

Modeling and Study Influence of the Temperature Parameter on Corrosion Factors in the Atmospheric Distillation Column of Crude Oil

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Abstract

Atmospheric distillation is the first step in separating crude oil into by-products. It uses the different boiling temperatures of the components of crude oil to separate them. But crude oil contains a large quantity of acids and corrosive gases, including sulfur compounds, naphthenic acids, carbon dioxide, oxygen, etc. However, the temperature has an important influence on the aggressive-ness of the corrosion factors in the atmospheric distillation column. This paper aims to investigate the role of temperature on corrosive products in the atmospheric distillation column. The results of the developed model show that the temperature increases the corrosion rate in the atmospheric distillation column but above a certain temperature value (about 600 K), it decreases. This illustrates the dual role played by temperature in the study of corrosion with-in the atmospheric distillation column.

Keywords

Atmospheric Distillation, Corrosion, Crude Oil, Materials, Temperature

1. Introduction

Our research covers three areas, namely: petrochemistry, materials science and thermodynamics, which are inseparable in the petroleum industry. Prospecting, depositing, refining and transporting products derived from crude oil require in-depth knowledge of the links between these three areas. Since the first researches and results on corrosion in mining, refining especially in the distillation and processing of crude oil, temperature has always been a determining factor. However, its behavior is complex; some believe that corrosion increases directly with temperature, others tend to minimize its effects on corrosion. At the beginning of researches on the link between temperature and corrosion, many specialists showed that corrosion increases with temperature. An old rule of thumb is that increasing the temperature to 283 K doubles the corrosion rate [1]. This approximation gives an idea of the influence that temperature can have on corrosion, although this rule can be misleading in certain situations. On the other hand, over time, some specialists have demonstrated the inhibition of the proliferation of corrosion beyond a certain temperature value for the corrosion of naphthenic acid, the corrosion by carbon dioxide and the corrosion of sulfur compounds [2] [3] [4].

Firstly, it is necessary to differentiate between the temperature of the wall and the temperature of the medium. It is the latter that is considered in this article and that we will use in the rest of our discussion. In furnaces and in the event of a significant difference between these two values, the one that prevails is the temperature of the walls if the temperature in the medium does not modify its composition [2].

At room temperature, naphthalene acids are not corrosive. However, it becomes more aggressive at temperatures where refining takes place [5]. Naphthalene acid becomes corrosive to carbon steel at temperature ranging from 473 to 493 K, respectively and reaches its peak activity at 583 K. The corrosivity of Naphthalene is minimal above 673 K due to its decomposition at high temperatures [5].

Temperature strongly affects the nature and morphology of corrosion deposits that form on the surface of low alloy steels. For temperatures above 343 K, the low solubility of $FeCO_3$ and the high saturation in the latter promote the formation of a protective iron carbonate deposit [3]. Below 343 K, the temperature activates the process of electronic dissolution of steel [6].

Sulfur corrosion intensifies with increasing temperature from 503 K and is maximal at temperatures (698 - 723 K) [7]. Beyond these temperatures, the corrosion of sulfur compounds decreases with increasing temperature up to 813 K. At temperatures above 698 K, the greatest amount of corrosive sulfur has reacted with the metal surface or decomposed and there is a formation of a dense coke deposit, which prevents corrosion from proliferating [4].

Temperature and pressure affect the nature of the phases (liquid, solid and gaseous) which in turn can cause significant corrosion damage [8]. The increase in temperature accelerates the electrochemical reactions of corrosion and the transfer of aggressive substances on the surface of metals. A rise in temperature causes a drop in the pH of the water. This results in a proliferation of corrosion. In another sense, the solubility of aggressive gases (H₂S, O₂, CO₂) decreases with increasing temperature. Therefore, temperature has a complicated effect on corrosion. Above a certain temperature, corrosion increases considerably and then

decreases due to the reduction in the solubility of corrosion-causing gases in aqueous solutions. Generally, it is between 333 - 353 K depending on the chemical composition of the liquid phase [9]. In addition, temperature increases the rate of sedimentation and the formation of a protective $FeCO_3$ layer [4].

It is therefore necessary to provide a scientific answer to this problem.

This paper aims to carry out a study on this problem in order to give the behavior of the corrosion factors with regard to temperature and to define by a mathematical modeling of the evolution of the mass loss according to the temperature within the atmospheric distillation column.

The rest of this article is subdivided into three parts. The first part is the materials and methods used, then the presentation and discussion of the results, and in the last part we have resumed this work and given the perspectives for developing, and eventually apply these results in industry.

2. Materials and Methods

2.1. Materials

To illustrate the effect of temperature on corrosion factors through programming softwares, the time (X) and temperature (Y) parameters are varied in order to observe the behavior of the representative curves of the mass loss ($P_1(X, Y)$ for the linear Equation (6) and $P_2(X, Y)$ for the second order polynomial Equation (7)).

Firstly we study the behavior of these two equations for times Y from 0 to 10 h and temperatures X from 600 to 1000 K in accordance with the operating temperatures of the atmospheric distillation column.

Secondly, the time parameter *Y* is varied from 0 to 1000 h and temperature stays from 600 tom 1000 K.

2.2. Methods

The rate of corrosion can be related to temperature, based on the Arrhenius equation [10]:

$$R = A \exp\left(\frac{-Ea}{RT}\right) \tag{1}$$

R is the speed constant of corrosion reaction; *A* is the Arrhenius constant; *R* is the noble gases constant (J/K·mol); *T* is temperature (K) and *Ea* is the activation energy of the reaction (KJ/mol).

Furthermore, the experimental results show that the corrosion rate increased with time to the power n, R is proportional to [10]:

$$t^n \exp\left(\frac{-1}{T}\right) \tag{2}$$

Therefore, a new exponential model is proposed to correlate corrosion rate data as a function of temperature T and time t [10]:

$$R = a_7 C^{a_8} \exp\left(\frac{-a_9}{T}\right) \tag{3}$$

 a_7 , a_8 , a_9 and C are constants.

Mathematical and statistical analyzes provide a powerful approach for the dependence of corrosion rate on temperature and time [11]. Statistical and mathematical relationships can be used to prevent the evolution of corrosion in the atmospheric distillation column under conditions different from the experimental conditions.

Mathematical regression can be used, as it is the predominant method for illustrating computer data [12].

Several mathematical equations can be suggested for the mathematical illustration of the mass loss of low carbon steels as a function of temperature and time [13] [14]. The linear Equation (4) and the second-order polynomial Equation (5) are examples [12]:

$$P_{a_1}(T,t) = a_0 + a_1 T + a_2 t \tag{4}$$

$$P_{a_2}(T,t) = a_0 + a_1T + a_2t + a_3Tt + a_4T^2 + a_5t^2$$
(5)

 P_{a_1} and P_{a_2} represent the mass loss in (g/m²) and t is the time in (hour h) and from a_0 to a_5 which are constants.

Equations (3) and (4) can be developed and the regression method is used for this purpose to evaluate the coefficients up to these equations. STATISTICA 7 software is used to estimate these coefficients. This software is based on the non-linear estimates of the Levenberg-Marquardt least squares method. The maximum number of iterations is 1000, the confidence level is 95% and the critical convergence is 10^6 .

These equations can be rewritten as follows [12]:

$$P_1(T,t) = -0.162 + 6.5 \times 10^{-4} T + 3 \times 10^{-3} t$$
(6)

$$P_{2}(T,t) = 0.545 - 1.9 \times 10^{-2} T + 2.26 \times 10^{-3} t + 2.04 \times 10^{-6} Tt + 2.3 \times 10^{-6} T^{2} - 7.5 \times 10^{-6} t^{2}$$
(7)

The numerical values of the coefficients $(a_0 - a_5)$ are given in Equations (6) and (7).

Equation (6) represents the mass loss with a computational correlation of $R^2 = 0.9834$. However, Equation (7) is slightly more rigorous with a correlation of 0.9904 [12]. In general, the correlation coefficient greater than 0.3 signifies a weak relationship between parameters and uncertain validity. Between 0.5 and 0.7, it indicates a significant relationship between the parameters and practical importance. On the other hand, a correlation of 0.9 signifies a significant relationship between the parameters and significant relationship between the parameters and practical importance. On the other hand, a correlation of 0.9 signifies a significant relationship between the parameters [13] [14].

Equations (6) and (7) represent the mass loss in the atmospheric distillation column with an acceptable validity criterion, and a good dependence of the parameters: time, temperature and mass loss.

To show the influence of temperature on the proliferation of corrosion we use the linear Equation (6):

• For time between 0 - 10 hours and temperature 600 - 1000 K (Figure 1(a)).



Figure 1. Influence of temperature between 600 to 1000 K on proliferation of corrosion for time between 0 to 10 h (a) and 0 to 1000 h (b).

• For a time between 0 to 1000 hours (6 months) and a temperature of 600 to 1000 K (Figure 1(b)).

To show the influence of temperature on corrosion inhibition we use the second order polynomial Equation (7):

- For time between 0 10 h and temperature 600 1000 K (Figure 2(a)).
- For a time between 0 to 1000 h and a temperature between 600 to 1000 K (Figure 2(b)).

The mass loss is given by the expression [15]:

$$P = \frac{M_i - M_f}{S} \tag{8}$$

where *P* is the mass loss in $(g/cm^2) M_i$ is the initial mass and M_f the final mass of the metal sample studied in (g) and *S* is the surface in (m^2) .

3. Results and Discussions

3.1. Results

3.1.1. The Linear Equation (6)

The linear Equation (6) in Figure 1 shows at Figure 1(a) and Figure 1(b) that despite these changes in the parameters, the mass loss increases considerably with temperature and time in the atmospheric distillation column. This constitutes the primary role of temperature on corrosion. These results relate the behavior of corrosion factors with temperature. Corrosion is accelerated if the temperature of the medium grows until a certain value.



Figure 2. Influence of temperature between 600 K to 1000 K on corrosion inhibition for time between 0 to 1000 h (a) and 0 to 10 h (b).

3.1.2. The Second Order Polynomial Equation (7)

The second order polynomial Equation (7) in **Figure 2** shows at **Figure 2(a)** and **Figure 2(b)** for different mass loss scales that the mass loss decreases with time and temperature.

The difference in mass loss scales is explained by the important difference in mass loss if time is varied from 10 to 1000 h. This influence of temperature in the corrosion factors in the atmospheric distillation column constitutes the secondary role of temperature on corrosion. These results show that above 673 K the corrosion is inhibited in the atmospheric distillation column.

3.2. Discussion

3.2.1. Influence of Temperature on the Proliferation of Corrosion

In fact, corrosion is caused in the atmospheric distillation column by certain substances present in the crude oil such as naphthenic acids, carbon dioxide and mainly by sulfur compounds. The corrosivity of these substances increases with temperature as shown in **Figure 1** and confirmed by the investigations of some authors in corrosion factors through the atmospheric distillation column. However, the corrosion of naphthenic acids causes significant damage to refinery installations when the temperature is between 493 - 673 K and temperatures lower than these favor low corrosion rates [2].

The corrosion caused by carbon dioxide increases until it reaches a peak at about 343 K [3]. As for sulfur corrosion, it intensifies with increasing temperature from 503 K and reaches a peak at temperatures (698 - 723 K) [4]. The temperature affects the nature of the phases (solid, liquid, gas) which can cause significant corrosion damage. Indeed, a rise in temperature accelerates the electrochemical reactions of corrosion and the transfer of aggressive substances on the surface of metals. This increase also causes a drop in the pH of the water, hence the increase in corrosion [8].

3.2.2. Influence of Temperature on Corrosion Inhibition

The corrosivity of the corrosion factors decreases with temperature above (600 K) as shown in **Figure 2** and investigated by some authors in the corrosion factors through the atmospheric distillation column. The corrosivity of Naphthalene is minimal above 673 K due to its decomposition at high temperatures [5].

Laboratory tests have shown that corrosion increases with an increase in temperature before decreasing considerably beyond a certain temperature value. Iron carbonate FeCO₃ acts as a protective layer in the case of corrosion by carbon dioxide, which reduces corrosion at high temperature [3]. Temperature strongly affects the nature and morphology of corrosion deposits that form on the surface of low alloy steels. Temperatures above 343 K cause the low solubility of the iron carbonate FeCO₃, hence the saturation of the medium with this substance, which constitutes a protective layer on the iron [3]. Beyond (698 - 723 K) the corrosion of sulfur compounds decreases with increasing temperature up to 813 K [4]. For temperatures above 698 K, most of the corrosive sulfur has already reacted with the surface or decomposed and there is formation of a dense coke deposit, which prevents the proliferation of corrosion [4].

The solubility of aggressive gases (H_2S , O_2 , CO_2) decreases with increasing temperature. Therefore, temperature has a complicated effect on corrosion. Above a certain temperature, corrosion increases considerably and then decreases due to the reduction in the solubility of corrosion-causing gases in aqueous solutions. Generally, it is between 333 - 353 K depending on the chemical composition of the liquid phase [9]. In addition, temperature increases the rate of sedimentation and the formation of a protective FeCO₃ layer [4].

Negative mass losses are due to deposits such as iron carbonate $FeCO_3$ and cokes, which form on the surface of metals thus increasing their mass [15].

To remedy this, scientists soak the steel in air after testing, then they put it in a chemical solution thermostated with ultrasound which eliminates the corrosion products formed on the surface by the molten salts and reveals the healthy metal [15].

This study of the influence of the temperature parameter on the corrosion factors in the atmospheric distillation column enabled us to establish **Table 1**. This table is a temperature scale of vulnerability of materials and inhibition of corrosion by certain factors at within the atmospheric distillation column of crude oil.

3.3. Activity Zone of Corrosion Factors in the Atmospheric Distillation Column

Figure 3 shows the distribution of the activity of the corrosion factors as a function of the temperature of the medium. The bright colors show the maximum activity of the corrosion factors in the distillation column, the lighter the color

 Table 1. Temperature scale of vulnerability and inhibition of corrosion by certain corrosion factors in the atmospheric distillation column.

Type of corrosion	Vulnerability temperatures	Corrosion inhibitor temperatures
Naphtaline corrosion	493 - 673 K	>673 K
Sulfur compounds corrosion	503 - 698 K	>425 K
Dioxide carbon corrosion	<343 K	>343 K





becomes, the more the vulnerability decreases. The red color represents corrosion by sulfur compounds; blue represents corrosion by carbon dioxide, orange corrosion by naphthenic acids distributed in the various petroleum cuts of the atmospheric distillation column.

In addition, the time parameter in the evolution of the mass loss would make it possible to evaluate the lifetime of the materials thus undergoing corrosion in the atmospheric distillation system.

4. Conclusion

The overall objective of this study was to define a temperature scale for understanding the corrosion mechanisms in the corrosion control process in the atmospheric distillation column. This work has shown that for the main corrosion factor compounds in the atmospheric distillation column there is a temperature scale of vulnerability and a temperature beyond which, corrosion is inhibited. Therefore, corrosion does not increase exponentially with temperature. The time parameter, which is also linked to the mass loss, could help to predict the lifespan of materials. In perspective in the fight against corrosion in the atmospheric distillation system, these results would permit to redefine certain methods of fighting and inhibiting corrosion based on the temperature parameter in order to reduce the significant cost of corrosion in the refining industry. In addition, it would be interesting to conduct a study in the different units of the atmospheric distillation system in order to choose the appropriate metal according to the operating temperature and the content of the crude products in corrosion factors.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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