The Effect of Different Operating Parameters on the Corrosion Rate of Carbon Steel in Petroleum Fractions

Nagham Salman Hassan
Technical College, Foundation Technic/Baghdad
Email:naghamalmaliky@yahoo.com

ABSTRACT

   The corrosion in petroleum pipelines was investigated by the studying the corrosion of carbon steel in crude oil and refined petroleum products which include gasoline, kerosene, and gas oil. Weight loss method was used in which test specimens of carbon steel, with a known weights, were immersed in the test media for a total exposure time of 60 days. The weight loss was measured at an interval of 10 days and the corrosion rate was determined. The results showed that corrosion rate are highest for gasoline followed by kerosene, gas oil and crude oil, in a decreasing order. The observed pattern in the corrosion behavior is consistent with the density and weight percent of hydrogen in the hydrocarbon products. The corrosion rate increases with decreasing density and increasing weight percent of hydrogen. Experiments were carried out at different temperatures (30, 60, 90 and 120°C) at a constant partial pressure of CO_2 (50psi) in 3.5% NaCl solution. The results indicated that as partial pressure of CO_2 and temperature increase, corrosion rate increases due to due to continuous dissolution of iron ion and formation of weak carbonic acid. The weak carbonic acid dissociates into carbonate and hydrogen ion, which increases the cathodic reaction on the metal surface.The presence of small amount of H_2S (0.4 ppm) increases the corrosion rate significantly.

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تــأثير عوامل مختلفة على معدل التاكل للفولاذ الكربوني في المشتقات النفطية

الخلاصة

التاكـل فـي خطـوط الانابيب النفطيـة تم بحثهـا بواسـطة التاكـل للفولاذ الكربـوني فـي النفط الخـام والمشتقات النفطية والتي تتضمن الكـازولين , النفط الابيض, وزيت الغـاز. تم استعمال طريقة الوزن المفقود في فحص عينات الفولاذ الكربوني مع اوزان معلومة والتي تم غمرها في اوساط الفحص لفترة كلية مقدارها 60 يوم, الوزن المفقود تم قياسة كل عشرة ايام وتم احتساب معدل التاكل. اظهرت النتـائج

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اعلى معدل تاكل يكون للكازولين ومن بعدها النفط الابيض وزيت الغاز والنفط الخام حسب الترتيب تنازليا.النمط الملاحظ في سلوك التاكل يتضمن الكثافة والنسبة الوزنية للهدروجين في المنتجات الهيدركربونية . معدل التاكل يزداد بانخفاض الكثافة وزيادة النسبة الوزنية للهدروجين. في الاجراء العملي عند درجات الحرارة المختلفة (120 ,90 ,60,30) عند ضغط جزئي ل CO_2 (50psi) وتركيز NaCl 3.5%. اظهرت النتائج ان زيادة درجة الحرارة والضغط الجزئي ل CO_2 يؤدي الى زيادة معدل التاكل مع زيادة انحلال ايون الحديد وتشكيل حامض الكربونيك الضعيف. حامض الكربونيك الضعيف لايتاثر بايون الكربون والهيدروجين اللذان يزدادان بفعل التفاعل الكاثودي على سطح المعدن. وجود مادة قليلة من H_2S (0.4 ppm) يزيد من معدل التاكل بشكل واضح.

الكلمات المرشدة: الفولاذ الكربوني, معدل التاكل, النفط الخام, المشتقات النفطية, الهيدركربون, الضغط الجزئي ل CO_2.

INTRODUCTION

Carbon steel, the most widely used engineering material, accounts for approximately 85%, of the annual steel production worldwide. Despite its relatively limited corrosion resistance, carbon steel is used in large tonnages in marine applications, nuclear power and fossil fuel power plants, transportation, chemical processing, petroleum production and refining, pipelines, mining, construction and metal-processing equipment.

The selection of pipe for a particular situation is dependent on what is going through the pipe, the pressure and temperature of the contents. Pipes are fabricated from different material types to suit stringent needs and services desired. The most commonly used material for petroleum pipelines is mild steel because of its strength, ductility, weldability and it is amenable to heat treatment for varying mechanical properties [Abdul Hameed, (2005), Bolton, (1994), Davies, and Oelmann, (1983), Smith, and Hashemi, (2006)]. However, mild steel corrodes easily because all common structural metals form surface oxide films when exposed to pure air but the oxide formed on mild steel is readily broken down, and in the presence of moisture it is not repaired [Badmos, and Ajimotokan, (2009)].

Carbon steels are generally used for the petroleum industry for transportation of crude oils and gasses from offshore to different refining platforms and from their to different destination of the applications. The carbon steel is susceptible to internal corrosion due to CO_2/H_2S environment [van Hunnik, Pots, Hendriksen,(1996) , Dugstad,(1998)] .The comparison of their corrosivity in the severe corrosive environment needs further investigation under the dynamic flow condition. The severity of corrosion depends on various working parameters such as partial pressure of CO_2, temperature, chloride concentration, H_2S level, surface films and oxide contents [Videm, Dugstad,(1996), Crolet, Thevenot, Nes¢ic, (1989)].

The presence of carbon dioxide (CO_2), hydrogen sulphide (H_2S) and free water can cause severe corrosion problems in oil and gas pipelines. Internal corrosion in wells and pipelines is influenced by temperature, CO_2 and H_2S content, water chemistry,

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flow velocity, oil or water wetting and composition and surface condition of the steel. A small change in one of these parameters can change the corrosion rate considerably, due to changes in the properties of the thin layer of corrosion products that accumulates on the steel surface [Das, Khanna, (2003)].

The surface films mainly consist of $FeCO_3$ and their influence on the corrosion rates were observed in CO_2 aqueous solutions [Dugstad, (1998), Nyborg, (1991)]. The formation of iron carbonate is temperature dependent and at higher temperature it forms the protective layers over the metal surface [De Waard, Lotz, Milliams, (1991), Palacios, Shadley, (1991)]. The effect of H_2S on CO_2 saturated solution has been investigated by adding little amount of H_2S (0.4 ppm) in the same working environment. The H_2S level from the surface has been easily skipped off due to the flow effect of liquid and the corrosion rate increases severely [De Waard, Lotz, Milliams, (1991)].

This work examines the corrosion of carbon steel in crude oil and its various refined products which include gas oil, gasoline, and kerosene. The aim of this study is to assess the corrosiveness of the various hydrocarbons to enhance material selection and effective surface treatments of pipelines for apt quality of passivity layers to prevent corrosion.

EXPERIMENTAL SETUP
A) Material and Instrument

The crude oil was obtained from the oil field while the refined products of crude oil, gas oil, gasoline, and kerosene were procured from the filling station and the pH of each medium was measured. Commercial grade carbon steel was used for the tests; Table 1 shows that the composition of carbon steel elements (state company of geological survey and mining). Specimens were machined from carbon steel alloy. Specimens were machined from carbon steel of dimensions 3×2×0.2 cm and 0.2cm diameter with central hole. The set of instrument and devices which have been used for testing are illustrated in Figure (1).

B) Procedure
Chemical corrosion tests (ASTM 4562)

1- For all the experiments, the specimens were machined and grinded and polished sequentially with silicon carbide paper of grades 600 grit then wished in distilled water and brush, and then with acetone or alcohol. Drying of the specimens was carried out using drying paper and specimens driers. They were then put in a dissector or (container) containing a silica gel bed.

2- After taking the initial weight and dimension, carbon steel specimen was immersed in various test media in beakers. Each test coupon was exposed for a total period of 60 days with six weight measurements taken at an interval of 10 days. The weighting is carried out after the specimens are cleaned with distilled

water and brush, and then with acetone or alcohol. Drying of the specimens was carried out using drying paper and specimens driers.

3- Experiments were carried out at four different temperatures (30, 60, 90 and 120°C) at a constant partial pressure of CO_2 (50 psi) in 3.5% NaCl solution. Each experiment was conducted using the same procedures for a total period of 24 hours with four fresh samples and corrosion rates were measured in millimeter per year (mpy).

4- The work was repeated in step (2) with different temperatures (30, 60, 90 and 120°C) by adding little amount of H_2S (0.4 ppm) after completion of the immersion test, the specimens were taking out. For preparing, cleaning from any localized attack.

This expression is readily calculated from the weight loss of the metal specimen during the corrosion test by the equation given below [Fontana, (1987), Avwiri, (2004)].

$$\text{Corrosion Rate (mpy)} = 534\ W/DAt \ \ldots\ldots\ldots\ldots\ (1)$$

Where:
W: weight loss (mg)
D: density of coupon material (g/cm^3)
A: area (inch^2), t: time of exposure (h)

Table(1)Composition of Carbon Steel Elements.

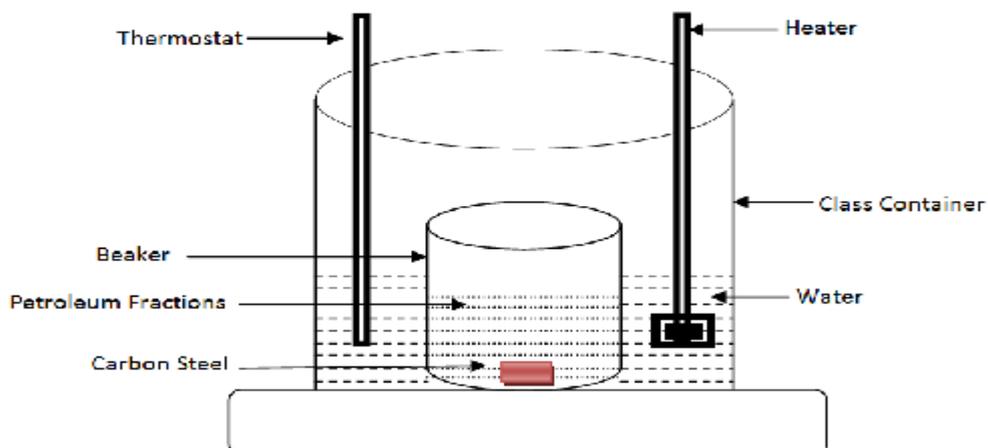| Steel	%Composition of Elements									
	C	Si	Mn	P	S	Ti	Ni	Mo	Cu	Fe
Carbone Steel	0.12	1.21	1.29	0.01	0.022	0.069	0.37	-	0.061	96.8 27

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Figure (1) The set of devices using for corrosion resistance test.

RESULTS AND DISCUSSION

The chemical composition, density and pH values of the crude oil and their fractions are shown in Table (2) (Daura refinery). Generally, the density appears to increase with decreasing weight percent of hydrogen content of the media. The densities of crude oil and kerosene are respectively 886 and 794 kg/m^3 while their weight percent hydrogen contents are 12.1 and 13.6 respectively. Corrosion rate is observed to decrease with decreasing weight percent of hydrogen content in the hydrocarbon media.

Uniform corrosion was observed in all the test coupons immersed in the media and the results of the corrosion rate measurements are as shown in Table 3. The corresponding plots of corrosion rate as a function of exposure time are shown in Figure 2. Corrosion rate appear have maximum value in gasoline and other media are in the following decreasing order, kerosene, gas oil and Crude oil. The observed pattern in the corrosion behavior is consistent with the density and weight percent of hydrogen in the hydrocarbon products. The corrosion rate increases with decreasing density and increasing weight percent of hydrogen.

**Table (2) Elemental compositions, densities and
pH values of Test Media.**

Elemental Composition	gasoline (wt.%)	kerosene (wt.%)	Gas oil (wt.%)	Crude oil (wt.%)
Carbon c	85	86.3	85.5	83.2
Hydrogen H	14.1	13.6	12.5	12.1
Sulfur S	0.15	0.1	1.2	3.9
Density (kg/m3)	748	794	845	886
pH value	6.6	7	6.3	6.5

The corresponding plots of corrosion rate as a function of temperature are shown in Figures (3 and 4). At low temperature, corrosion rate of samples slowly increases due to continuous dissolution of Fe^{2+}ion in the solution as a result of formation of porous $FeCO_3$, which is not protective in nature, however as the temperature increases from 30 to 60^oC, the $FeCO_3$ film becomes less porous, more adherent to the metal surface and protective in nature and hence the corrosion rate decreases. Beyond 60^oC, the corrosion rate increases and it is higher at $90\ ^0C$ due to accumulation of more porous inner $FeCO_3$ film on the metal surface which initiates formation of cracks and finally spallation of $FeCO_3$ film [Palacios, Shadley, (1991)].The corrosion rates of all the various media are higher at 90^oC. Further increase in temperature the corrosion rate decreases significantly due to the formation of denser, adherent and homogeneous layer of iron carbonate, which is, protects the metal to further corrosion [De Waard, Lotz, Milliams, (1991),and DeWaard, Lotz, (1994)]. As the partial pressure of CO_2 in the solution increases the formation of weak carbonic acid (H_2CO_3) favors, which increases the corrosion rate. But at higher temperature the bicarbonate ions (HCO_3^{-}) formed on the surface gives more carbonate ions (CO_3^{2-}) results in formation of more insoluble iron carbonate which increases the solution pH and corrosion rate decreases significantly as shown in Figures 3 and 4 at 120^oC. In many literatures, it has been reported that $FeCO_3$precipitation is temperature dependent and for its precipitation super saturation with the Fe^{2+} ion is required which is 5-10 times higher than the thermodynamically calculated values of solubility [De Waard, Milliams,(1975),Das, Khanna,(2004)].

The surface morphology of carbon steel in kerosene and gas oil as shown in Figure 5 indicates cracking and spallation of $FeCO_3$ film at 90^oC. However, at 120^oC, the $FeCO_3$ film is showing protective nature and good adherence on the metal surface as shown in Figure 6 Similarly carbon steel in crude oil and gasoline at 90^oC indicate crack formation and less adherence of the protective film with the base metal and thus corrosion rates are higher, but at higher temperature the oxide layer is more protective

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in nature and adheres on the metal surface, which restricts access of H_2O to the surface. Since water reduction is the only cathodic reaction in the deaerated neutral solution therefore, the corrosion rate depends on how rapidly H2O diffuses to the metal surface through the barrier of oxide film and on diffusion of Fe2+ out through the film. Thus any change in temperature, bulk concentration and disturbance of the oxide film will affect the reaction rate [Ismaeel Andijani and Turgoose, (1999)]. The corrosion rate can be reduced substantially under conditions where iron carbonate ($FeCO_3$) can precipitate on the steel surface and form a dense and protective corrosion product film. This occurs more easily at high temperature or high pH in the water phase. When H_2S is present in addition to CO_2, iron sulphide (FeS) films are formed rather than $FeCO_3$, and protective films can be formed at lower temperature, since FeS precipitates much easier than $FeCO_3$ [Das, Khanna,(2004)].

CONCLUSIONS
1. Corrosion rate is highest in gasoline, and it follows decreasing order for the other media, kerosene, gas oil, and Crude oil.

2. Corrosion rate is observed to decrease with decreasing weight percent of hydrogen content in the hydrocarbon media.

3. The temperature increases the solubility of iron carbonate in the solution resulting in the precipitation of $FeCO_3$ on the surface and forms the protective layer.

4. Higher temperature the bicarbonate ions (HCO^{3-}) formed on the surface gives more carbonate ions (CO_3^{2-}) results in formation of more insoluble iron carbonate which increases the solution pH and corrosion rate decreases.

REFERENCES
[1]. Abdul Hameed A., "Evaluation of Quality of Steels Produced Locally" B. Eng. Thesis, Department of Mechanical Engineering, University of Ilorin, Ilorin, Nigeria (2005).

[2]. Bolton, W. "Engineering Materials Technology", 2nd Ed, B. H Newnes Ltd., Oxford, London, England (1994).

[3]. Davies, D. J. and Oelmann, L. A. "The Structure, Properties and Heat Treatment of Metals", First Ed., Pitman Publishing New Zealand Ltd, Wellington, England (1983).

[4]. Smith, W.F. and Hashemi, J. "Foundations of Material Science and Engineering", Fourth Edition, McGraw-Hill, New York (2006).

[5]. Badmos, A.Y. and Ajimotokan, H.A. "The Corrosion of Mild Steel in Orange Juice Environment", Technical Report No: 2009-02, Department of Mechanical Engineering, University of Ilorin, Nigeria, 8pgs (2009).

[6]. van Hunnik, E.W.J. B.F.M. Pots, E.L.J.A. Hendriksen, "The Formation of Protective $FeCO_3$ Corrosion Product Layers in CO_2 Corrosion," CORROSION/96, paper no. 6 (Houston, TX: NACE, 1996).

[7]. Dugstad, "Mechanism of Protective Film Formation During CO_2 Corrosion of Carbon Steel," CORROSION/98, paper No. 31 (Houston, TX: NACE International, 1998).

[8]. Crolet, J.-L. N. Thevenot, S. Nes¢ic, "Role of Conductive Corrosion Products on the Protectiveness of Corrosion Layers," CORROSION/ 96, paper No. 4 (Houston, TX: NACE, 1996).

[9]. Videm, K. A. Dugstad, Corrosion of Carbon Steel in an Aqueous Carbon Dioxide Environment. Part 2. Film formation, Mats. Perf. Vol.28, No. 46–50, (1989).

[10]. Das, G.S. A.S. Khanna, Corrosion Mechanism of Pipeline Steel in CO_2/H_2S Environment, NMD (2003).

[11]. Nyborg, R. "Initiation and Growth of Mesa Corrosion Attack During CO_2 Corrosion of Carbon Steel," CORROSION/98, paper No. 48 (Houston, TX: NACE, 1998).

[12]. De Waard, C. U. Lotz, D.E. Milliams, Predictive Model for CO_2 Corrosion Engineering in Wet Natural Gas Pipelines, Corrosion Vol.47, No. 976–985, (1991).

[13]. Palacios, C.A. J. R. Shadley, Characteristics of Corrosion Scales on Steel in a CO_2 Saturated NaCl brine, Corrosion Vol.47, No.122–127, (1991).

[14]. Fontana, M.G. "Corrosion Engineering", Third Edition, McGraw-Hill International Edition, New York (1987).

[15]. DeWaard, C. U. Lotz, Prediction of CO_2 Corrosion of Carbon Steel, in: Prediction of CO_2 Corrosion in the Oil and Gas Industry, Institute of Materials Publisher, UK, pp. 30–49, (1994).

[16]. Avwiri, G.O. "Corrosion Resistance of Copper and Brass in Various Media", Journal of Corrosion Science and Technology, Vol. 1 No. 1, 58-60 (2004).

[17]. De Waard, C. D. E. Milliams, Carbonic Acid Corrosion of Steel, Corrosion Vol. 31, No.177–181, (1975).

[18]. Ismaeel Andijani and S. Turgoose "Studies on Corrosion of Carbon Steel in Deaerated Saline Solutions in Presence of Scale Inhibitor[1] " WSTA IV Gulf Conference, Bahrain, 13-18 February, (1999).

[19]. Das, G.S. A.S. Khanna, Corrosion Behavior of Pipeline Steel in CO_2 Environment CRSMS 03 /Transaction IIM June (2004).

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Table (3) Corrosion rate of carbon steel in the test media.

Exposure Time *(Days)*	gasoline *(mpy)*	kerosene *(mpy)*	Gas oil *(mpy)*	Crude oil *(mpy)*
10	2.51	1.24	0.633	0.743
20	2.20	1.24	0.693	0.763
30	2.33	1.24	0.824	0.888
40	2.40	1.45	0.977	0.761
50	2.45	1.40	1	0.842
60	2.50	1.5	1.09	0.760

**Table (4) Corrosion rate of carbon steel in the test media exposed for 24 h in
3.5% NaCl at constant partial pressure of CO_2/H_2S (50Psi).**

Temperature (^{o}C)	gasoline *(mpy)*	kerosene *(mpy)*	Gas oil *(mpy)*	Crude oil *(mpy)*
30	5.51	3.45	2.21	1.52
60	8.32	5.86	4.20	3.76
90	11.28	9.02	7.23	6.04
120	5.78	3.87	2.67	1.98

**Table (5) Corrosion rate of carbon Steel in the test media exposed for 24 h in
3.5% NaCl at constant partial pressure of CO_2/H_2S (50Psi).**

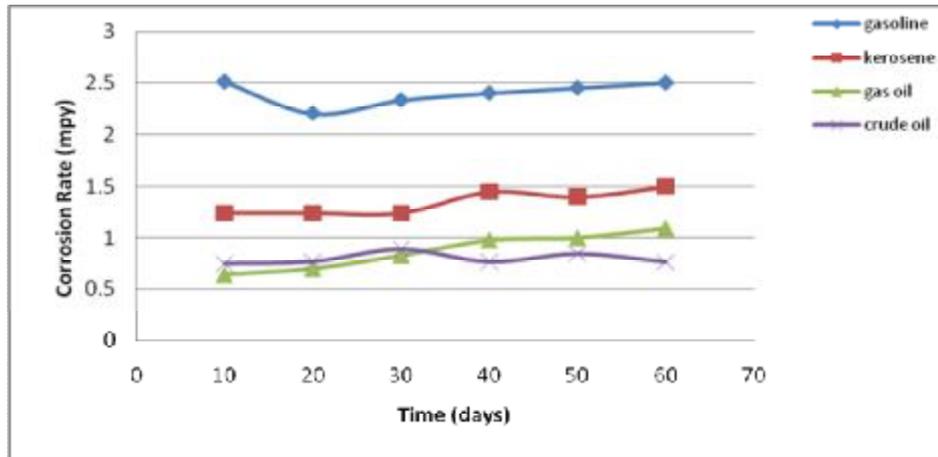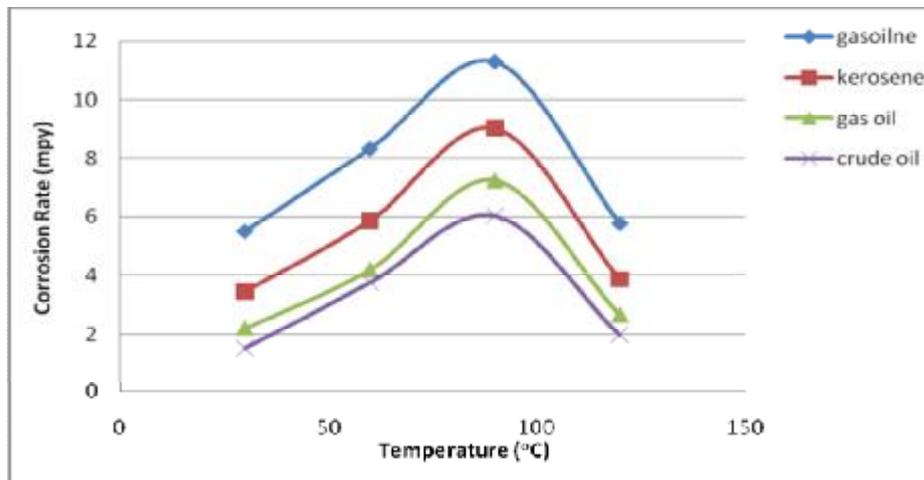| Temperature (^{o}C)	gasoline *(mpy)*	kerosene *(mpy)*	Gas oil *(mpy)*	Crude oil *(mpy)*
30	7.73	6.48	6.01	4.62
60	9.63	8.96	7.02	7.56
90	15.42	15.21	12.87	9.55
120	7.66	2.78	4.88	2.89

Figure (2) Variation of Corrosion Rate Vs Time for different Media.

Figure (3) Corrosion rate of carbon steel in the test media exposed
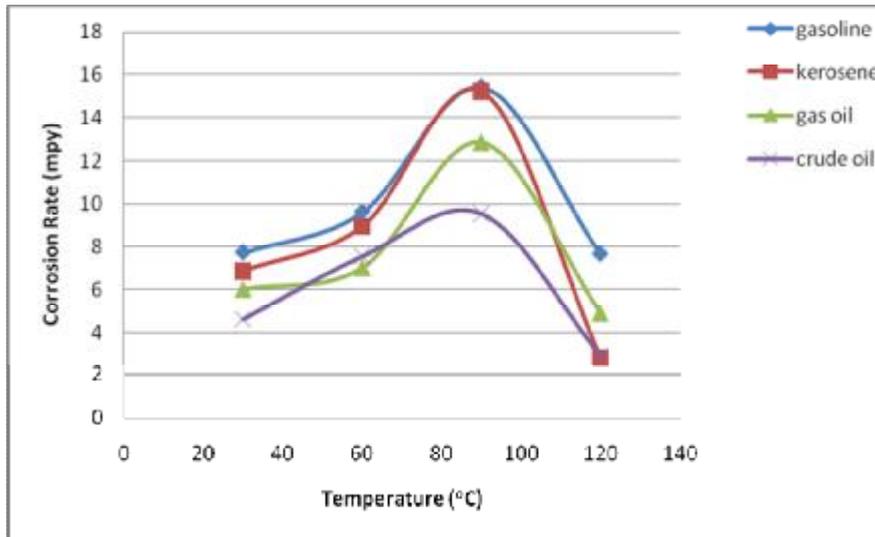**for 24 h in 3.5% NaCl at constant partial pressure of CO_2 (50Psi) .**

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Figure (4) Corrosion rate of carbon steel in the test media exposed for 24 h in 3.5% NaCl at constant partial pressure of CO_2//H_2S (50Psi) .
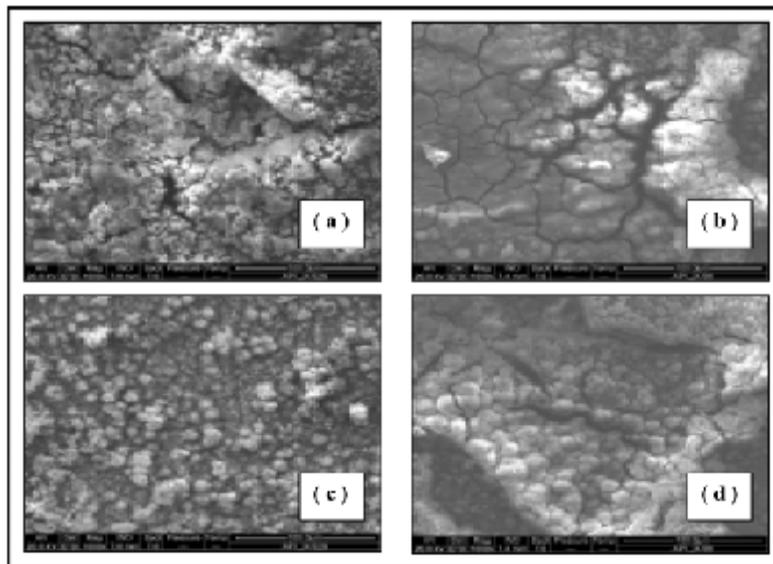

Figure (5) ESEM micrographs showing surface morphology of carbon steel in (a) kerosene (b) gas oil exposed at 90^oC and (c) kerosene and (d) gas oil exposed at 120^oC.
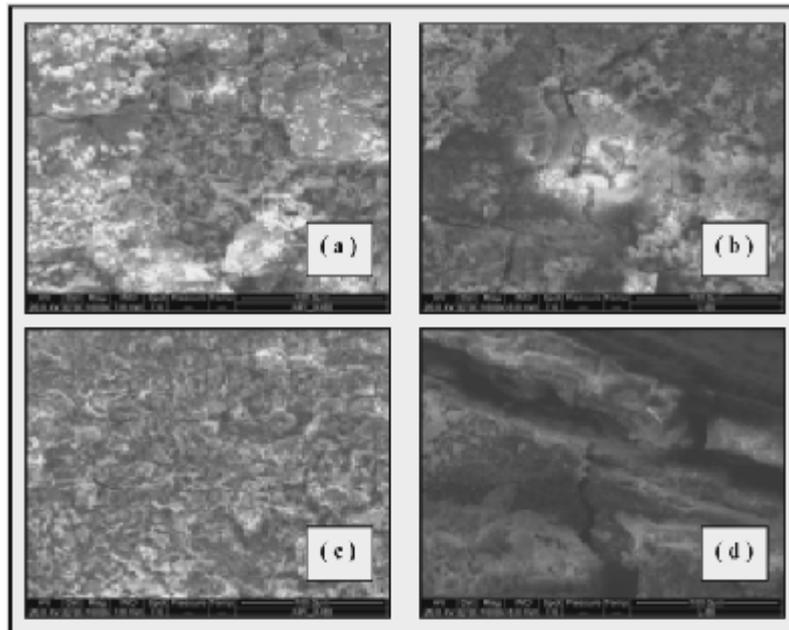
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Figure (6) ESEM micrographs showing surface morphology of carbon steel in (a) crude oil (b) gasoline exposed at 90°C and (c) crude oil and (d) gasoline exposed at 120°C.