Vol. 22, n.° 2, julio-diciembre de 2024
ISSN impreso: 1657-6527 • ISSN en línea: 2145-8502

FUENTES
EL REVENTÓN ENERGÉTICO

ANALYSIS OF ALTERNATIVES FOR WATER AND SALTS SEPARATION FROM CRUDE OIL IN THE DESALINATION SECTION OF A COLOMBIAN REFINERY

ANÁLISIS DE ALTERNATIVAS PARA LA SEPARACIÓN DE AGUA Y SALES DEL PETRÓLEO CRUDO EN LA SECCIÓN DE DESALINIZACIÓN DE UNA REFINERÍA COLOMBIANA

ANÁLISE DE ALTERNATIVAS PARA SEPARAÇÃO DE ÁGUA E SAIS DO PETRÓLEO BRUTO NA SEÇÃO DE DESSALINIZAÇÃO DE UMA REFINARIA COLOMBIANA

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Recibido: 14 de marzo de 2024. Aprobado: 22 de agosto de 2024. Versión final: 5 de diciembre de 2024.

Abstract

The goal of this article is to present a proposal to optimize the performance of desalinated and dehydrated crude oil in a Colombian refinery, improving the separation of the present phases and ensuring that the salt and water levels in the outgoing crude remain constant and within specifications. First, a diagnosis of the current state of the process is carried out. Then, to evaluate the impact of relevant variables on desalination efficiency, a mathematical model was developed that allows for the reproduction, with a reasonable level of precision, of the actual process values. Based on this model, the optimal operating conditions were determined. It is concluded that the main limitation of the current desalination process lies in the inadequate characterization of the crude load, the low efficiency of the chemical treatment for breaking emulsions, and the high content of salts and hydrocarbons in the wash water. Therefore, it is recommended to redesign the characterization procedures, chemical treatment injection, and wash water handling to improve emulsion breaking and promote coalescence in desalination plants.

Keywords: Desalination; Dehydration; Crude oil; Colombian refinery; Separation phases; Desalting efficiency; Optimal working conditions.

Como citar: Parra Avendaño, J., Arturo-Calvache, J. E., Camacho-Galindo, S., Guerreiro, J. S., Fernandes Lucas, E., Guerrero-Martin, L. E., & Prieto-Moreno, L. A. (2024). Analysis of alternatives for water and salts separation from crude oil in the desalination section of a Colombian refinery. *Fuentes, El reventón energético, 22*(2), 93-110. https://doi.org/10.18273/revfue.v22n2-2024007

Resumen

El objetivo de este artículo es presentar una propuesta para optimizar el desempeño del crudo desalado y deshidratado en una refinería colombiana, mejorando la separación de las fases presentes y asegurando que los niveles de sal y agua en el crudo saliente se mantengan constantes y dentro de las especificaciones. En primer lugar, se realiza un diagnóstico del estado actual del proceso. Luego, para evaluar el impacto de las variables relevantes sobre la eficiencia de desalación, se desarrolló un modelo matemático que permite reproducir, con un nivel razonable de precisión, los valores reales del proceso. A partir de este modelo, se determinaron las condiciones óptimas de operación. Se concluye que la principal limitante de la desalinización actual radica en la inadecuada caracterización de la carga de crudo, la baja eficiencia del tratamiento químico para el rompimiento de emulsiones y el alto contenido de sales e hidrocarburos en las aguas de lavado. Por tanto, se recomienda rediseñar los procedimientos de caracterización, inyección del tratamiento químico y manejo de las aguas de lavado para mejorar el rompimiento de las emulsiones y favorecer la coalescencia en las plantas desalinizadoras.

Palabras clave: Desalinización; Deshidratación; Petróleo crudo; Refinería colombiana; Separador de fases; Eficiencia de la desalinización; Condiciones óptimas de trabajo.

Resumo

O desenvolvimento deste artigo consiste em gerar uma proposta para melhorar o desempenho do produto bruto dessalinizado e desidratado de uma refinaria colombiana, favorecendo a separação das fases presentes, mantendo constantes e dentro das especificações os teores de sal e água no produto bruto. Foi realizado um diagnóstico do estado atual do processo e, para avaliar o efeito das variáveis de interesse na eficiência da dessalinização, foi desenvolvido um modelo matemático capaz de dar repetibilidade, com certo nível de precisão, aos valores reais e, a partir disso, foram avaliadas as condições ideais de trabalho. Sugere-se que o principal ponto fraco da dessalinização atual se deve à caracterização inadequada da carga bruta, à baixa eficiência do tratamento químico para quebrar a emulsão e ao alto teor de sais e hidrocarbonetos na água de lavagem, para os quais se recomenda redesenhar os procedimentos de caracterização e injeção do tratamento químico e das águas de lavagem para promover a quebra adequada das emulsões e favorecer a coalescência nas plantas de dessalinização.

Palavras-chave: Dessalinização; Desidratação; Petróleo bruto; Refinaria colombiana; Fases de separação; Eficiência de dessalinização; Condições ideais de trabalho.

1. Introduction

Oil fields typically exhibit an increasing formation of water cuts that vary according to the reservoirs age and recovery method. When oil and part of water formation get contact due to high shear during production and transport of crude oil, water in oil (w/o), emulsions are formed (Figure **1**) (Wong et al., 2015; Shafiei et al., 2023). They are highly problematic because they retain a variety of contaminants, mostly Sodium, Magnesium and Calcium chlorides (Abdullah et al., 2023; Yacine et al., 2023). Salt comes in different forms, most often dissolved in water emulsified formation droplets in crude oil, or crystallized and suspended solids, which can compromise the mechanical integrity of process equipment (Li et al., 2023; Hao et al., 2024). Because of this, the crude oil must be processed to separate the associated water, either in emulsified or free form, aiming to reduce the salt content to a specified percentage (Zulfiqar et al., 2024; Chen et al., 2024).

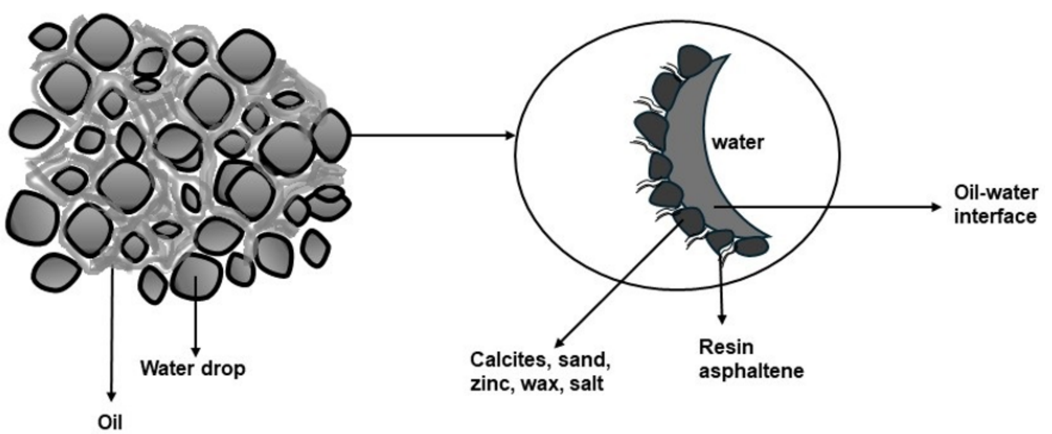

Figure 1. Water-oil emulsion.

The negative effect of these emulsions lies in the difficulty transportation of high viscosity liquids that require higher pumping energies, the formation of salt deposits such as flakes where change from water to steam occurs, corrosion in pipes and equipment occurs due to the presence of hydrochloric acid formed in the decomposition of chloride salts at high temperatures (approximately 350 °C) also by the presence of other metals in inorganic compounds that produce catalyst poisoning/intoxicating (Pereira et al., 2015; Tahouni et al., 2023).

Not to mention that the income is lost due to the presence of these salts in the form of brine, since the latter decreases the API gravity of the oil since it increases its specific gravity due to increase in its density produced by water, therefore decreases the sale price of crude oil and increases transportation costs by increasing oil viscosity, typically producing a 2 % increase in viscosity in a 30° API crude and a 4% increase in viscosity in a 15° API crude (Guoju, 2023; Escandon, 2023; Rincón et al., 2014). Overall, an increase of one part per million (ppm) of water and brine reduces the cost of crude oil by about $0.85-1.3 per barrel (Yu et al., 2024; Fuentes et al., 2022)

In economic terms, the most frequent problem caused by salts and water during crude oil production and refining is corrosion in pipes, vessels, valves and processing instrumentation. The costs associated with controlling such issues, as the replacement of corroded pipes and other metal installations, as well as hard work have increased as wells are drilled deeper and in increasingly hostile environments, at 33 %, corrosion becomes the most important failure for the integrity of assets ranging from wells and drilling rigs in the upstream segment, to pipelines and refineries in the midstream and downstream segments.

According to Kiani et al. (2016), the global cost of corrosion was estimated at $2,505 MMUS, which was equivalent to 3.4 % of global GDP in that year. However, if treatment and prevention practices are used in an appropriate and controlled manner, it is estimated that savings between 15 and 35 % of the cost of corrosion could be achieved; that is, between $ 375 and $ 875 MMUS annually on a global basis (Bowman et al., 2016; Kania, 2023).

In the Combined Distillation Unit of the Cartagena refinery, a dehydration and desalting section was installed, prior to loading into the atmospheric furnace. In this section, demulsifier and washing water are injected into the crude oil, before the entry of this to the electrostatic desalination plants, where the process of removal of contaminants is covered by inducing electric dipoles in the water droplets for their subsequent coalescence and separation by gravity (Figure 2).

However, the desalination process has an overall efficiency of no more than 74 % compared to 95 % that should be reported according to literature. Based on this premise and as a result of the repetitive fouling by chlorides, water and sediments in the downstream units of the Cartagena refinery. For the purposes of this research, a comprehensive approach will be formulated to optimize the performance of crude oil dehydration and desalting processes, whose purpose is mainly to reduce susceptibility to corrosion and containment losses with potential damage to the environment, people, and infrastructure.

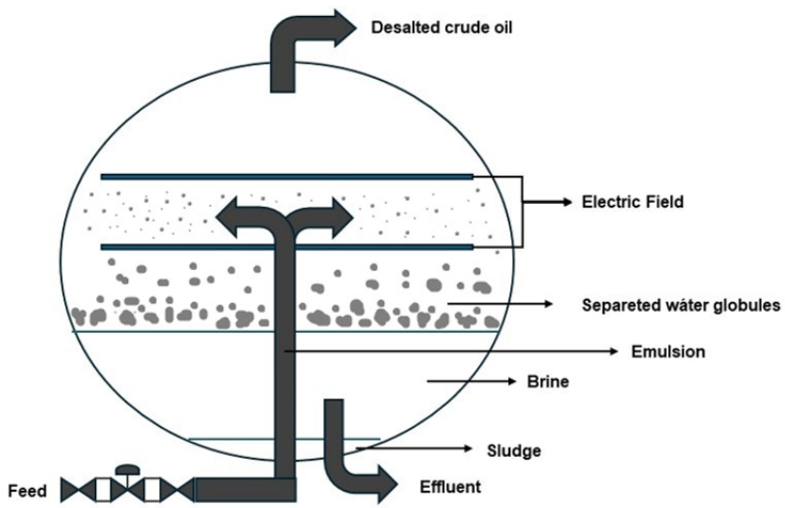

Figure 2. Operation of electrostatic desalination.

Throughout a diagnosis of the process carried out in the refinery to establish an initial root cause analysis, a mathematical model is presented to represent the current dehydration process with a sufficient degree of reliability with a previous statistical validation and a sensitivity analysis of literature are established to improve the integral efficiency of dehydration / desalting of crude oil.

2. Materials and Methods

The methodology is developed in three stages, a general description of the process carried out in the field, the evaluation and validation of the mathematical model that presents the best fit to the process data and the sensitivity analysis to evaluate the variables that exert the greatest impact on dehydration.

2.1 Process Description

After exploration and extraction, treatment facilities typically begin with the separation of fluids from the producing well into three components: oil, gas and associated water along with sediments. Initially the crude goes through a first stage of dehydration and desalting whose purpose is to eliminate much of the remaining free water and a part of the emulsified water, the salt content is generally not measured at this point, but once the water is removed it can be expected that the crude that leaves the dehydrator contains lower concentrations of salt. Once in the refinery, the oil is typically free of associated gases and free of unemulsified water according to Table 1, ready to be treated in the Combined Distillation Unit where it is suitable to follow its downstream course.

Typically, heavy crudes treated in Colombia contain large proportions of surfactants that stabilize the emulsions w/o further complicating their treatment, so that a simple sedimentation by gravity or chemical demulsification does not result in the timely separation of the phases of crude oil and water. Therefore, in the oil industry, some of the typical methods of crude oil dehydration (chemical, thermal, mechanical and electrical) are usually combined, depending on the type of oil and the availability of resources. In general, a combination of thermal and chemical methods is used with a mechanical or electrical one to increase the speed and efficiency of water/crude emulsion breakage and with this achieve the dragging of salts dis-solved in water and those crystallized salts in the form of suspension.

Table 1. Characteristics of loaded crude in the refinery

Parameters	Average Value	Minimum Value	Maximum Value	Deviation
Flow Rate (kbpd)	159.67	152.42	163.16	3.06
Water Content (%)	0.6	0.05	1.81	0.35
Salt Content NaCl (PTB)	3.60	0.52	13.80	3.18
API Degrees	22.66	21.48	23.59	0.55
Viscosity at 100 ^{0}F (cP)	29.77	22.24	52.97	8.02
Charging Temperature (^{0}F)	98.90	96.59	100.67	1.20
Specific Gravity **	0.92	0.91	0.92	0.003
Aromatics Content (%)	46.00	20.10	50.10	10.31
Resin Content (%)	13.94	10.90	32.20	7.66
Asphaltine Content (%)	21.5	20.5	22.5	1.41

**Specific gravity taken at 600 F.
***Data from January 2019.

Among the main subprocesses of the Combined Distillation Unit is the second stage of dehydration and desalting in electrostatic dehydrators, where the inorganic salts present in the crude oil are separated taking advantage of their solubility with both free and emulsion water, this in order to remove in greater detail unspecified amounts of emulsified brine and trapped salt crystals that remain in the crude oil. For single-stage desalination units, efficiencies of 90 to 95 % are achieved and two-stage processes achieve an efficiency of 99 % or higher.

In the following diagram (Figure **3**) it is evident that the mixture of crude oil-water whose characteristics are presented in Table 1 passes through a series of heat exchangers to increase its temperature and receives an injection of demulsifier and waste water from the second desalination plant, this process increases the mass transfer of inorganic salts to water and also reduces global water requirements. The mixture thus enters the valve whose function is to provide an adequate pressure drop to facilitate contact between fluids and promote the removal of corrosive salts from crude oil. This mixture enters through the bottom of the desalination plant D-001, passes through the distributors and reaches the center of the electric field between the electrodes of the equipment where the coalescence of the drops intensifies. By difference in densities the fluids are separated, the upper product is the treated crude oil and the lower product is the brine whose temperature is recorded.

The treated crude oil again receives an injection of demulsifier and 9 % of washing water in relation to the flow of loaded crude oil (3 % from the discard water of D-002 as internal recycle and 6 % from the acidic water zone) whose characteristics are shown in Table 2.

Table 2. Characteristics of water loaded to D-002.

Parameters	Average Value	Minimum Value	Maximum Value	Deviation
Flow Rate (kbpd)	9.86	9.41	9.96	0.15
Water Content (%)	11.32	1.47	22.18	15.50

Then the crude passes through the mixing valve and enters through the bottom of desalination plant 2 where both fluids are separated by the same mechanism mentioned in the first stage. The crude oil free of corrosive salts and other contaminants leaves through the top of the D-002 and enters through the tube side to the bank of Exchangers E011A / B where it is heated with light diesel that flows on the hull side and then receives an injection of defoamer.

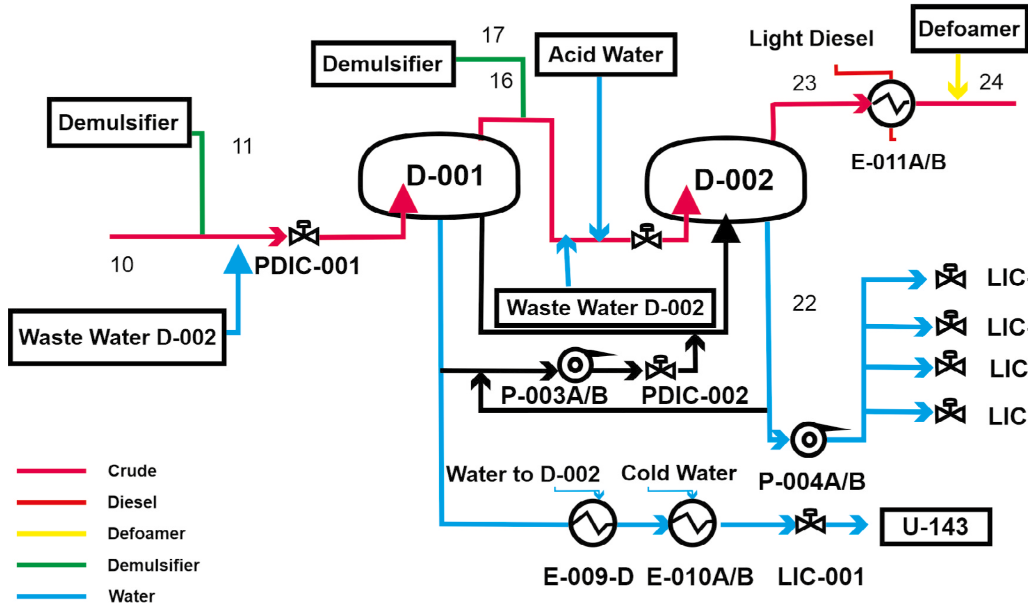

Figure 3. Two-stage desalting and dehydration unit.

This process is important for the plant since the properties with which the fluid enters the unit must be controlled, including viscosity, flow, composition, temperature, salt, water and solids content, in the same way it is sought to preheat the crude oil to reach the temperatures required in the subsequent desalination equipment and additional operating conditions within the electrostatic equipment must be controlled (Table 3 and 4).

Table 3. Operating conditions D-001.

Parameters	Average Value	Minimum Value	Maximum Value	Deviation
Operating Temperature (^{0}F)	272.20	258.00	282.00	5.95
Operating Pressure (psig)	199.15	195.70	201.28	1.66
Dewatering Efficiency (%)	75.66	10.03	86.69	17.88
Desalting Efficiency (%)	58.23	17.37	85.90	28.76
Pressure Drop (psig)	13.14	11.87	14.70	0.73
Primary Voltage (V)	508.4	462.00	597.00	33.24

Table 4. Operating conditions D-002.

Parameters	Average Value	Minimum Value	Maximum Value	Deviation
Operating Temperature (^{0}F)	258.66	247.00	269.00	5.45
Operating Pressure (psig)	185.97	184.88	186.51	0.43
Dewatering Efficiency (%)	92.82	85.48	112.779	5.99
Desalting Efficiency (%)	73.13	44.27	92.92	17.16
Pressure Drop (psig)	8.17	6.00	9.82	1.56
Primary Voltage (V)	787.80	732.00	930.00	53.26

2.2 Mathematical Model Validation

The mathematical model used to evaluate the operating conditions specifically represents the dehydration of crude oil, that is, the separation of the aqueous and oily phases, assuming the removal of salts, dragged with water. This model was developed in conjunction with the Leopoldo A. Miguez de Mello Research and Development Center (CENPES) of PETROBRAS S.A., one of the largest oil companies in the world, which positively influences the reliability of the selection.

2.2.1 Model proposed by da Cunha (2008)

The authors' study purpose is to analyze the variables of the electrostatic dehydration process of oil and propose a representative model of the experimental data obtained in the pilot unit of electrostatic treatment of the CENPES of Petrobras S.A and of the tests carried out on the desalination plants of two refineries of the company.

In addition, a comparison is made between the efficiency of electrostatic dehydration of the pilot and industrial units, based on the doubling of the conditions tested in the re-fineries to the pilot unit, in this way a broader empirical mathematical model of the process is proposed, based on the results obtained and whose purpose will be to predict the performance of the industrial units.

As free variables, the study considered the physicochemical properties important for the performance of the electrostatic dehydration process, including the content of water, salt, resins, aromatics, asphaltenes, metals, sulfur, nickel, vanadium, iron and nitrogen of crude oil, in addition to its viscosity, density, API degrees, interfacial tension, conductivity, acid index and distribution of emulsion droplet size, on the other hand, the density of the aqueous phase in emulsion was taken into account.

Based on the analysis of these factors, it is concluded that the free variables that will be included in the model will be: the dynamic viscosity of crude oil at operating temperature and the density of both phases. It is important to note that the salt content in crude oil was finally not included as a free variable, since it is considered that mathematical models of dehydration process infer desalination efficiency.

The operational variables tested for each crude oil analyzed were: water content in the synthetic emulsion, the voltage gradient between electrodes, the operating temperature and the residence time between electrodes. In this way, it is decided to consider in the model only the voltage gradient and the residence time as direct operating variables since the effect of temperature is implicit in the analyzed properties of crude oil and water. As a response variable, the water content in the treated crude oil was measured. The Equation 1 was the proposed by da Cunha (2008).

$$BS\&W_{fM} = A * \frac{\mu_p^B}{\Delta\rho^C * T_{RPM}^D} * {GT_M}^E \qquad (1)$$

2.2.2 Evaluation of the model in the real data

Considering the operating variables and physicochemical properties of the crude oil entering the desalination and dehydration unit, to evaluate the fit of the model proposed by Cunha to the real data in the field, the sum of squares of the residuals between the predicted and observed values is used to estimate the error instead of using the pure error. The results presented in Table 4 are obtained.

da Cunha's model depends on a series of variables related to the nature of the phases present, such as the viscosity of the crude oil at operating temperature, the difference in densities between the aqueous and oily phase, and the response variable that is the water content in the treated crude, also takes into account the operating conditions of the process such as the flow of injected crude, the distance between electrodes, the voltage applied to the grids, and the cross-sectional area of the equipment in question (Equation 1). It is urgent to clarify that this model focuses directly on achieving an adequate water withdrawal, assuming the correct dilution of salts in this, so the modeling will be carried out specifically for desalination plant 1 since it is the equipment that presents low dehydration efficiency. To achieve adequate salt carryover, additional proposals focused on emulsion treatment and crude oil washing should be considered.

The A, B, C, D and E parameters depend on the type of crude oil treated and must be estimated from a multivariable nonlinear regression, these parameters account for the ability of the model to predict the behavior of the real data in the field. The available in-formation included some process flows with their water and salt content, working temperatures and voltages, as well as some of the most important properties of crude oil. The determination of the missing properties was made from mathematical correlations avail-able in the literature (Equation 2, 3, 4 and 5). As a first step, the explanatory variables of the model should be available for estimation. The Equation 2 represents the water density with respect to temperature. The Equation 3 represents the crude oil density with respect to temperature, and crude oil dynamic viscosity is represented for the Equation 4.

$$\rho_{water} = 0.99965 + 2.0438E-4 * T - 6.1744E-5 * T^{1.5} \qquad (2)$$

$$BS\&W_{fM} = A * \frac{\mu_p^B}{\Delta\rho^C * T_{RPM}^D} * {GT_M}^E \qquad (3)$$

$$LogLog(v_{crude} + 0.7) = A_1 + B_1 Log((T - 32) + 491.67)$$

$$v = \frac{\mu}{\rho_{Oily}} \qquad (4)$$

From Equation 4, values of viscosity dynamic at different temperatures, it is possible to determine the constants A 1 and B1 by means of least squares fit, in this way obtain a mathematical expression to predict μ as a function of T. The Equation 5 represent the A1 parameter estimation, and the Equation 6 represents the B1 parameter estimation.

$$A_1 = \frac{\sum_{i=1}^{n} Log\left[Log\left[\frac{\mu}{\rho_{oily}}+0.7\right]\right] - B_1 \sum_{i=1}^{n} LogT_i}{n} \quad (5)$$

$$B_1 = \frac{\sum_{i=1}^{n} Log\left[Log\left[\frac{\mu}{\rho_{oily}}+0.7\right]\right] LogT_i - \frac{1}{n}\sum_{i=1}^{n} LogT_i \sum_{i=1}^{n} Log\left[Log\left[\frac{\mu}{\rho_{oily}}+0.7\right]\right]}{\sum_{i=1}^{n}(LogT_i)^2 - \frac{1}{n}(\sum_{i=1}^{n} LogT_i)^2} \quad (6)$$

As for the voltage gradients, the desalination plants work each with two three-phase transformers located on top of the equipment that operate with voltages of 480 V in alternating signal and feed a load at the output of 28 kV, said load is fed through a bushing called bushing or pressure seal, which is connected to the grids that are re-sponsible for inducing the electrostatic effect in the emulsion. The electric field of greater intensity is then produced between the energized plates, depending on the secondary voltage delivered by the transformer, and the distance between grids, this relationship is expressed in Equation 7 as:

$$GT_C = \frac{V_s}{x} \quad (7)$$

The voltage transformation ratio between the primary and secondary winding according to Faraday’s Law, assuming an ideal behavior (without power losses) is ex-pressed in equation 8.

$$\frac{V_p}{V_p} = \frac{V_s}{x} \quad (8)$$

This relationship allows to identify the secondary voltage delivered by the transformer as a function of the primary voltage recorded in the field and the transformation ratio Ns / Np. As for the distance of the electric field, only the first and second electrode of the configuration are energized by the transformers, while the third electrode is grounded, the distance to be considered for the considerations of the model will be that between the first and second electrode (19.98 cm), as shown in Figure 4.

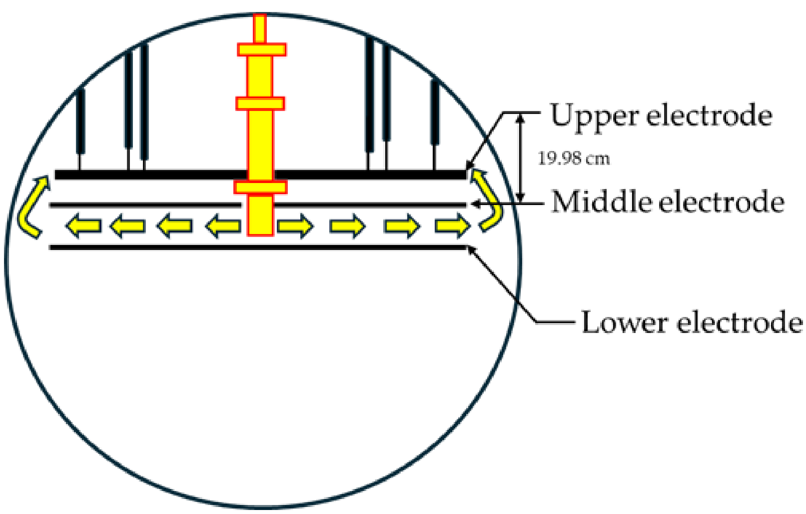

Figure 4. Desalinator cross section.

Equation 9 evaluates the final content of basic sediment and water (BSWf), expressed in mass content. For the residence time between electrodes equation 10 is used (Mello Duarte, 2008).

$$BSW_f = \frac{m_{Water}}{m_{Water}+m_{Crude}} * 100 \quad (9)$$

$$T_{RP} = \frac{A_t * L_e}{Q_D} \quad (10)$$

2.2.3 Multivariable nonlinear regression

Based on the values calculated based on the current procedure in the refinery, a multivariable nonlinear regression was performed to determine the value of the model parameters, particular to each type of crude oil. According to Ratkowsky (1990), In statistics, nonlinear regression is a type of regression analysis where observational data are modeled by a function that depends on one or more independent variables and is a nonlinear combination of the model parameters. The data are then fitted using an iterative approximation method.

The methods of successive approximations are based on numerical method techniques, which aim to find the coefficients of the independent variables that guarantee the best possible fit with the dependent variable. It is intended to analyze the validity of the strength of the regression fit in the mathematical modeling equation for crude oil dehydration, which, according to its nature, is a multiple nonlinear equation (more than one dependent variable with at least one degree different from 1 of one of the predictor variables); The above in order to validate if it is a suitable model to be used in the calculation of estimates. It should be clarified that an appropriate adjustment of the regression with respect to the real data, allows to use the model to predict the behavior of the process when some variable is changed. The objective function used for parameter estimation was the minimization of the square mean of the differences between the calculated and experimental output values: Table 5 represents the calculated coefficients for a 95 % confidence interval, which indicate the range in which the estimates of the actual parameters will vary 95 % of the time.

Table 5. Analysis of variance non-linear ANOVA (Parra, 2020).

Number of experimental data = 21 R^2 = 0.907				
Parameter	**Estimation**	**Deviation**	**Confidence -95%**	**Confidence 95%**
A	9.818E-22	0.00	-6.35E-20	6.54E-20
B	6.26	1.49	3.09	9.43
C	-9.66	4.37	-18.94	-0.39
D	-22.82	4.07	-31.46	-14.17
E	-3.97	1.95	-8.12	0.17

The first thing that is validated is whether or not there is a significant model between the dependent variable and the independent variables, for this an analysis of nonlinear variance is run. The results are described as follows (Table 6).

Table 6. Correlation matrix of parameter estimates.

Source	Sum of Squares	GL	Mean Square
Regression	124.66	5	24.93
Residue	5.44	16	0.340
Total without correction	130.11	21	
Total corrected	58.78	20	

The nonlinear analysis of variance shows that it has a significant model (the Regression / Residue ratio is higher critical value), that means that the set of variables significantly explain the behavior of the dependent variable. On the other hand, to measure the association and strength of the model, the software calculates the coefficient R2, called the coefficient of determination and looks for how much variance is explained by the model of independent variables.

The R2 coefficient obtained was 0.907, which is a value very close to 100 % which means that the variance explained by the dependent variables is 91 % (the other per-centage is explained by variables exogenous to the model), which allows us to confirm that the combination of the model is relevant and adequate to estimate the value of the dependent variable.

It is worth mentioning that the correlation coefficient could be higher due to two main factors: t the iterations by the software reached their maximum allowed memory and the number of data was sufficient to capture the normality of the set and allow a better fit.

It is important to note that, unlike linear regression methods, nonlinear models do not need to meet the assumptions that are necessary in linear regression: independence, homoscedasticity and independence of residuals. This implies that it was not necessary to make validations with respect to the residual's behavior.

In addition to R2, it is expected that the explanatory variables will be homogeneous with each other, a situation that is fulfilled for this model; since the correlation matrix (Table 7) shows values very close to 1 or -1 (for the most part). Another dynamic that confirms the goodness of the model.

Table 7. Matrix of correlations of parameter estimates (Parra, 2020; da Cunha, 2008).

	A	B	C	D	E
A	1.000	0.782	-0.825	0.739	-0.458
B	0.782	1.000	-0.886	0.220	-0.223
C	-0.825	-8.886	1.000	-0.243	0.125
D	0.739	0.220	-0.242	1.000	-0.585
E	-0.458	-0.223	0.125	-0.585	1.000

Each of these parameters, that represents type of crude, it is possible to compare the predictions of the final water content in the treated crude oil with the observed data. However, it is observed that the predictive model manages to capture the real behavior of the process, not to mention that the mean square error (MSE) is 0.25 and the maximum relative error (RE) observed in the estimates is 1.14, so it is concluded that the model is valid to represent the dehydration of crude oil in the refinery (Figure 5).

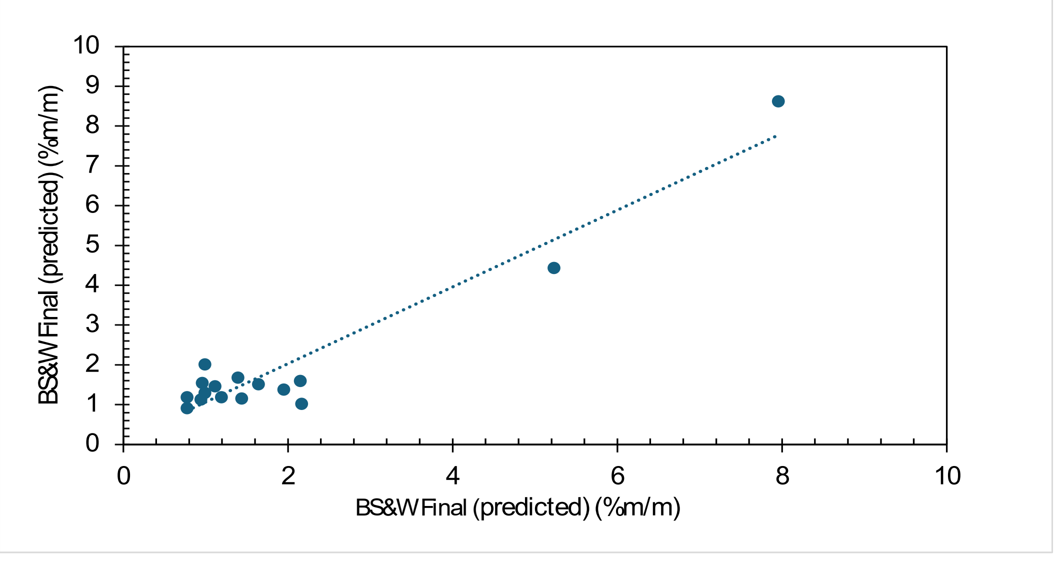

Figure 5. Prediction of the selected dewatering model.

3. Results and discussion

3.1 Load Characterization.

Generally, the load and crude oil streams analysis is performed in the refinery. However, to study the root cause of the variability in the efficiency of the desalination process, a sampling matrix and a robust characterization of the loaded crude was carried out to determine the compounds present that can affect the removal of salts, water and sediments from treated crude oil. The results are presented in Tables 7 and 8.

Table 8. Sampling matrix of the streams of interest (Parra, 2020).

Sample \ parameters	Chlorides not extracted	Chlorides extracted	Solids	Insoluble in N and C7*	Insoluble in toluene	BS&W
Crude oil load per unit	Present	Present	Present	Present	Present	Present
D-001 treated crude	Present	Present	Present	Present	Present	Present
D-002 treated crude	Present	Present	Present	Present	Present	Present

These results show that indeed the loaded crude oil contains chlorides not extractable by electrostatic desalination, which can come from inorganic chlorides encapsulated in asphaltenes or organic chlorides, in addition to solids, sediments, water and metal compounds whose adverse effect on the efficiency of the process has already been mentioned (Table 9).

It should be considered that compatibility problems may arise with the mixture of crudes diet entering the refinery, when mixing crudes of a paraffinic nature with asphaltene crudes, which leads to the destabilization of asphaltenes, which can stabilize emulsions and encapsulate other types of compounds such as metals, affecting the properties of the crude itself, mainly conductivity.

There is a high content of non-extractable chlorides by desalination whose presence may be due to; As mentioned in the previous section, inorganic chlorides encapsulated by asphaltenes and solids present, or A, organic chlorides such as carbon tetrachloride, perchloroethylene, chlorobenzene, among other compounds, which are soluble in the oily phase and have limited solubility in the aqueous phase due to the presence of covalent bonds between carbon and chlorine atoms, This type of salts are not extractable by the electrostatic desalination plants located in the unit, so like the encapsulated salts, they will remain in the treated crude load and continue their course downstream where they are hydrolyzed forming HCl.

Table 9. SARA analysis and other properties of load crude (Parra, 2020).

Load Crude oil properties	Average value
API Gravity	22.66
Nickel (mg/kg)	47
Vanadium (mg/kg)	135
Calcium (mg/kg)	23.5
Total Sulfur (mg/kg)	12130
Iron (mg/kg)	4.3
Water and Sediments (%)	0.41
Aromatis (%)	46.0
Resin (%)	13.94
Asphaltenes (%)	2.17
Extractable chlorides (PTB)	5.18
Total chlorides (PTB)	4.77
Filterable chlorides (%mass)	0.04

To evaluate the salt content in the cargo, it is proposed to implement standard methods and procedures for the measurement of nondesalinable chlorides in hydrocarbons routinely in each unit and to ensure that the content of organic and total chlorides in the crude oil is kept below a certain level. Such methods include the determination of inorganic hydrocarbon chlorides under ASTM Designation 51250 by selective ion method, and the determination of organic chlorides in the crude oil washed naphtha fraction by X-ray fluorescence spectrometry under ASTM Designation 4929-C51. For these analyses, the acquisition of a compact analyzer to measure total chlorine in liquid hydrocarbons such as aromatics, distillates, heavy fuels, crude oils and aqueous solutions is proposed.

Regarding the content of asphaltenes, sediments, solids, and their influence on the stability of the emulsion, it is always recommended to evaluate the diet that enters the unit to avoid mixtures of paraffinic crudes with asphaltene crudes, causing the destabilization and agglomeration of the asphaltenes present, which promote the stabilization of the emulsion, the increase of oil in the effluents and the accumulation of dirt in the cold preheating heat exchangers.

Because the average efficiency of desalination and dehydration in the electrostatic treaters is between 58.23 and 75.69 % respectively for the first desalination plant and, 73.13 and 93.82 % for the second desalination plant (Figure **6** and **7**) and there is no evidence of adequate removal of solids in the equipment, it is proposed to re-evaluate the current chemical treatment that includes the addition of washing water and demulsifying chemicals to the crude oil, prior to entering the cold preheating exchangers. Such treatment may include options such as injecting primary demulsifiers into both crude oil and water.

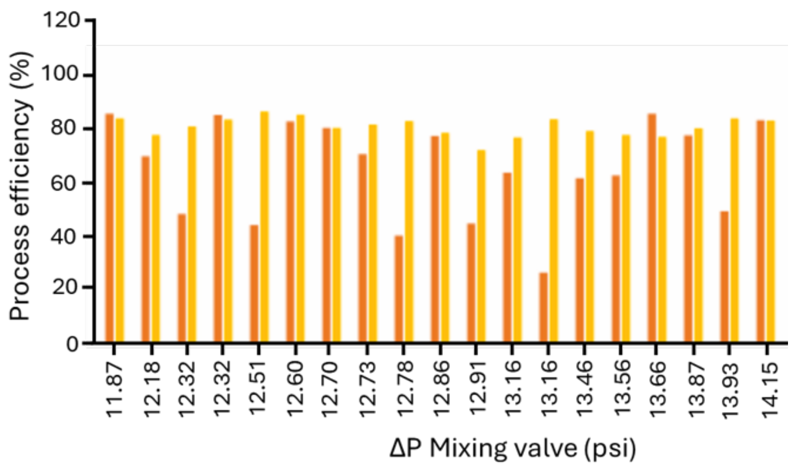

Figure 6. Dehydration and desalting efficiency in D-001.

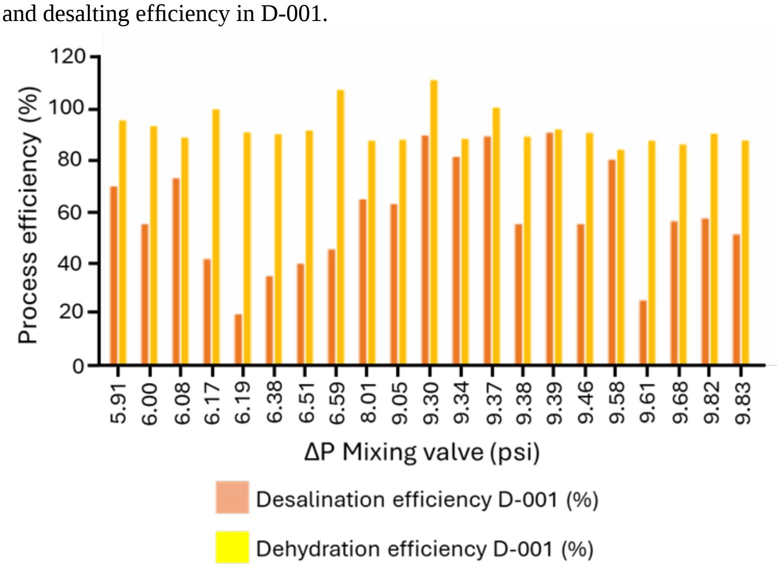

Figure 7. Dehydration and desalting efficiency in D-002.

The increased load of solids can exceed the ability of desalination plants to remove them efficiently, so the chemical program must be carefully evaluated taking into account the management of the solid waste system impregnated with hydrocarbons considering the location and manner of injecting crude stabilizers and wetting agents. As always, chemical programs must be carefully evaluated, not only the preparation of the chosen chemistry when accessing the complete treatment program but also the application technology, as it is another condition that can affect the performance of the program. Therefore, how and where the chemical treatment is applied is almost as important as the selection of the chemistry itself.

3.2 Washing Waters

The quality of the washing water negatively influences the process because it presents variability of content in salts, solids and other compounds that affect the transfer of mass, a chloride content was evidenced in the injection water higher than the control limit in the refinery that is 30 ppm, not to mention that there is hydrocarbon drag in values above that allowed for reuse in desalination (100 ppm) and variations very significant pH, so it is not recommended to use these currents as washing water to desalination plants, because a high and variable chloride content affects the process of mass transfer in the salt from the oily phase to the aqueous, as it decreases the effect of electrocoalescence due to the increase in conductivity in the mixture and therefore the decrease in voltage.

On the other hand, this variation increases the loss of hydrocarbon dragged in the water, because in theory the process of electrocoalescence within the desalination plants has no effect on emulsions of crude oil in water commonly called inverse emulsions and instead, at high temperatures the solubility of the hydrocarbon in the aqueous phase will increase promoted in turn by the already existing concentration of crude oil in the water.

Therefore, it is proposed to evaluate the use of another source of washing water or, failing that, to characterize the sour waters of the UDC drums continuously and readjust the limits established for their injection to the desalination plants, likewise it is recommended to modify and continuously inspect the dosage of the pH modifiers to keep the washing water to the acid desalination plants and at constant levels, This modification promotes the elimination of amines and ammonia as it contributes to their partitioning in water.

3.3 Separation of Phases

The main factor to be evaluated at this point is the electrical performance of the equipment, because according to field inspections, the power consumption has increased with respect to the values normally recorded (24-40 % of kVA design) also increasing the current intensity in the emulsion, which causes the reactance circuit to begin to greatly reduce the voltage obtained to control the load, leading to a decrease in performance in desalination plants. This situation may be due to the conductivity of the emulsion, the process temperatures, or the level of water in the electrocoalescence zone. For conductivity analysis, a sample of crude oil is analyzed and the results are shown below (Figure **8**).

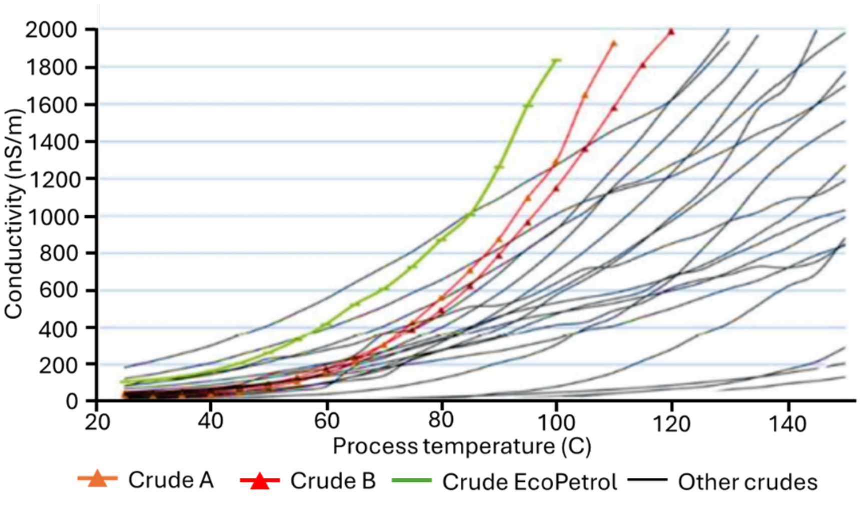

Figure 8. Conductivity of crude oil in refinery.

3.4 Mixing Valves

The reason why the mixing system is important, is that the electrodes work to flocculate the droplets and form larger droplets to promote coalescence and sedimentation, if the droplets are distributed properly, the attractive force will be enough to promote their shock, but if an overmixing occurs, the diameter of droplets will be so small that the attractive forces will not be able to unite the scattered droplets and these would come out in The crude oil together with the salts, which is the current case of the refinery, similarly, if a sub-mixture is produced, the emulsion will not break and the emulsified dispersed water droplets will come out in the crude along with the salts, so both processes can be the cause of the current desalination performance. Therefore, it is proposed to establish an optimal configuration of the mixing valves for different types of crude oil experimentally and considering the ΔP limit for the desalination plant D-001 would be 14 psi

3.5 Sensitivity Analysis D-001

Making use of the mathematical model proposed by da Cunha (2008), it is intended to evaluate the effect of: the voltage gradient applied to the emulsion, the process temperature and the crude oil flow, on the final water content in the dehydrated product of the first desalination plant, since it presents low and variable dehydration efficiency (average of 75.66 % and deviation of 17.88 %) compared to the second desalination plant, assuming a correct solubilization of the salts present in the emulsion.

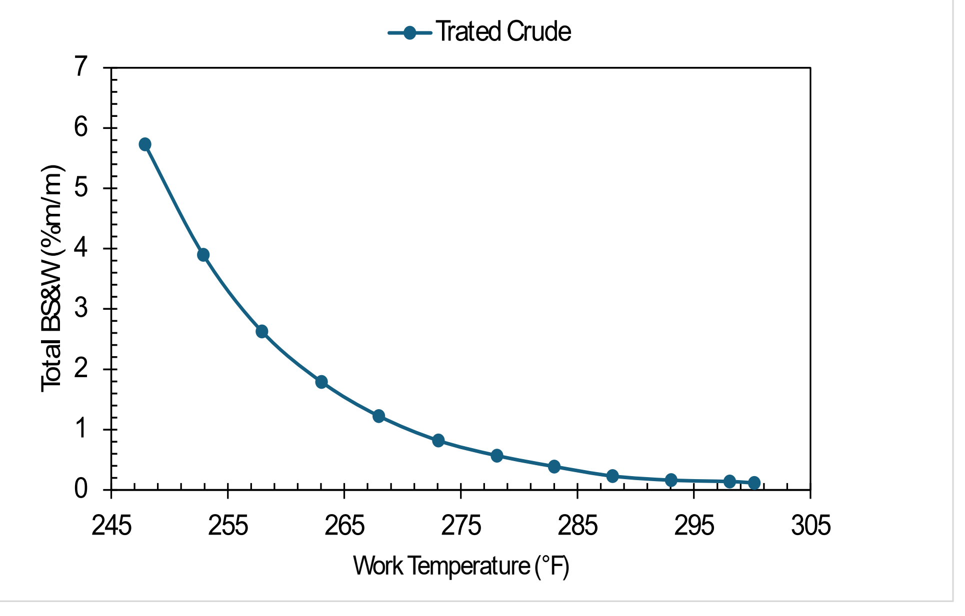

Figure 9. Process temperature analysis.

The Figure **9** shows that, when the crude oil is heated above 275 °F the water content begins to present lower values and its variability decreases, this is because, the heating causes a decrease in the viscosity of the oil phase, which allows particles or drops of water to flow more freely within the emulsion promoting its melting. Similarly, heating the W/O emulsions seeks to reduce the thickness and cohesion of the surfactant film that surrounds the water droplets. Therefore, it is proposed to work at a temperature of 285 °F that does not affect the internal insulation of the equipment and at pressures close to 200 psig, which is the normal working pressure of desalination plants to avoid loss of light.

In Figure **10**, the behavior of the dehydration efficiency seen as the final water content in the crude oil is shown, with respect to the crude oil load, both the temperature and the voltage remained constant.

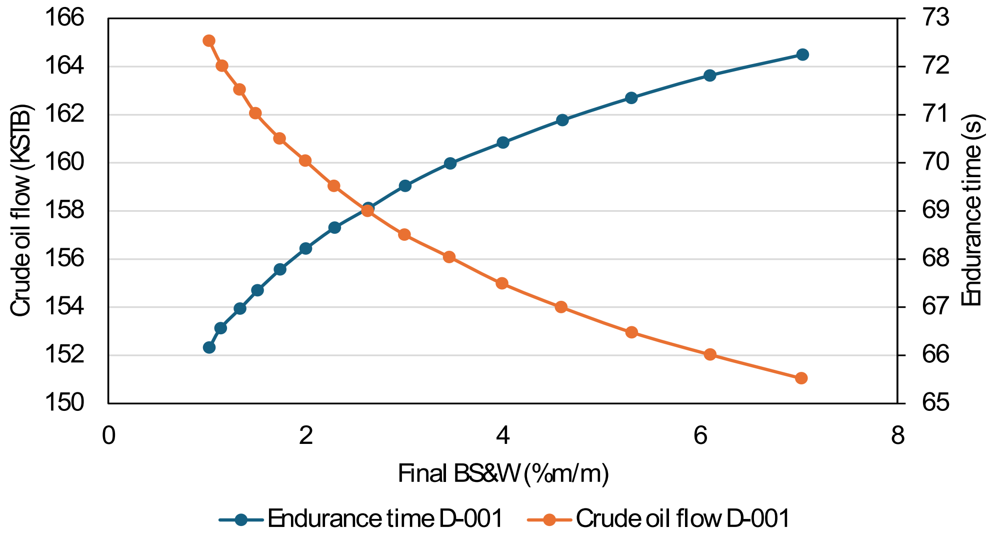

Figure 10. Dehydrated crude oil flow analysis.

Crude oil's flow related to the residence time between electrodes, through an inversely proportional relationship, which indicates that as the flow increases, the residence time decreases favoring the efficiency of dehydration. As is well known, initially, prolonged residence times of the emulsion in the equipment favor the separation of the fluids present, since they allow the collision of a greater number of dispersed droplets, thus increasing the probability of sedimentation of the aqueous phase and decreasing the content of the same in the treated crude. However, after a given time, the diameter of droplets and the percentage of water decrease due to the progress of coalescence, also reducing the probability of colliding of the droplets so that they continue to separate by sedimentation, according to the behavior of the process observed, this given time occurs when an average crude flow of 160 to 165 kbpd is reached. After that time, the efficiency of the process is decreased. Therefore, it is proposed to work with 160 kbpd and time of 66 seconds between the electrodes since it is a continuous process.

As for the voltage applied to the emulsion, the transformers have a primary input voltage of 480 V and deliver an output voltage of 28 kV, which is the configuration initially established to apply to the desalination grids, responsible for performing the electrostatic effect. However, due to the properties of crude oil, the voltage applied to the emulsion can vary and is recorded and controlled, maintaining an average of 485 V, so the analysis of this variable is limited to voltage values be-tween 470 and 490 V, keeping the temperature and load flow constant.

From Figure 11, an inversely proportional relationship can be observed between both variables, since the efficiency of dehydration is favored at higher voltages, this due to the force of attraction between the drops of water dispersed in the crude oil, which must be of sufficient magnitude so that, when colliding, the films of surfactants and other com-pounds that surround them break, allowing coalescence. This force of attraction can be estimated from equation 3, mentioned in chapter 1, in which it is established that the greater the voltage gradient applied and the diameter of the water droplet, the greater the force of attraction between droplets and there-fore their melting and subsequent sedimentation, due to this, it is proposed that the applied primary voltage continue to be controlled and maintained at values close to 485 V and having as a limit the capacity of the transformer which is 28 kV.

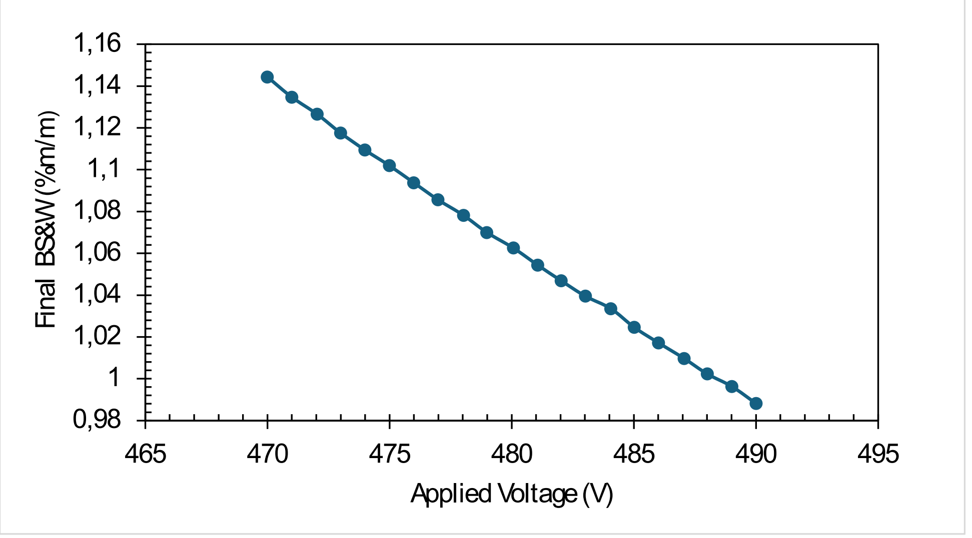

Figure 11. Treated crude oil D-001.

4. Conclusions

As per the diagnostic assessment conducted on the existing crude oil dehydration and desalting processes within the refinery, three distinct zones have been discerned: the loading and preheating phase within the exchanger train, the injection of water subsequent to preheating in the exchanger train, and the injection of wash water coupled with the separation zone. Through the examination of flow diagrams and consideration of average operational conditions, it has been ascertained that the crude exhibits elevated and fluctuating salt concentrations. Moreover, a disparity in dehydration efficiency between units D-001 and D-002 has been identified.

Consequently, there exist preliminary opportunities for improvement to enhance the overall quality of the crude product. These improvement initiatives are aimed at addressing issues such as the high and variable salt contents, as well as the observed discrepancies in dehydration efficiency, particularly in unit D-001 relative to D-002. The proposed enhancements intend to mitigate system disturbances and optimize the performance of the crude oil dehydration and desalting processes at the refinery.

Several representative mathematical models for crude oil dehydration were documented and subjected to comparison using the PUGH methodology. Among these models, the one presented by da Cunha was chosen, with a higher emphasis on the accuracy of the response variable. The selection process was based on the comprehensive evaluation facilitated by the PUGH methodology.

After the model selection, a successful validation was conducted, yielding a non-linear correlation coefficient (R2) of 0.907. This signifies that approximately 91 % of the variance in the final water content of the treated crude oil can be accounted for by the independent variables incorporated in the chosen model. The high R2 value indicates a robust correlation, emphasizing the efficacy of the model in accurately predicting and explaining the final water content in the treated crude oil.

The chosen model is employed for conducting a sensitivity analysis on D-001 with the aim of enhancing water withdrawal efficiency in the equipment. It is proposed that employing flow rates of 160 STBD, temperatures of 285 °F, a mixing time of 68 seconds between the desalter electrodes, and voltages of 485 V will contribute to the improvement of the desalting process. The specified conditions of 485 V are anticipated to enhance process efficiency, particularly when applied in conjunction with complementary separation procedures.

It is advisable to monitor and adjust the salt and hydrocarbon content within the separation tanks of other process units continuously. If deemed necessary, consider extending the residence time to promote effective separation between crude oil and water.

Additionally, it is recommended to assess the feasibility of acquiring two curtain valves within the sour water injection section. This measure aims to ensure a controlled flow while preventing damage to the valve internals.

Acknowledgments: The authors acknowledge the international cooperation agreement between the UNIVERSIDADE FEDERAL DO PARÁ (UFPA, Brazil) and the UNIVERSIDAD DE AMÉRICA (FUA, Colombia) - PROCESO 23073.053603/2022-70

Conflicts of Interest: The authors declare no conflict of interest.

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