARA composition of the different crude oils, the Colloidal Instability Index for Blend – 1 & 2 can be represented as;

$$CII_{B1} = \frac{\sum_{i=1-3} (w_i + x_i)}{\sum_{i=1-3} (y_i + z_i)} \quad (11a)$$

And

$$CII_{B2} = \frac{\sum_{i=1-4} (w_i + x_i) - \sum (w_3 + x_3)}{\sum_{i=1-4} (y_i + z_i) - \sum (y_3 + z_3)} \quad (11b)$$

With eqns. (11a) and (11b), the Asphaltene precipitation in a crude blend which gives indication of blend compatibility and stability is easily determined.

4.3 Determination of A/R

The Asphaltene and resin compositions for the Crudes oil blends is given by;

Blend – 1:

$Asphaltene$: $x_1 + x_2 + x_3$ $\quad (12a)$

$Resins$: $y_1 + y_2 + y_3$ $\quad (12b)$

Therefore, A/R is:

$$\left(\frac{A}{R}\right)_{B1} = \frac{\sum_{i=1-3} x_i}{\sum_{i=1-3} y_i} \quad (13)$$

Blend – 2:

$Asphaltene$: $x_1 + x_2 + x_4$ $\quad (14a)$

$Resins$: $y_1 + y_2 + y_4$ $\quad (14b)$

$$\left(\frac{A}{R}\right)_{B2} = \frac{\sum_{i=1-4} x_i - x_3}{\sum_{i=1-4} y_i - y_3} \quad (15)$$

4.4 Determination of $S_{BN(Mix)}$ and $I_{N(Max)}$ based on SARA composition

From Eq. (4), the Solubility Blending Number is given by;

$$S_{BN} = I_N \left(1 + \frac{100}{HD}\right)$$

But from Figure 3 and 4 of the work of Mahmoud and Aboujadeed (2017), a relationship between the Oil, n – heptane and Toluene, being the test liquid is given in Table 5:

Table 5: n – Heptane Dilution Test

Oil/ Test Liquid	oil	N - heptane	Toluene
1.6 ml	0.267	0.333	1.00
3.6 ml	0.6	0.930	2.07
6.2 ml	1.04	1.55	3.61

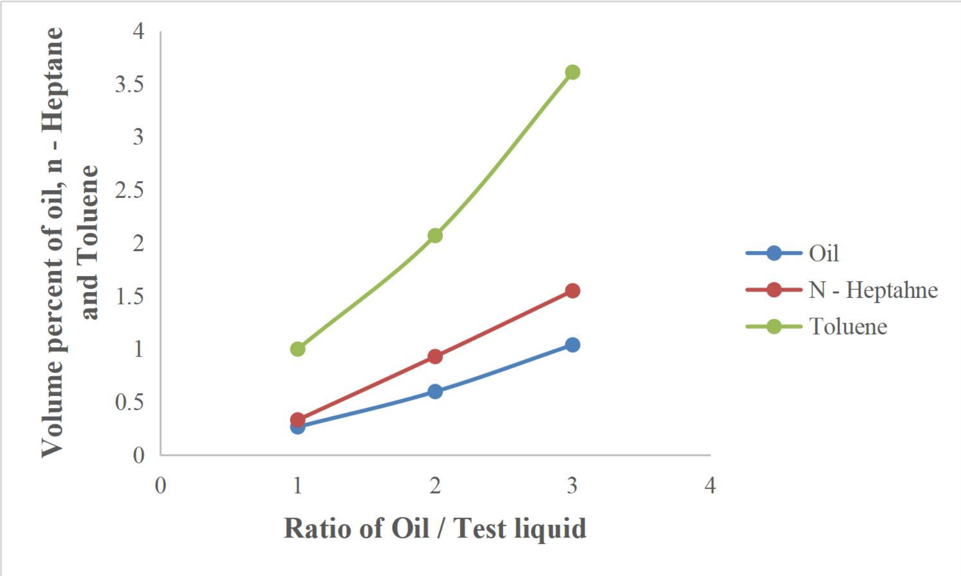


Figure 1: Graph of n – Heptane Dilution Test
(Adapted from Mahmoud and Aboujadeed, 2017)

Figure 1 gives a direct relationship between the volume percent of Toluene in the n – heptane and Toluene mixture and the Oil / Test liquid ratio, which has a directed correlation with the Insolubility Index, Solubility Blending number and consequently Asphaltene composition as given in Equation (4).

5.0 Results and Discussion

Crude oil is composed of many components, being one of the most complex multicomponent mixtures known to mankind. Some Scientist and authors have even attempted to give it rather definite and rigid number of components. It is however common knowledge that the number of components of crude oil depends on the type of separation and mode of specification used (Chaudhuri, 2011). The most elementary specification is that based on its distillation using true boiling point (TBP). In this specification, crude oil components are defined more by their application, viz: Liquified Petroleum Gas (LPG), Gasoline, Kerosene, Atmospheric and Vacuum Gas Oils (AGO and VGO), etc. A second specification of crude oil is based on the nature of its chemical composition. Here, crude oils are often defined to be composed of four components: Paraffins, Olefins, Naphthenes and Aromatics (PONA).

Yet another specification, though similar to the second above, but with some modifications defines the composition of crude oil as Saturates, Asphaltenes, Resins and Aromatics (SARA). For purposes of the present study, this is preferred and applied throughout this work. It is important to note that the different specifications of crude oil components serve different scientific purposes, and thus are all useful. The SARA specification of crude oil is particularly useful as Asphaltene precipitation in crude oil is a measure of its stability. It finds even greater application in crude oil blending, where Asphaltene precipitation is used as basis of measurement of blend compatibility, as shown below in the work. With the simple mathematical procedure given in this work, the precise SARA composition of individual crude oil in each of two blends were established based on four crude oil types of Libya. The foregoing enabled the determination of crude oil blend compatibility and stability using appropriate equations in section 4, which results are given in Table 6 and figure 2.

Table 6: Fractional Composition of Individual Crude Oils and Solubility Indices

S/N	w	x	y	z	V_i	V_iS_{BNi}	HD
1	0.6308	0.0063	0.2276	0.1041	0.644	1.288	1.0
2	0.6344	0.0052	0.2687	0.0917	0.10	0.305	1.22
3	0.4891	0.0038	0.4880	0.0190	0.25	0.14	1.4
4	0.7682	0.0154	0.0009	0.2155	0.007	0.01	1.45

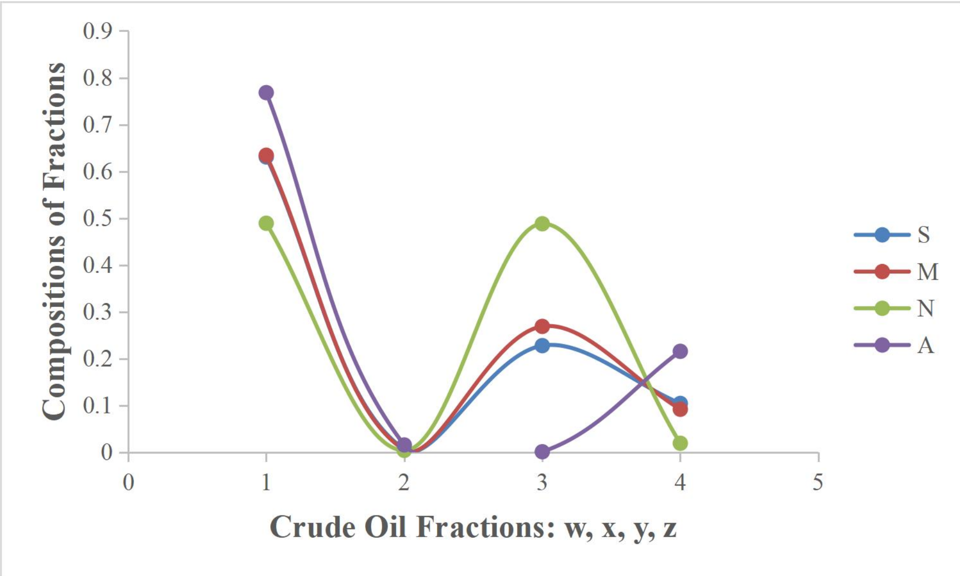


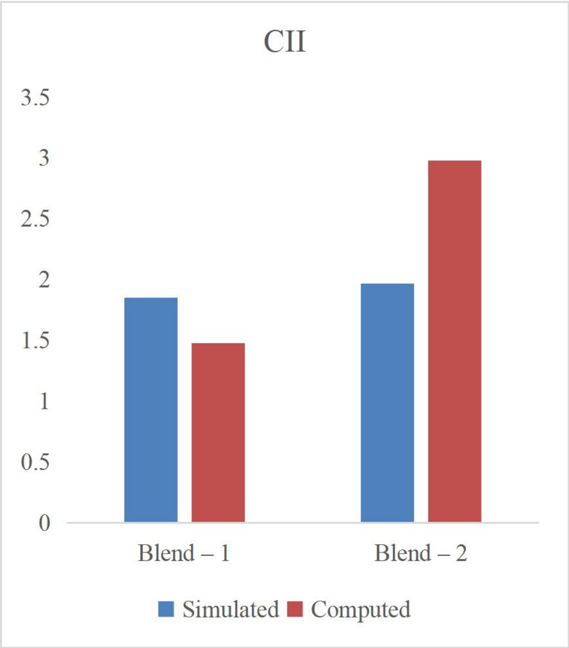
Figure 2: Fractional Compositions of the Different Crude Oils

From the work of Mahmoud and Aboujadeed (2017), it is seen that Colloidal Instability Index (CII) for crude Blend – 1 and Blend – 2 are 1.85 and 1.97 respectively, while it was 1.48 and 2.98 respectively from the developed models in this work, giving only marginal deviations of 0.37 and 1.01 respectively between results of the two studies. Similarly, the measure of stability by Asphaltene to Resins ratio (A/R) was 0.024 and 0.031 for the previous work, and 0.045 and 0.054 respectively for the present work giving deviations of 0.021 and 0.023 respectively as shown in Table 7 and Figure 3(a) – (c).

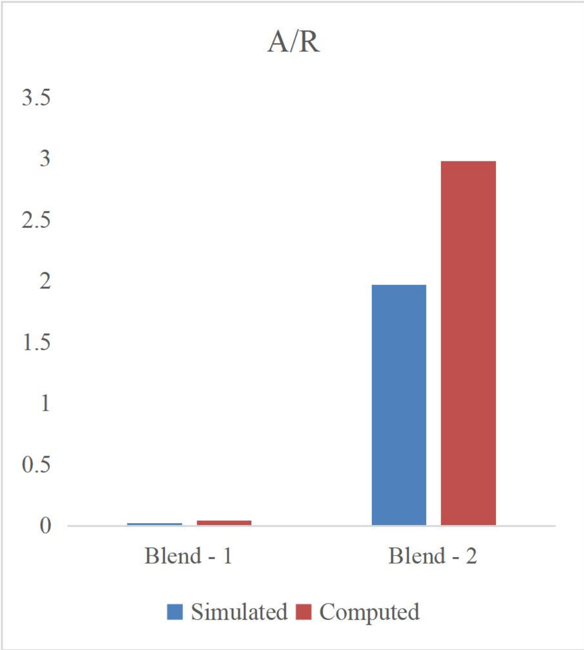
Table 7: Results of Blend Stability Between Simulated and Model Computed

Name	Blend-1 (Simulated)	Blend-1 (Computed)	Deviation	Blend -2 (Simulated)	Blend -2 (Computed)	Deviation
CII	1.85	1.48	0.37	1.97	2.98	1.01
A/R	0.024	0.045	0.021	0.031	0.054	0.023
R	1.17	1.74	0.57	1.17	1.78	0.61

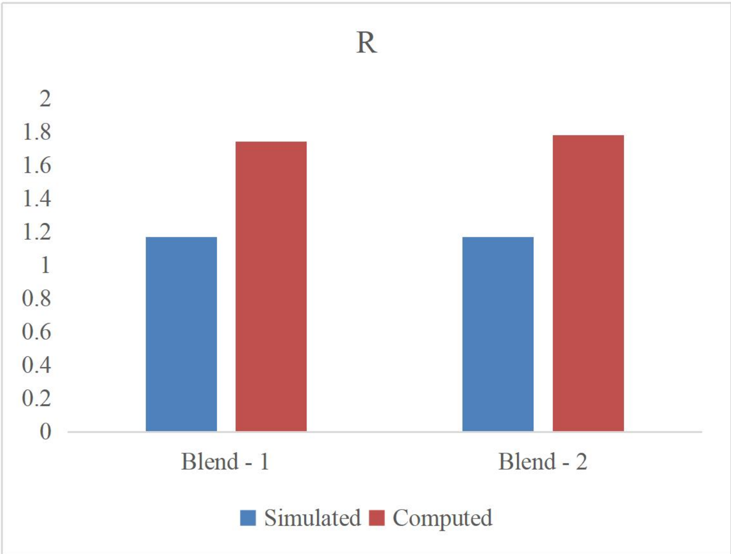
Finally, blend compatibility and stability based on ratio (R) of the Solubility Blending Number and Insolubility Index gave 1.17 for both Blends in the previous work and 1.74 and 1.78 for Blend – 1 and Blend – 2 respectively in the present work, giving deviations of 0.57 and 0.61 respectively (Figure 4).



(a)



(b)



(c)

Figure 3: Blend Stability of Simulated and Computed Models Based on CII, A/R and R

6.0 Conclusion

Crude oil blend formulation and recipe development has been topical in recent times, especially given the ever – increasing dependence of world energy needs on fossil fuel. Different approaches have been applied in crude oil refinery feedstock preparation (Dinesh, 2016), and even blending for transportation of bulk crude oil cargo. However, most of these solutions are theoretically complicated and not easily deployable. Results of the present work are in good agreement with that of Mahmoud and Aboujadeed (2017) for all parameters of blend stability determination using Colloidal Instability Index and Asphaltene to Resins ratio (A/R) and Flocculation Index. In each case, both studies gave stable blends as shown above. Main contribution of this work to the subject matter is in its unambiguous and precise nature, and its simplicity, both of formulation and application, shown in the flowchart algorithm in Figure 5.

Declarations

Credit authorship contribution statement
IPW: Conceptualization. Wrote the original draft, Methodology, Validation, Resources, project administration, and review of manuscript.

Declaration of competing interest
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