Original Article

Prediction Of Stability Of The Asphaltene Fraction In Crudes Del Campo Pacoa (Ecuador)

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Abstract

The present study will evaluate the concentration and stability of the asphaltenes of 5 crudes obtained from the different producing levels of the Pacoa field as well as the mixture of all of them in the central tank at static surface conditions (1 atm) and 60ºF from the methods of "Stability index (IE)", "Colloidal stability index (IEC)", "Stankiewiez stability criterion (CES)", culminated with the "Sepulveda stability criterion (ACC: qualitative and quantitative analysis)" and La Mancha method.

Keyboard: concentration and stability; asphaltenes ; crudes; Pacoa field

INTRODUCTION

Asphaltenes are polar molecules of high molecular weight consisting of polynuclear aromatic hydrocarbons that constitute between 0 and 20% of the total mass of oil. Physically, they are dark colored semi-Christian solid particles that remain dissolved in crude oil in dynamic equilibrium with resins. However, this equilibrium can be altered by changes in the thermodynamic conditions of the system, modifications in pressure or by changes in composition and/or pH derived from the mixture of crude oil with each other or with other compounds (Grey and Ayola, 2015; Padilla and Watt, 2015). The rupture of the equilibrium produces the flocculation of the asphaltenes and therefore their precipitation negatively affecting the recovery of oil, as well as pumps, valves, production lines and surface facilities (Pereira, 2006).

The S.A.R.A analysis based on the differences in molecular weight, polarity and solubility of the crude oil components is an important tool for the type of study to be carried out, since on the one hand it provides information regarding the proportions of the fractions that make up the crude oil and on the other hand, in the scientific literature, different methods have been reported that use relationships of these fractions to obtain a highly reliable prediction about the behavior and stability of asphaltenes (Gordillo et al., 2010; Sepúlveda Gaona, Bonilla Manrique, & Medina Majé, 2010).

The Pacoa field is located in the southern area of the oil block I of the Costa del Ecuador region, has a production of 42 bbl/day from 48 producing wells of the Rosario and Socorro formations (B, C, D and E). Of the total of wells, the 5 selected produce in singularity of producer level and the rest their simultaneous production of several simultaneous levels. The production is stored in the individual tanks of each well and finally collected in a central tank where the percentage of mixture or the stability of the collected crudes is not controlled. If the collected crudes present instability to the change of temperature or to the mixture, asphaltene sludge would be generated that increases the maintenance of the facilities, as well as generates an environmental liability of dangerous handling.

The present study will evaluate the concentration and stability of the asphaltenes of 5 crudes obtained from the different producing levels of the Pacoa field as well as the mixture of all of them in the central tank at static surface conditions (1 atm) and 60ºF from the methods of "Stability index (IE)", "Colloidal stability index (IEC)", "Stankiewiez stability criterion (CES)", culminated with the "Sepulveda stability criterion (ACC: qualitative and quantitative analysis)" and La Mancha method.

METHODOLOGY

API SEVERITY

API gravity was determined in crude oil samples according to Hunt (1996). Approximately 5 ml of total oil was measured with the hygrometer. To validate accuracy and reproducibility, this method was applied three times for each crude.

SARA ANALYSIS

An aliquot (approximately 5 ml) of complete crude oil was separated into its constituent fractions, Saturated, Aromatic, Resins and Asphaltenes (SARA). Asphaltenes were precipitated by adding n-heptane in a ratio of 1:40 v/v following standard procedure ASTM D3279 ((ASTM International, 2001)); each sample was passed through a batch reactor in constant stirring for 1 hour at 60 °C, followed by a 12-hour idle period. Then the precipitated asphaltenes were filtered out. Maltene fractions were adsorbed on silica gel liquid chromatography column. Finally, they were fractionated into saturated (using n-hexane eluent), aromatics (toluene) and resins (30% methanol in toluene), and collected separately.

COLLOIDAL INSTABILITY INDEX (ICC)

The ICC predicts the stability of asphaltenes in a crude oil relating these plus the most unfavorable compounds for its stability in oil with the petizing agents that favor stability in them.

ICC= [(Asphaltenes+Saturated) /(Resins+Aromatics)]

Asomaning and Watkinson (2000) established that for ICC>0.9 asphaltenes are unstable in the medium, for ICC in the range of 0.7 to 0.9 there is uncertainty about their stability and for IIC<0.7 asphaltenes are stable.

COLLOIDAL STABILITY INDEX (IEC)

The IEC states that the asfaltenos of unstable crudes are more polar than in stable crudes, so it studies the polarity of the crude components using the fractions obtained from S.A.R.A analysis and the dielectric constant in stable and unstable crudes (Red and Hascakir, 2017; Rogel, Ovalles, Moirand Schabron, 2009)

$$IEC = \frac{(\varepsilon^{asf} * \%Asfaltenos) + (\varepsilon^{sat} * \%Saturados)}{(\varepsilon^{res} * \%Resinas) + (\varepsilon^{arom} * \%Aromáticos)}$$

ε asf = 18.4 and ε res = 3.8; for stable crude oils ε^{asf} = 5.5 and ε^{res} = 4.7, and for all crude oils ε^{sat} = 1.921 and ε^{arom} = 2.379. Therefore, the IEC is calculated with the ratio between the sum of the products of (ε^{asf}*%Asphaltenes) and (ε^{sat}*%Saturated), over the sum of the products (ε^{res}*%Resin) and (ε^{arom}*%Aromatics).

The stability limit for this index is set at Si IEC<0.95, indicates that crude oil is stable, otherwise crude oil will be unstable and therefore there is a risk of precipitation of the asphaltenic fraction (Likhatsky & Syunyaev, 2010).

STABILITY INDEX (IE)

The study of the relationship of the asphaltenic fraction of a crude oil against the fraction of resins has been widely used in the prediction of stability, since both fractions form the non-volatile part of the petroleum and the resins are the peptizing agents of the asphaltenes and keeps them in solution. The reported values of the A/R ratio for stable crudes are less than 0.35 (Asomaning, S., 2003).

STANKIEWICZ STABILITY CRITERIA (CES)

The Stankiewicz stability criterion is a graphical method based on the representation of the Asphaltenes / Resins versus Saturated / Aromatic relationships, allowing a rapid identification of the behavior of asphaltenes by separating a stable zone from an unstable one (Stankiewicz et al., 2002).

SEPULVEDA STABILITY CRITERION (ACC)

The ACC consists of a qualitative-quantitative study with different relationships of the fractions obtained from the SARA analysis: (R/A), (S/A), (AR/A), (AR/(S/A)), ((R*AR) /(S*A) and (S/(AR*A)). These relationships are plotted and three zones are identified which are given a specific value 1 (Unstable), 5 (Metastable) and 10 (Stable). The limit of each region derives from the maximum value of the R/A ratio and with this the stability ((R/A) /2), metastability (((R/A) /4) and instability fields will be established. Finally, a summation of each crude sample is made and if it is greater than 30 the crude oil is stable, between 15-30 the crude oil is metastable and less than 15 the crude is unstable (Sepúlveda Gaona et al., 2010).

STABILITY CROSS PLOT (SCP)

The stability criterion of Sepúlveda 2010 is a graphical method based on the analysis of the SARA fractions and the ACC, to study the behavior of crude oil through its representation of 4 different compositional relationships: (SPC1) [(Resins / Asphaltenes) / (Saturated / Aromatic)] Vs [Resins / Asphaltenes] (SCP 2), [Saturated/Aromatic] Vs [Resins/Asphaltenes] (SCP 3) and [(Resins/Asphaltenes)/ (Saturated/Aromatic)] Vs [Aromatic/(Saturated*Asphaltenes)] (SCP 4); in order to obtain a single result that characterizes the stability of asphaltenes in crude oil.

DISCUSSION AND RESULTS

The 5 samples of the present study according to the specific gravity measured (API) can be classified as medium crudes except for PAC 40 crude which is shown as a light crude and Matachivato crude classified as heavy.

The five crudes analyzed are shown as unstable according to the IE since all values are greater than 0.35 (S. Asomaning & Watkinson, 2000; Santos et al., 2022; Olvera et al., 2022) indicating that the percentage of the fraction of resins with respect to the fraction of asphaltenes is not sufficient to maintain the latter in solution. Similarly, the IEC index also points to the instability of all crude oils since the range of values for the relationship studied is greater than 0.95 ((Likhatsky and Syunyaev, 2010)). Another factor supporting the instability thesis is the CES study. According to the CES diagram, all the crudes analyzed are presented as unstable, since the S/Ar ratio is greater than 2 and the A/R ratio is greater than 0.2 ((Stankiewicz et al., 2002).

On the other hand, the CrossPlot stability analysis is in line with the above, SPC 2 shows all unstable crudes, however, SPC 1 and SPC4 shows that Matachivato crude is in the stable field and in SPC3 is above the metastability line. This data of Matachivato is consistent with the results obtained from IE where the only crude oil with a value lower than 0.3 is Matachivato inferring this stability.

The only analysis that shows all crudes as stable is the qualitative stability analysis of Sepúlveda (2010), although in some relationships most crudes are shown as metastable or unstable in the final sum the values obtained are in the range 41-55 inferring general stability.

The slick method points to the incompatibility of the PAC40, PAC36, PAC39, PAC 17 crudes while the Matachivato crudes and the central tank show a practically imperceptible halo which indicates stability in the asphaltenes.

Finally, from the general study of stability extracted from all methods all seem to indicate that the crudes analyzed PAC30, PAC39, PAC17, PAC 40 and Central Tank are shown as unstable while Matachivato seems to indicate that it is metastable or stable.

CONCLUSIONS

- The analyzed crudes are classified as medium by their API severity minus the Matachivato crude which is heavy.
- PAC30, PAC39, PAC17, PAC 40 and Central Tank crudes are unstable, while Matachivato crude is predicted to be metastable or stable.
- The crudes PAC40, PAC36, PAC39, PAC 17 are incompatible so their mixture induces asphaltene precipitation. However, the sample taken in the central tank and in Matachivato are stable from the point of view of the stain test.

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SUPPLEMENTARY MATERIAL:

TABLE 1:

	S	A	R	A	ICC	IE	IEC	A/R	S/Ar	(R/A),	(S/A),	(AR/A),	(Ar/(S/A))	((R*AR) /(S*A)	(S/(AR*A)
Tank Central	**62**	**25.17**	**8.83**	**4**	**1.94**	**0.45**	**0.49**	**0.5**	**2.5**	**2.2**	**15.5**	**6.3**	**1.6**	**0.9**	**0.6**
Matachivato	**58.4**	**28.9**	**10.1**	**2.6**	**1.56**	**0.26**	**0.61**	**0.3**	**2.0**	**3.9**	**22.7**	**11.3**	**1.3**	**1.9**	**0.8**
PAC 17	**66.3**	**20.9**	**8.8**	**4.0**	**2.37**	**0.46**	**0.59**	**0.5**	**3.2**	**2.2**	**16.6**	**5.2**	**1.3**	**0.7**	**0.8**
PAC 39	**72.3**	**17.5**	**6.6**	**3.5**	**3.14**	**0.53**	**0.89**	**0.5**	**4.1**	**1.9**	**20.6**	**5.0**	**0.9**	**0.5**	**1.2**
PAC 36	**70.3**	**16.6**	**8.4**	**4.7**	**3.00**	**0.56**	**0.63**	**0.6**	**4.2**	**1.8**	**14.9**	**3.5**	**1.1**	**0.4**	**0.9**
PAC 40	**71.5**	**10.3**	**9.7**	**8.5**	**4.00**	**0.88**	**0.47**	**0.9**	**6.9**	**1.1**	**8.4**	**1.2**	**1.2**	**0.2**	**0.8**

Figure A. Stanckiewicz Chart

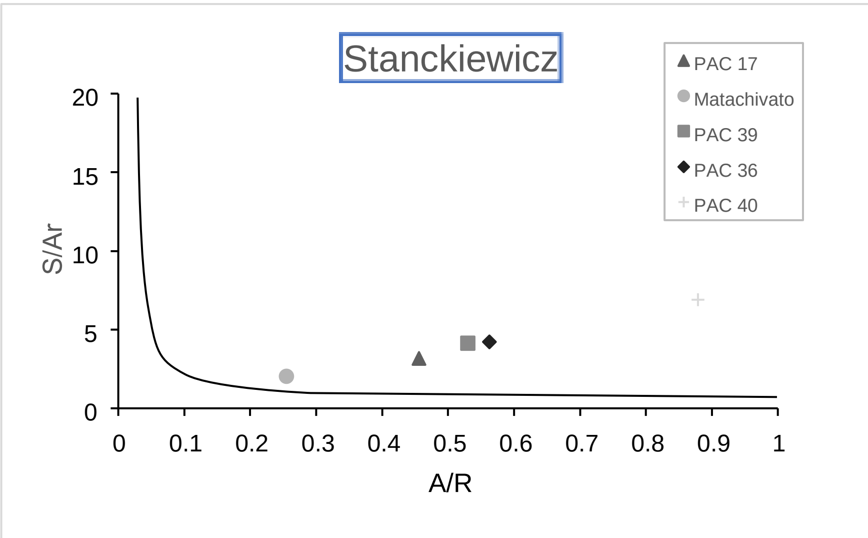
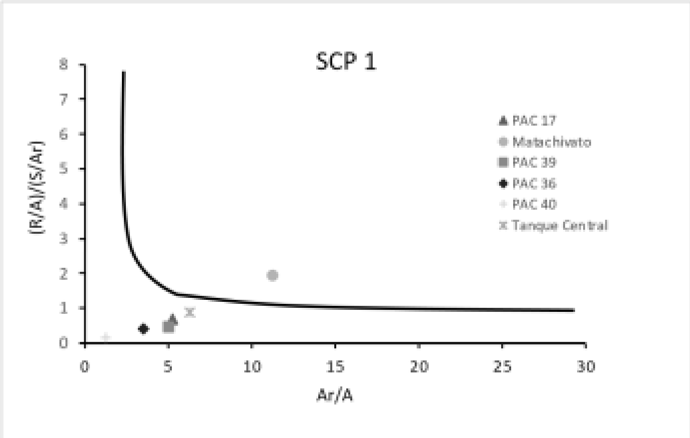
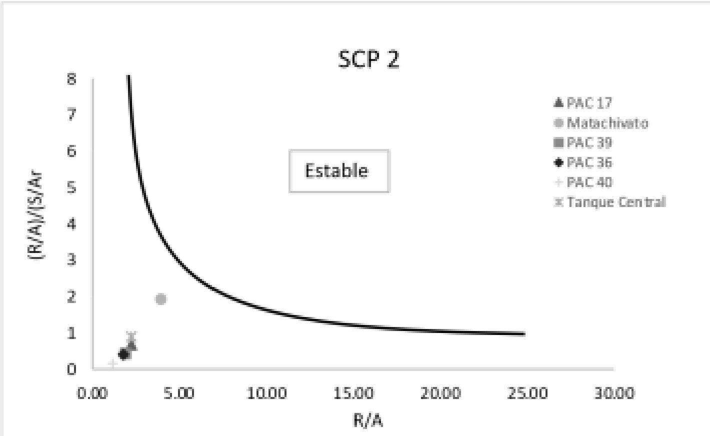
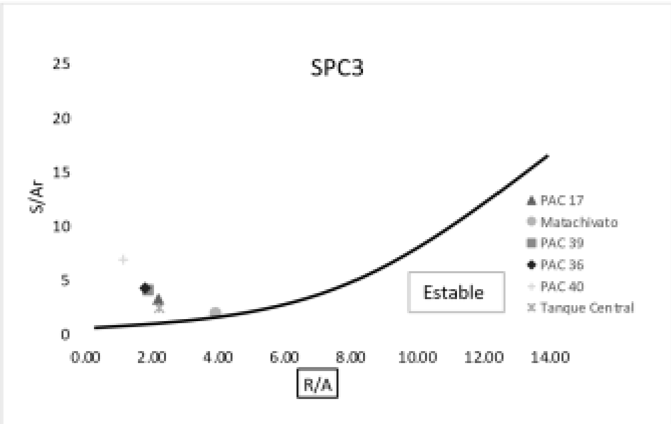


Figura B: Stability Cross Plot (SPC)







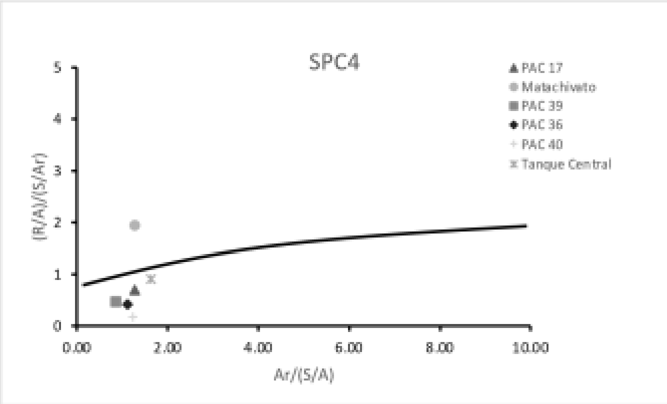
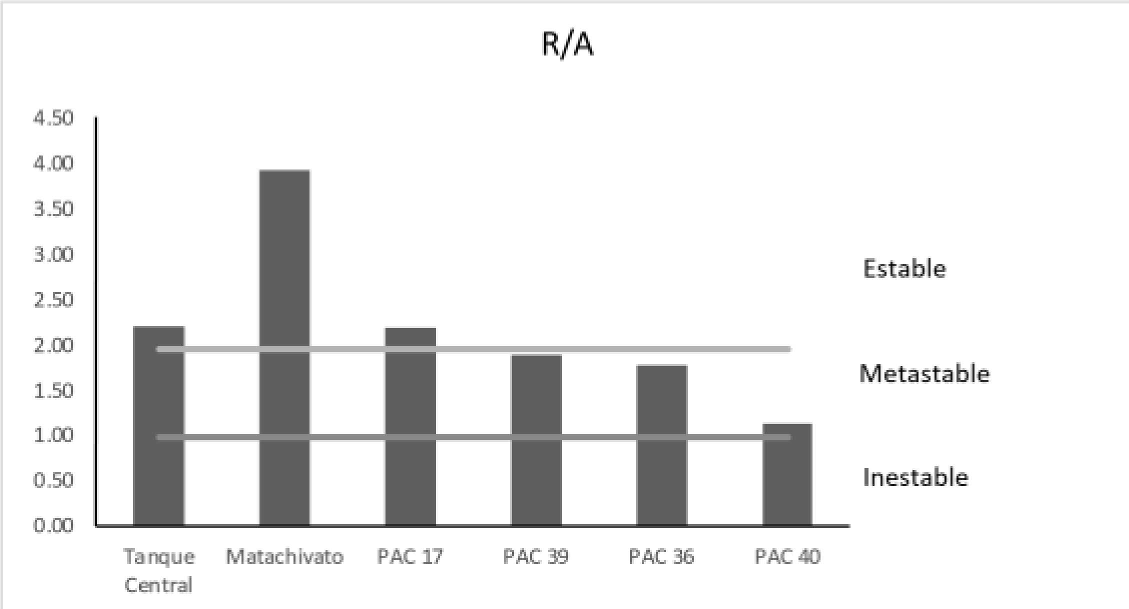

SPC4
PAC 17
Matachivato
PAC 39
PAC 36
PAC 40
Tanque Central
(R/A)/(S/Ar)
Ar/(S/A)
0.00
2.00
4.00
6.00
8.00
10.00
0
1
2
3
4
5

Figure C:


R/A
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
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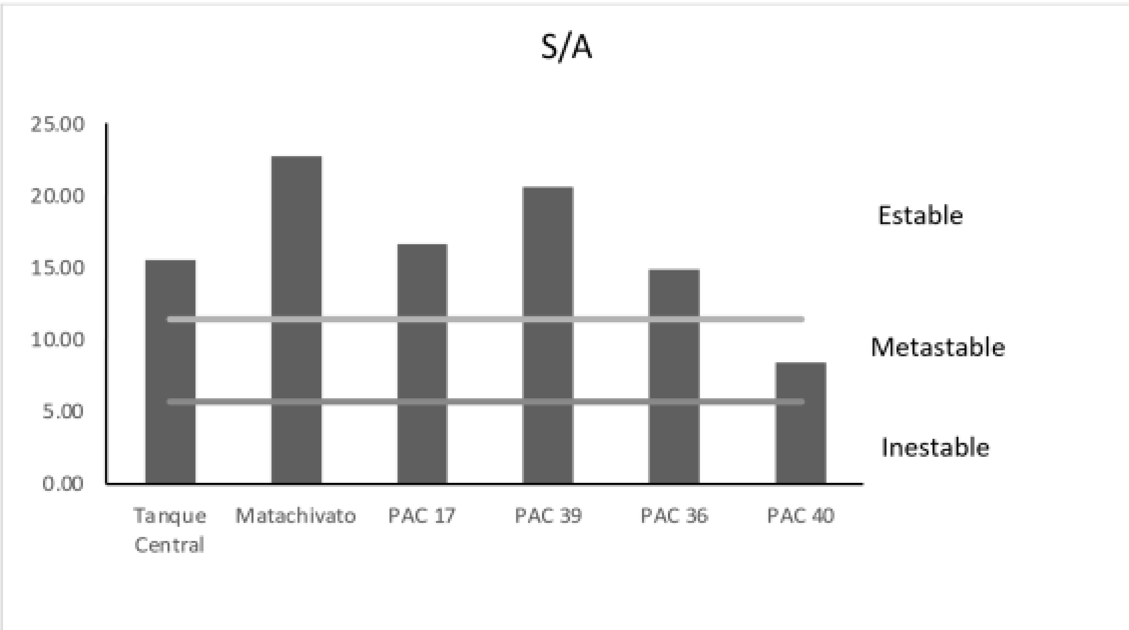
Estable
Metastable
Inestable
Tanque Central
Matachivato
PAC 17
PAC 39
PAC 36
PAC 40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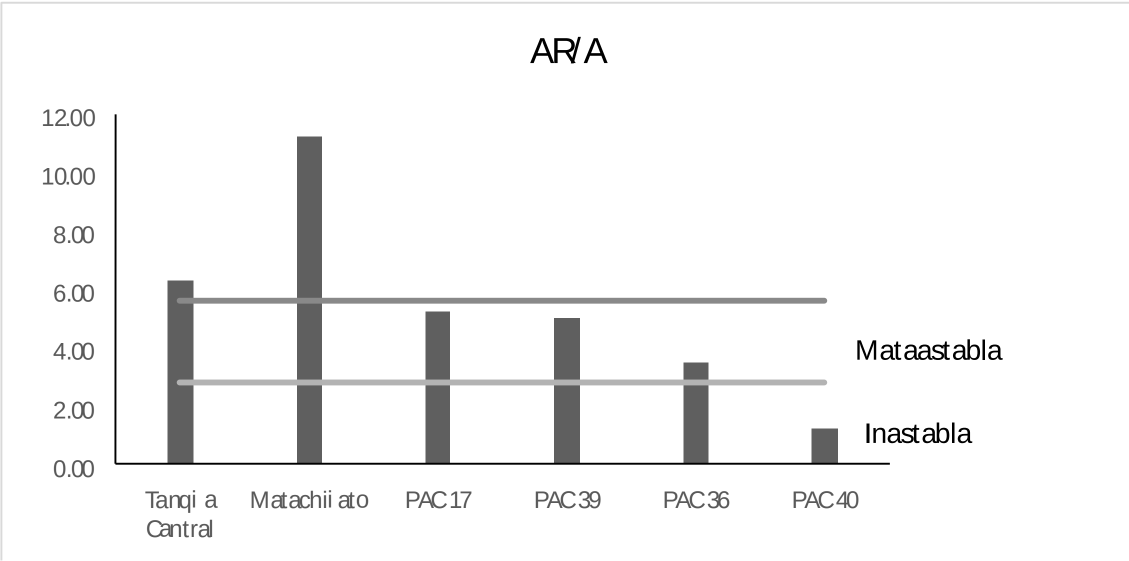
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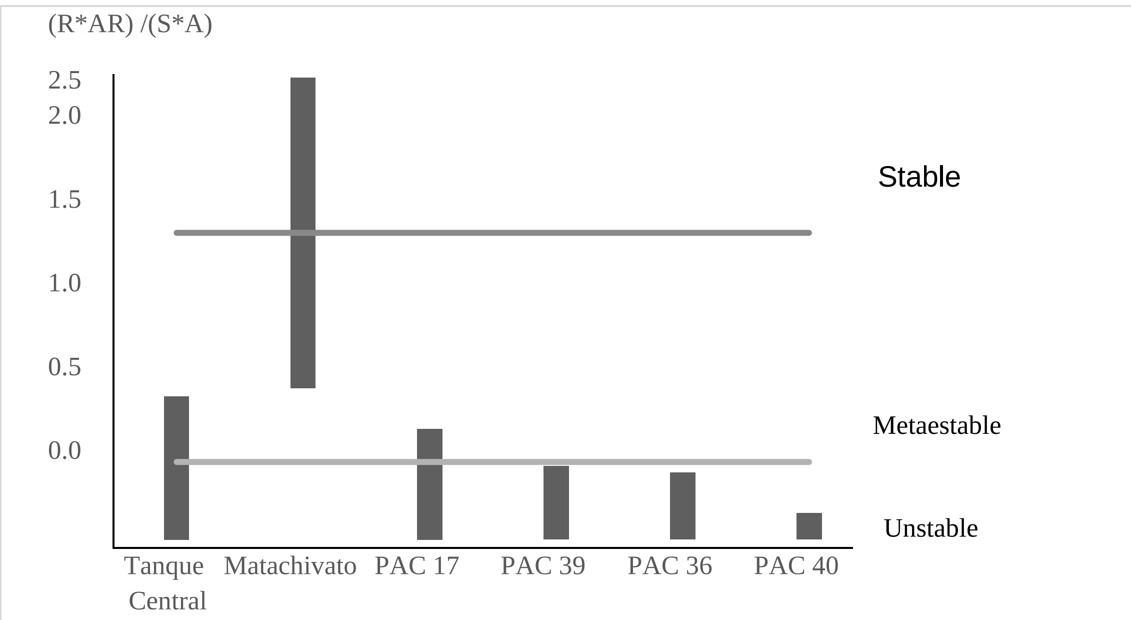
(R*AR) /(S*A)
2.5
2.0
1.5
1.0
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Stable
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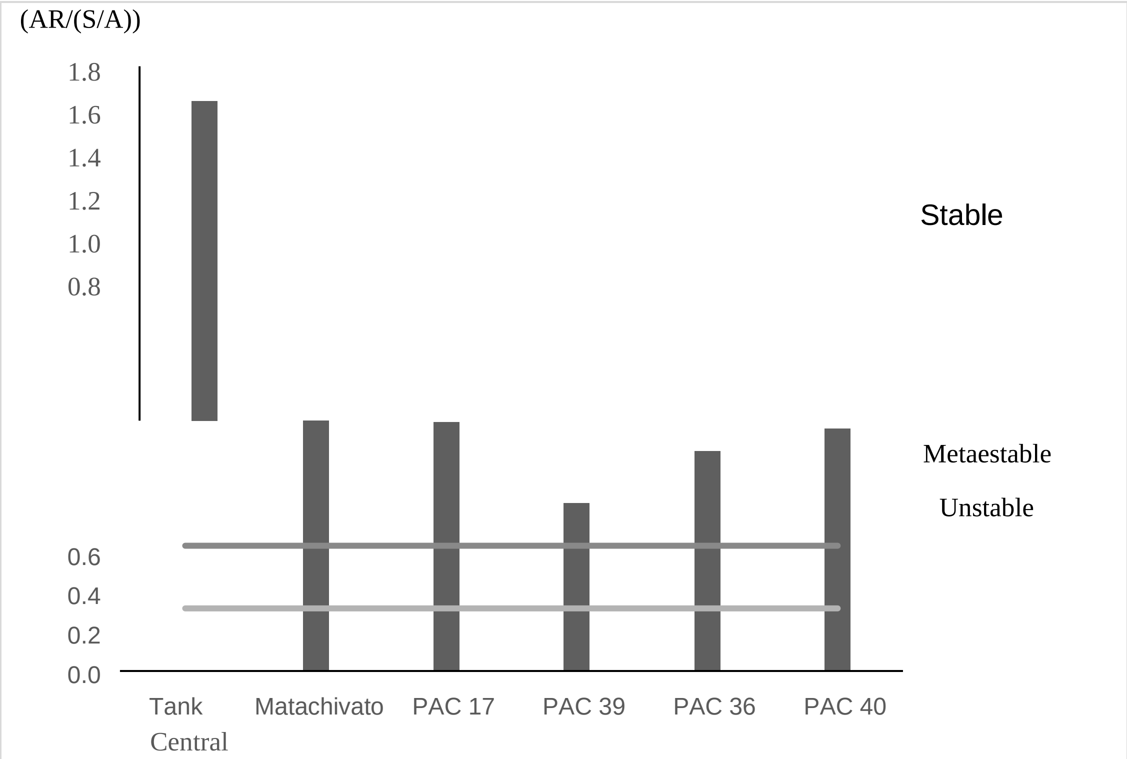
Tanque Central
Matachivato
PAC 17
PAC 39
PAC 36
PAC 40


(AR/(S/A))
1.8
1.6
1.4
1.2
1.0
0.8
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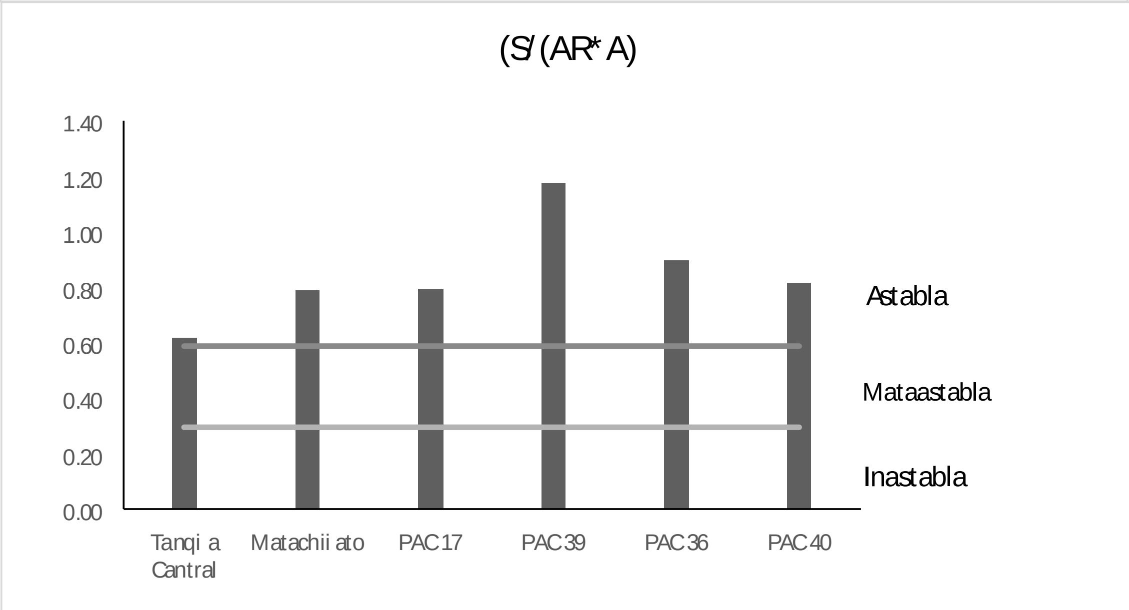
Stable
Metaestable
Unstable
Tank Central
Matachivato
PAC 17
PAC 39
PAC 36
PAC 40


(S/(AR* A)
1.40
1.20
1.00
0.80
0.60
0.40
0.20
0.00
Astabla
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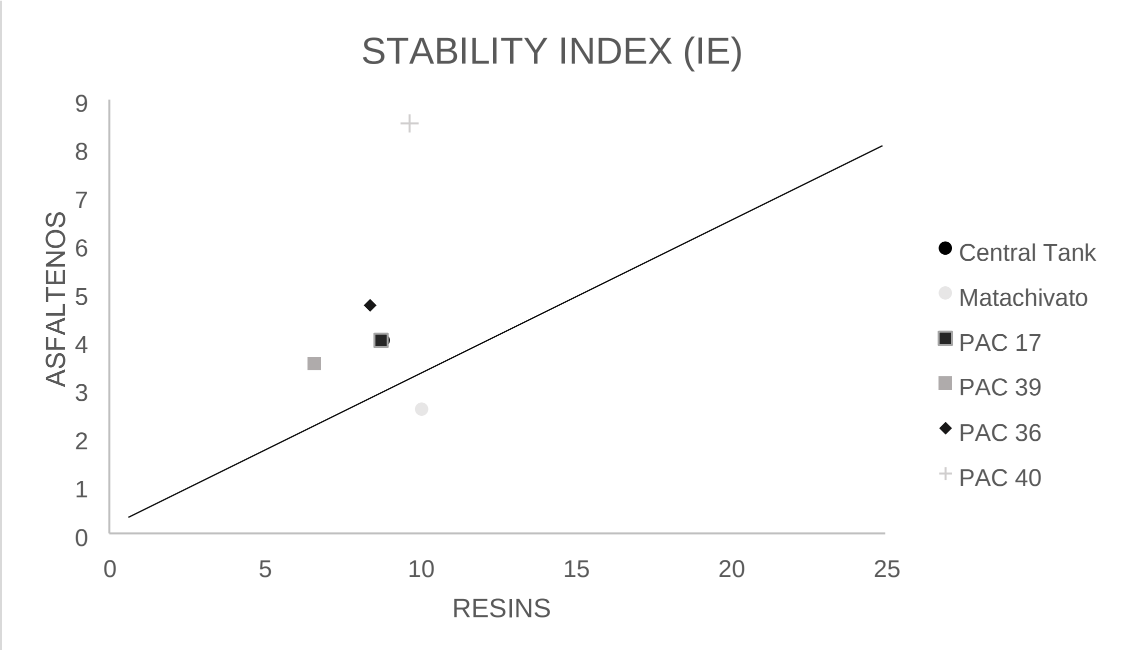
Tanqi a Cantral
Matachii ato
PAC17
PAC39
PAC36
PAC40

FIGURE D:


STABILITY INDEX (IE)
ASFALTENOS
RESINS
0
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7
8
9
0
5
10
15
20
25
Central Tank
Matachivato
PAC 17
PAC 39
PAC 36
PAC 40