Proceedings of the International Conference on Heat Exchanger Fouling and Cleaning - 2024 (Peer-reviewed)
April 21–26, 2024, Lisbon, Portugal; Editors: H.U. Zettler and E.M. Ishiyama

PRECIPITATION INDEX: A POTENTIAL ALTERNATIVE TO PREDICTING CRUDE STABILITY OF PETROLEUM OILS

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ABSTRACT

Predicting asphaltene stability in crude and heavy oil streams under stationary conditions can provide early insights into fouling propensity of such streams. Composition based indices like the Colloidal Instability Index (CII) and Stability Index (SI) have been extensively used by refiners to understand asphaltene precipitation in crude oils based on the Saturate, Aromatic, Resin and Asphaltene (SARA) content in the oils. In the present work, a new predictor, i.e., the Precipitation Index (PI) is proposed as an alternative to the CII and SI. The PI was used to predict asphaltene stability for 111 crude oil samples for which SARA data was available/estimated from literature. A “confusion” matrix was used to statistically evaluate the performance of the PI in comparison to the CII, SI and a property-based index, i.e. ANJIS for 68 of the 111 samples for which stability related information was available based on operational experience. This PI was found to predict stability relatively better than the other three indices and can be potentially used for preliminary screening of asphaltene stability in crude oils.

INTRODUCTION

Petroleum or crude oil since the 1950’s has been the predominant source for meeting global energy demands. However, petroleum exploration and refining is often constrained by deposition of asphaltenes in oil reservoirs, flow/process pipelines and processing equipment’s. Asphaltenes have long been referred to as “cholesterol” associated with petroleum processing. Asphaltene precipitation leads to challenges of reservoir clogging, alteration in wettability characteristics of reservoir rock, oil viscosity changes and fouling of operating facilities, thus resulting in sub-optimal operation and increased shutdown time [1]. Several strategies have been researched and adopted over the years to mitigate this long-standing problem. Understanding and managing crude oil stability, particularly the behavior of asphaltenes, is essential for optimizing industrial performance and minimizing disruptions when crude oil is processed. Addressing this challenge requires thorough research into the physicochemical interactions governing asphaltene behavior, which is vital for developing strategies to prevent or mitigate their adverse effects. However, oil exploration companies and refiners have preferred prevention over mitigation strategies. Prevention strategies are based on predicting asphaltene precipitation and hence its stability in petroleum streams under stationary conditions. This provides an early insight into the asphaltene deposition propensity of such streams.

Asphaltenes (A) forms one of the four main components used to characterize petroleum streams, the other three being Saturates (S), Aromatics (A) and Resins (R). Collectively known as SARA, these compounds provide information on the polarity and polarizability of a specific stream [2]. While aromatics and resin suppress asphaltene precipitation, saturates dissolve resins and promote flocculation of asphaltenes [3]. The stability of the oil system is eventually dependent on the peptizing power of the resins, the solvent effect of the aromatics and the precipitating tendency of saturates in flocculating asphaltenes.

Over the years, several indices have been extensively used for the purpose of predicting asphaltene stability in crude and heavy oils. These indices have been developed based on either the knowhow of SARA composition or thermo-physical properties of such oils. Of the SARA based indices, the Colloidal Instability Index (CII) is popular and commonly used [4]. This index assigns a range of

ISBN: 978-0-9984188-3-4; Published online www.heatexchanger-fouling.com

numerical values within which an oil is stable or unstable. This index is expressed as a ratio of the sum of asphaltenes and saturates to the sum of aromatics and resins, thus

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

A stream with a CII value less than 0.7 is considered to be in solution or stable. Such streams are less prone to fouling because the combined fraction of resins and aromatics are considered sufficiently high to keep the asphaltene fraction soluble in the oil. On the other hand, streams with CII values greater than 0.9 are considered unstable and results in precipitation of asphaltene from solution. Uncertainty exists with regard to predicting stream stability when the CII value is between 0.7 to 0.9. In this range of uncertainty, an oil is predicted to be metastable. To overcome this issue of metastability, a new index known as Precipitation Index (PI) is proposed as an alternative. This short communication presents results related to the performance of the PI in comparison to the CII which is often used extensively in the oil industry to predict stability.

THE PRECIPITATION INDEX (PI)

The proposed Precipitation Index (PI) takes into account of opposing effect of solvent (aromatics + resins) to anti-solvent (saturates) on the percentage asphaltene content in the oil and is defined as:

$$\mathrm{PI} = \frac{[(\mathrm{Aromatics} + \mathrm{Resins}) - \mathrm{Saturates}]}{\mathrm{Asphaltenes}} \quad (2)$$

If the value of the PI is positive, the oil can be considered to be stable. For negative values of this index, the oil is unstable.

COMPARISON OF PI WITH CII

Table 1 reports the stability prediction for 28 crude oils (CR1 – CR28) using the CII and PI. The CII and PI values were estimated using SARA data reported in literature for CR1 – CR8 [5] and CR9 – CR28 [6]. The Table also includes stability reported for these oils based on operational experience. As against the CII which predicts 11 oils to be metastable, the PI is found to agree in all the cases with stability observed in refinery experience.

Table 1. Crude oil stability predicted using the Colloidal Stability Index (CII) and Precipitation Index (PI) for crude oils CR1to CR28

No.	Sample Code	CII	PI	Refinery Experience
1	CR1	M	S	S
2	CR2	M	S	S
3	CR3	M	S	S
4	CR4	M	S	S
5	CR5	M	S	S
6	CR6	M	S	S
7	CR7	M	S	S
8	CR8	M	S	S
9	CR9	U	U	U
10	CR10	S	S	S
11	CR11	M	S	S
12	CR12	M	S	S
13	CR13	U	S	S
14	CR14	S	S	S
15	CR15	U	S	S
16	CR16	S	S	S
17	CR17	M	S	S
18	CR18	U	U	U
19	CR19	U	U	U
20	CR20	U	U	U
21	CR21	U	U	U
22	CR22	U	U	U
23	CR23	U	U	U
24	CR24	U	U	U
25	CR25	U	U	U
26	CR26	U	U	U
27	CR27	U	U	U
28	CR28	U	U	U

CR: Crude oil; S: Stable; U: Unstable; M: Metastable

For the PI to be acceptable as an alternative to CII, it must predict oil stability with the same efficacy as the CII, if not better. In this regard, the PI stability predictions were compared with the predictions obtained using the CII for 43 additional oils. The SARA data for 27 of these oils were provided by BPCL Corporate Research & Development Centre (CRDC) and the data for the remaining 16 oils were taken from literature [7]. The PI and CII values along with the SARA values for these oils (CR29 – CR71) are presented in Table 2. Predictions from both indices were found to agree for 39 of the 43 oils confirming again that the PI can be used as alternative to the CII.

Table 2. CII and PI results for crude oils CR29 to CR71

Sample Code	CII	PI
CR29	U	U
CR30	S	S
CR31	U	S
CR32	U	U
CR33	U	U
CR34	U	U
CR35	U	U
CR36	U	S

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CR37	U	U
CR38	M	S
CR39	U	U
CR40	U	U
CR41	U	U
CR42	U	U
CR43	U	U
CR44	S	S
CR45	S	S
CR46	S	S
CR47	S	S
CR48	S	S
CR49	S	S
CR50	S	S
CR51	S	S
CR52	S	S
CR53	U	U
CR54	S	S
CR55	U	S
CR56	U	U
CR57	U	U
CR58	U	U
CR59	U	U
CR60	U	U
CR61	U	U
CR62	U	U
CR63	U	U
CR64	U	U
CR65	U	U
CR66	U	U
CR67	U	U
CR68	U	U
CR69	U	U
CR70	U	U
CR71	U	U

PERFORMANCE METRICS FOR THE PI

To establish the suitability of PI over CII in predicting crude and heavy oil stability, a detailed analysis was carried out using an approach adopted by Ali et al. [8]. The analysis was based on a 2 × 2 "confusion" matrix which assesses the performance of a stability index or "classifier" using a set of data for which refinery experience is available. The matrix structure comprises of two predictions, i.e., Stable (S) and Unstable (U) with four possible outcomes. The outcomes are termed as follows:

- True Positive (TP): Sample is stable (positive) from operational experience and predicted to be stable (positive) by the index or "classifier"
- False Negative (FN): Sample is stable (positive) from operational experience and predicted to be unstable (negative) by the index or "classifier"
- True Negative (TN): Sample is unstable (negative) from operational experience and predicted to be unstable (negative) by the index or "classifier"
- False Positive (FP): Sample is unstable (negative) from operational experience and predicted to be stable (positive) by the index or "classifier"

The terms "positive" and "negative" are also referred to as "class". Five performance parameters were subsequently estimated using the above outcomes, thus:

Accuracy (ACC)

It is a measure of the correct predictions made by a "classifier" from all the predicted "classes". It is defined as the ratio of total correct predictions to the total number of predictions made and is expressed mathematically as [8] – [10].

$$\mathrm{ACC} = \frac{\mathrm{TP} + \mathrm{TN}}{\mathrm{TP} + \mathrm{TN} + \mathrm{FN} + \mathrm{FP}} \quad (3)$$

True Positive Rate (TPR) or Sensitivity

It is a measure of the correct predictions made by a "classifier" from all the actual "positive classes" (operational experience). It indicates the correctly classified stable samples out of the total number of actual stable samples and is estimated using [8] – [10].

$$\mathrm{TPR} = \frac{\mathrm{TP}}{\mathrm{TP} + \mathrm{FN}} \quad (4)$$

True Negative Rate (TNR) or Specificity

It is a measure of the correct predictions made by a "classifier" from all the actual "negative classes" (operational experience). TNR expresses the correctly identified unstable samples out of the total number of actual unstable samples present using the equation [8] – [10].

$$\mathrm{TNR} = \frac{\mathrm{TN}}{\mathrm{TN} + \mathrm{FP}} \quad (5)$$

Positive Predictive Value (PPV) or Precision

Positive Predictive Value (PPV) is a measure of the "classifier" performance with respect to its ability to correctly predict stable samples. It is expressed as the ratio of the correctly predicted stable samples to the total number of predicted stable samples and is calculate using [8] – [10].

$$\mathrm{PPV} = \frac{\mathrm{TP}}{\mathrm{TP} + \mathrm{FP}} \quad (6)$$

Negative Predictive Value (NPV)

Negative Predictive Values (NPV) is a measure of the "classifier" performance with respect to its

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ability to correctly predict unstable samples. It is defined as the ratio of the correctly predicted unstable samples by the model to the total number of unstable samples predicted and is computed using [8] – [10].

$$\mathrm{NPV} = \frac{\mathrm{TN}}{\mathrm{TN} + \mathrm{FN}} \tag{7}$$

TPR and TNR values close or equal to 1 indicates good accuracy of predicting index or "classifier". Values of PPV or NPV near or equal to 1 indicate high precision of the "classifier". Fig. 1 summarizes the above information along with the confusion matrix.

		PREDICTED			
		Stable	Unstable		
ACTUAL	Stable	True Positive (TP)	False Negative (FN)	Total Stable (TP + FN)	TPR $\frac{TP}{TP + FN}$
	Unstable	False Positive (FP)	True Negative (TN)	Total Unstable (FP + TN)	TNR $\frac{TN}{TN + FP}$
		PPV $\frac{TP}{FP + TP}$	NPV $\frac{TN}{FN + TN}$	Accuracy $\frac{TP + TN}{TP + TN + FN + FP}$	

Fig. 1. 2 × 2 "confusion" matrix

Apart from oils CR1 to CR28, the stability of 40 additional oils was predicted using the CII and PI. Refinery experience with regard to stability for these 40 oils was reported in literature [5,6], [8,9], [11]. The stability of all 68 oils was also predicted using another SARA based index, i.e. the Stability Index (SI). This index is expressed as a ratio of composition of asphaltenes to resins in an oil sample. Oils are considered stable if the SI value is lower than 0.35 [12]. This index however does not account for the effect of anti-solvent properties of saturates in the oil. The stability of the CR31, CR36, CR38 and CR55 in Table 2 was predicted using the SI and found to be in agreement with PI. Table 3 summarizes the values of the performance evaluation parameters for the three indices.

Table 3. Performance evaluation parameters for CII, SI and PI

No.	Terms	Index/Classifier		
		CII	SI	PI
1	TP	14	30	25
2	TN	21	11	21
3	FN	26	10	15
4	FP	7	17	7
5	ACC	0.51	0.60	0.68
6	TPR	0.35	0.75	0.63
7	TNR	0.75	0.39	0.75
8	PPV	0.67	0.64	0.78
9	NPV	0.45	0.52	0.58

The ACC value of PI is better than the CII and SI in the 68 samples examined indicating that the PI offers relatively higher accurate predictions. The TPR value of PI (0.63) is significantly higher than the TPR value of CII (0.35). The PI thus predicts stable samples better than the CII. The SI however is the best among the three indices in predicting stable samples.

The TNR value of 0.75 for CII and PI are comparable and higher than the SI value of 0.39. These two indices predict unstable samples better than SI. The PPV value of PI is higher than that of CII and SI. A higher value of PPV suggests that less unstable samples are falsely classified as compared to stable oil samples. This is confirmed by a lower FP value (7) for CII and PI as against the FP value (17) for SI.

The SI classifies a lesser number of stable samples as unstable in comparison to the CII and PI. The FN value of SI is 10 as against 26 and 15 for CII and PI respectively. The higher FN value (26) for CII also results in a lower NPV value (0.45) for this index in comparison to the PI (0.58) even though the TN value for both indices (21) is the same. The higher FN value in PI is offset by its higher TN value (21) and results in a relatively higher NPV value for this index as compared to the NPV value of SI (0.52) for which the TN value is 11.

More recently Saboor et al. [8] have proposed the Abdus, Nimra, Javed, Imran & Shaine (ANJIS) index based on non-linear regression of stability values using a Colloidal Stability Index (CSI) which accounts for polarities of the SARA components in an oil, thus

$$\mathrm{ANJIS} = \frac{(\mathrm{Sa})^{1.7269} + (\mathrm{A})^{5.186}}{(\mathrm{Ar})^{1.525} + (\mathrm{R})^{4.302}} \tag{8}$$

If the ANJIS index is less than 0.03, then the oil is classified as stable. The oil is unstable if this index is greater than or equal to 0.03. The performance parameters for the 68 oils were also estimated using the ANJIS index and compared with PI. The results are tabulated in Table 4.

Table 4. Performance evaluation parameters for ANJIS and PI

No.	Terms	Index/Classifier	
		ANJIS	PI
1	TP	24	25
2	TN	19	21
3	FN	16	15
4	FP	9	7
5	ACC	0.63	0.68
6	TPR	0.60	0.63
7	TNR	0.68	0.75

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8	PPV	0.73	0.78
9	NPV	0.54	0.58

The PI predicts all the performance parameters better than the ANJIS index. Also, the superior performance of the ANJIS model reported in literature as against other indices was based on stability outcomes for 17 crude oil samples only. Based on the above analysis, the PI offers an excellent alternative to the CII and even the SI in predicting stability of crude oil samples when SARA data is available. The PI unlike the CII does not categorize oils as metastable or uncertain. The PI however must be used with caution when the crude oil is high in saturates (50% and above) i.e. paraffinic crudes and low in asphaltene (< 0.5%) content. In such cases, the CSI and K model which are based on the thermo-physical properties of oil can be used to predict stability [4].

CONCLUSION

The performance of a new SARA based index, i.e., Precipitation Index (PI) in predicting asphaltene stability was investigated for 111 crude oils for which SARA data was obtained from a refinery R&D Centre or provided in/estimated from literature. An oil is considered stable or unstable if the value of PI is positive or negative respectively. Predictions from the Colloidal Instability Index (CII), Stability Index (SI) and PI were compared for 68 of the 111 oils for which stability data from refinery experience was available. The PI was found to show better agreement with this data as compared to the CII and SI. Unlike the CII, which cannot predict oil stability for values of this index between 0.7 and 0.9, the PI provides a definitive prediction for such oils.

A statistical analysis using a "confusion" matrix was used to analyze the performance of the CII, SI and PI. In terms of performance evaluation parameters like ACC, TPR, PPV and NPV, stability predictions using the PI was significantly better than the CII. The PI predicted stable samples better than the CII. The SI predicted stable samples better than the CII and PI as against unstable samples. The PI performed better when compared with the ANJIS index which is based on knowhow of the SARA content and dielectric constants of the oil samples evaluated. Based on the results obtained, the PI is proposed as an alternative to the CII in predicting crude oil stability. The suitability of PI for oils with high saturate content (> 60%) will need further investigation.

NOMENCLATURE

CR	Crude Oil
Sa	Saturates
Ar	Aromatics
R	Resins
A	Asphaltenes
PI	Precipitation Index
CII	Colloidal Instability Index
SI	Stability Index

Keywords
Asphaltenes, SARA, Precipitation Index, Colloidal Instability Index, Stability Index

Declaration of Competing Interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper

Acknowledgements

The financial support provided for this work by Center for High Technology (CHT) / Oil Industry Development Board (OIDB), India is gratefully acknowledged. The authors would like to acknowledge the support received from Bharat Petroleum Corporation Limited (BPCL), Corporate R & D in timely providing refinery samples which were subsequently utilized in this work.

Credit Author Statement

Srinivas Krishnaswamy: Conceptualization, Methodology, Reviewing and Editing, Supervision, Funding acquisition; **Pragya Singh.**: Investigations, Data curation, Writing-Original draft; **Krishnaswamy Ponnani**: Conceptualization, Methodology; **Ankur Verma:** Resources, Investigations; **Jaya Rawat:** Resources, Funding acquisition

REFERENCES

[1] E. S. Boek, A. D. Wilson, J. T. Padding, T. F. Headen, and J. P. Crawshaw, "Multi-scale Simulation and Experimental Studies of Asphaltene Aggregation and Deposition in Capillary Flow," Energy Fuels, vol. 24, no. 4, pp. 2361–2368, Apr. 2010, doi: 10.1021/ef9010059.

[2] I. Muhammad, N. Tijjani, I. J. Dioha, A. Musa, H. Sale, and A. M. Lawal, "SARA Separation and Determination of Concentration Levels of Some Heavy Metals in Organic Fractions of Nigerian Crude Oil," Chem. Mater. Res., vol. 3, no. 4, p. 7, 2013.

[3] S. Ashoori, M. Sharifi, M. Masoumi, and M. Mohammad Salehi, "The relationship between SARA fractions and crude oil stability," Egypt. J. Pet., vol. 26, no. 1, pp. 209–213, Mar. 2017, doi: 10.1016/j.ejpe.2016.04.002.

[4] R. Xiong et al., "Method for Judging the Stability of Asphaltenes in Crude Oil," ACS

ISBN: 978-0-9984188-3-4; Published online www.heatexchanger-fouling.com

Omega, vol. 5, no. 34, pp. 21420–21427, Sep. 2020, doi: 10.1021/acsomega.0c01779.

[5] R. Kumar, R. K. Voolapalli, and S. Upadhyayula, "Prediction of crude oil blends compatibility and blend optimization for increasing heavy oil processing," Fuel Process. Technol., vol. 177, pp. 309–327, Aug. 2018, doi: 10.1016/j.fuproc.2018.05.008.

[6] A. A. Sulaimon, J. K. M. De Castro, and S. Vatsa, "New correlations and deposition envelopes for predicting asphaltene stability in crude oils," J. Pet. Sci. Eng., vol. 190, p. 106782, Jul. 2020, doi: 10.1016/j.petrol.2019.106782.

[7] L. G. M. Moura, M. F. P. Santos, E. L. Zilio, M. P. Rolemberg, and A. C. S. Ramos, "Evaluation of indices and of models applied to the prediction of the stability of crude oils," J. Pet. Sci. Eng., vol. 74, no. 1, pp. 77–87, Oct. 2010, doi: 10.1016/j.petrol.2010.08.011.

[8] S. I. Ali, S. M. Lalji, J. Haneef, M. A. Khan, and C. Louis, "Comprehensive Analysis of Asphaltene Stability Predictors under Different Conditions," Pet. Chem., vol. 61, no. 4, pp. 446–454, Apr. 2021, doi: 10.1134/S0965544121050091.

[9] A. Saboor, N. Yousaf, J. Haneef, S. I. Ali, and S. M. Lalji, "Performance of asphaltene stability predicting models in field environment and development of new stability predicting model (ANJIS)," J. Pet. Explor. Prod. Technol., vol. 12, no. 5, pp. 1423–1436, May 2022, doi: 10.1007/s13202-021-01407-8.

[10] M. Bekkar, H. K. Djemaa, and T. A. Alitouche, "Evaluation Measures for Models Assessment over Imbalanced Data Sets," J. Inf. Eng. Appl., vol. 3, no. 10, p. 27, 2013.

[11] O. León et al., "Adsorption of Native Resins on Asphaltene Particles: A Correlation between Adsorption and Activity," Langmuir, vol. 18, no. 13, pp. 5106–5112, Jun. 2002, doi: 10.1021/la011394q.

[12] A. P. W. S. Asomaning, "Petroleum Stability and Heteroatom Species Effects in Fouling of Heat Exchangers by Asphaltenes," Heat Transf. Eng., vol. 21, no. 3, pp. 10–16, Jul. 2000, doi: 10.1080/014576300270852.

ISBN: 978-0-9984188-3-4; Published online www.heatexchanger-fouling.com