CORROSION PROPERTIES OF TEMPERED MEDIUM CARBON STEEL IN 1.0 M HCl AND HOMEMADE VINEGAR

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ABSTRACT. The consumable palm wine has never been used in heat treatment process of steels. This research therefore focuses on the utilization of the consumable palm wine and other palm tree products as quenchants. The mechanical and physical properties of the samples were also evaluated to determine which of the quenchants that influences the hardness and corrosion rate values of medium carbon steel the most. The corrosion test was performed in 1.0 M of HCl solution and homemade vinegar using potentiodynamic polarization method. The results revealed a hardness value of 431, 351, 359 and 265 HB for the samples quenched in palm wine, palm kernel oil, palm oil and as-received, respectively. The corrosion rates of palm oil tempered samples showed more susceptibity to corrosion in HCl solution with a value of $2.261e^{+003}$ mil/year. Vinegar offers the highest corrosion rate with a value of $4.017e^{+002}$ mil/year for palm wine tempered. The corrosion rate of the as-received samples pulled the lowest values while on the treated samples, palm kernel oil showed the least corrosion rate values.

KEY WORDS: Consumable palm wine, Palm oil, Hardness, Corrosion rate, Austenitization, Quenching

INTRODUCTION

The need for higher requirements for the corrosion resistance of engineering materials has prompted numerous research in petroleum, transportation, chemical, pharmaceutical, clean energy and other industries to proffer solution to this challenge, since it is becoming near impossible to find an environment which is non-corrosive [1]. Corrosion is an electrochemical process that returns metals to their stable natural states via interactions with some belligerent environments [2–5]. A common practice to obtain high strength performance levels in steel that could be able to withstand harsh environment is to select a good composition, mechanical processing techniques and heat treatment methods [6]. Heat treatment is a sequence of heating and cooling operation, timed and applied to a metal or alloy in the solid state in a way that will produce the desired properties, which means, it is an operation or combination of operations of heating and cooling of a solid or an alloy metal aimed to endow it with specific predetermined physical and mechanical properties of valuable importance [7]. Conventional quenching and tempering heat treatments have long been used on steels to produce good combinations of strength and toughness from the martensitic structure [8]. This is because tempering of as-quenched martensitic steel is known to cause secondary hardening if the softening effect caused by annealing is offset by the precipitation of alloy carbides in the material. The precipitation and coarsening of secondary phases during heat treatment processes comprising austenitizing, quenching and tempering, are a key point towards obtaining the desirable microstructure [9–11].

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So far, there are no heat treatment where consumable palm wine was used as a quenchant, nor are there any corrosion research that used vinegar as the corrosion environment. This is solely because vinegars are mostly used for cleaning of metal surfaces due to its pickling capability. Studying the corrosion resistance of metals in mild acids (e.g. vinegar) as well as its open circuit potential will be very insightful to beam the search light into what happens in the interaction between the vinegar solution and the metal surface and to see if medium carbon steel commands excellent corrosion resistance in vinegar.

EXPERIMENTAL

10 mm × 10 mm × 0.5 mm rolled sheet of medium carbon steel was used in this work. The steel specimens were secured from Finke Steel Inc. (Sorel, QC, Canada). Compositional analysis of the medium carbon steel was conducted using Spark Optical Emission Spectrometer model ARL Quanta Desk rating 350 VA. The result of this analysis is presented in Table 1 as earlier reported in a related study [12]. About 23 samples were cut from the medium carbon steel with hand sharer and washed in methylated spirit to remove dirt. 5 out of the samples were reserved for the as-received condition. For the heat treatment, a steel pipe was cut opened, labeled and used as holders were 6 out of remaining 18 samples were placed in 3 of each of the half steel pipes to enable easy removal due to the smallness of samples. Thereafter, they were placed into a Muffle furnace model number LABC1210 for heat treatment at a temperature of 950 ºC to obtain austenite phase and later held for 45 min at that upper critical temperature to allow the samples have enough time for proper homogenization. They were later quenched respectively in 200 mL of palm wine, palm kernel oil, and palm oil as were measured with beaker and poured into three stainless steel cups. The furnace was then switched off and allowed to cool within 24 h to room temperature, the next day the quenched samples were placed back into the furnace for tempering heat treatment. The tempering was carried out at a temperature of 400 ºC and soaked for 1:30 h followed by air cooling under steady room temperature of 27 ºC. A Leeb hardness testing machine model PRLH210 produced by Inspection Technology Co., Ltd was used to measure the hardness of the samples after heat treatment and quenching, and after subsequent tempering respectively in HB.

A homemade vinegar was prepared using orange peels of mass 150 g, 201 g of granulated sugar and half a litre of water. The 0.5 L of water was first poured into a 1000 mL conical flask. The orange peels were stuffed into the flask close to the brim followed by pouring of the sugar into the flask and shaking it, to ensure that the sugar granules were well diluted. The lid of the conical flask was covered with clean white towel and tied with rubber bonds. The mixture was kept in a room and allowed to ferment for 30 days, sieved and the filtrate used for the experiments.

The heat-treated samples were polished with SiC abrasion papers of about 600 grits, and washed with methylated spirit to remove dirt and dried before corrosion test was performed with the aid of electrochemical analyser model CH1604E. Potentiodynamic polarization test was done to evaluate the corrosion behaviour of the steel specimens in the as-received, and tempered forms. This test was done according to ASTM G8-96 standard. Potentiodynamic polarization test was performed using a 3-electrode cell, in which a saturated calomel electrode (SCE) was used as a reference electrode, a graphite electrode served as a counter electrode and the steel sample was the working electrode [12]. The 1.0 M of HCl acid and the homemade vinegar were the electrolytes where the working electrode was immersed. Each corrosion test was performed in 200 mL of simulated 1.0 M of HCl and homemade vinegar at room temperature. Potentiodynamic polarization test was carried out at an applied potential range of -1.5 V (vs. SCE) to +1.5 V (vs. SCE) at a scanning rate of 0.01 V/s. The corrosion parameters such as corrosion rate and Tafel plots were obtained from the computer controlled potentiostat. Prior to each corrosion test, the working electrode was allowed to stabilize in the solution before the corrosion test was done. The open circuit potential (OCP) which is a passive experiment was done to find the equilibrium or resting potential of the system and the corrosion behavior of materials [13]. The polished sample

was placed in the cell and the graphite electrode was disconnected so as to switch on the potentiostat from current mode to voltage mode using only two of the electrodes, the working electrode and SCE. The two electrodes were engaged to monitor the OCP, while it was observed that the OCP changed with time [14].

Table 1. Chemical composition of the medium carbon steel [12].

Element	Percentage weight
Carbon (C)	0.47%
Iron (Fe)	98%
Manganese (Mn)	0.5–0.8%
Phosphorous (P)	0.03%
Sulfur (S)	0.03%
Silicon (Si)	0.17–0.37%
Chromium (Cr)	$\leq 0.25\%$

Table 2. Phytochemical constituents of palm wine [15].

Phytochemicals	Result
Alkaloids	-
Saponins	-
Tannins	-
Cardiac glycosides	+

Absent -, present +.

Corrosion test calculation

The corrosion test was carried out on the samples using the potentiodynamic polarization method which makes use of electrochemical analyzer to read off the corrosion current (i_{corr}) and potential and which the necessary information needed to determine the rate of corrosion of the material. However, the corrosion rate is based on the kinetics of both anodic and cathodic reactions which according to Faraday's law, follows a linear relationship as given below:

$$R_m = \frac{M i_{corr}}{nF\rho} \tag{1}$$

where R_m is rate of corrosion, i_{corr} is corrosion current, M is the atomic weight of the metal, ρ is the density, n is the number of charges, which indicates the number of electrons exchanged during the dissolution reaction, and F is Faraday's constant (96.485 C/mol). The ratio M/n is also sometimes referred to as equivalent weight [12].

RESULTS AND DISCUSSION

Tempered medium carbon steel is mostly less hard, brittle and much more ductile than those of the as-quenched medium carbon steel. This is because the precipitation of ε-iron carbide in the initial stage of the tempering will contribute to the hardening of the steel, while the depletion of the carbon from the metal matrix will contribute to the softening of the steel. At the finally stage of tempering heat treatment, a mixed solution of ε-iron carbides and low-carbon martensite would further soften the metal, while also at the same time will lead to the precipitation of cementite which contributes to the hardening effect on the metal, until when (α + C) structure are obtained, then this will further results to more softening of the metal from the growth of cementite particles [6].

Figure 1 describes the results of the evaluation of the samples as revealed by the various quenchants from palm produce in their as quenched and tempered conditions affected the hardness of the material. The quenching increased the hardness from the as-received, palm kernel oil, palm wine and palm oil in that order as shown on Figure 1. The results revealed a hardness value of 265, 351, 359 and 431 HB for the as-received, palm kernel oil, palm wine and palm oil respectively, while those of palm oil tempered, palm wine tempered and palm kernel oil tempered were found to be 292, 377, and 405 HB, respectively. It was further discovered that the novel palm wine quenchant provided the best hardness and quenching medium in the as-quenched state, while the palm kernel oil sample that was quenched and tempered produced a better hardening effect on the test sample after tempering. Tempering was able to reduce the hardness of samples quenched in palm wine and palm oil remarkably, Figure 1. By implication, it is believed that the tempering has improved the ductility of the samples impressively.
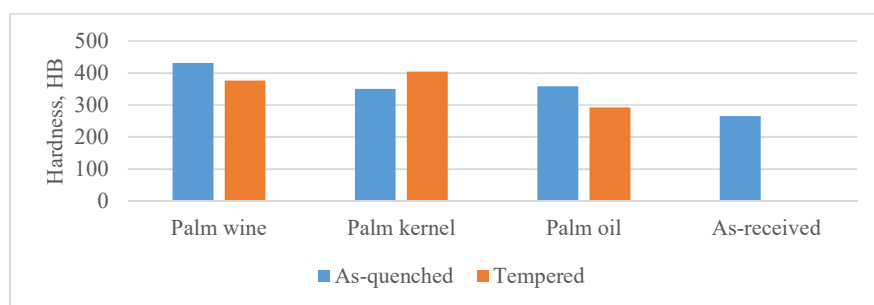

Figure 1. Comparison of hardness values in as-quenched and tempered conditions.

Table 3. Corrosion rate values and other Tafel polarization parameters from the as-received and tempered samples in 1 M of HCl.

Samples	E_{corr}/V	I_{corr}/A	b_c (V)	b_a (V)	CR (mil/year)
As-received	-0.40	0.025	4.000	3.250	$1.617e^{+003}$
Palm wine	-0.25	0.039	3.300	6.379	$1.753e^{+003}$
Palm oil	-0.30	0.031	3.450	3.403	$2.261e^{+003}$
Palm kernel	-0.35	0.050	3.750	4.587	$1.445e^{+003}$

Table 4. Corrosion rate values and other Tafel polarization parameters from the as-received and tempered samples in vinegar.

Samples	E_{corr}/V	I_{corr}/A	b_c (V)	b_a (V)	CR (mil/year)
As-received	-0.30	0.006	25.316	40.00	$1.859e^{+002}$
Palm wine	-0.15	0.001	3.650	3.800	$4.017e^{+002}$
Palm oil	-0.15	0.003	3.800	3.850	$3.136e^{+002}$
Palm kernel	-0.20	0.003	3.900	10.050	$3.264e^{+002}$

The electrochemical corrosion parameters extracted by extrapolating the Tafel polarization curves, which includes the cathodic reduction current density (E_{corr}), anodic inhibition current density (I_{corr}), cathodic, and anodic Tafel slopes (b_c, b_a) in the solution respectively as seen on Table 3 and 4. From this two tables, the corrosion rate values of $1.445e^{+003}$ mil/year was as obtained from palm kernel oil tempered in the 1.0 M of HCl, while $1.731e^{+003}$ mil/year as obtained from palm oil tempered shows more tendency for higher corrosion rate. The corrosion rate values of the as-received is moderately fair in 1.0 M of HCl. All the samples did very in 1.0 M of HCl in their different tempered conditions irrespective of what media they will quenched with.

The homemade vinegar proved a corrosion rate of $1.384e^{+002}$, $1.417e^{+002}$, $2.106e^{+002}$, and $2.306e^{+002}$ mil/year for the as-received, palm kernel tempered, palm wine tempered and palm wine respectively in their inhibited conditions. Vinegar offers the highest corrosion rate values. The corrosion rate of the as-received samples in vinegar pulled the lowest corrosion rate value. In general vinegar offers the highest corrosion rate values showing increase in corrosion attack.

In both Tables 3 and 4, the results obtained shows the corrosion current increased in all the samples, while the corrosion potentials were all negative values. The observed trend reveals that the cathodic Tafel slope values a bit lower in all the samples irrespective of the corrosion environment.
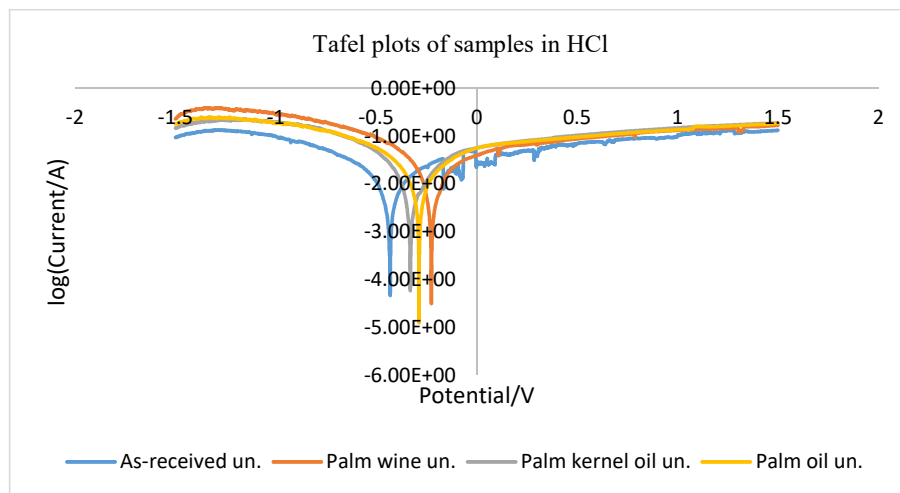

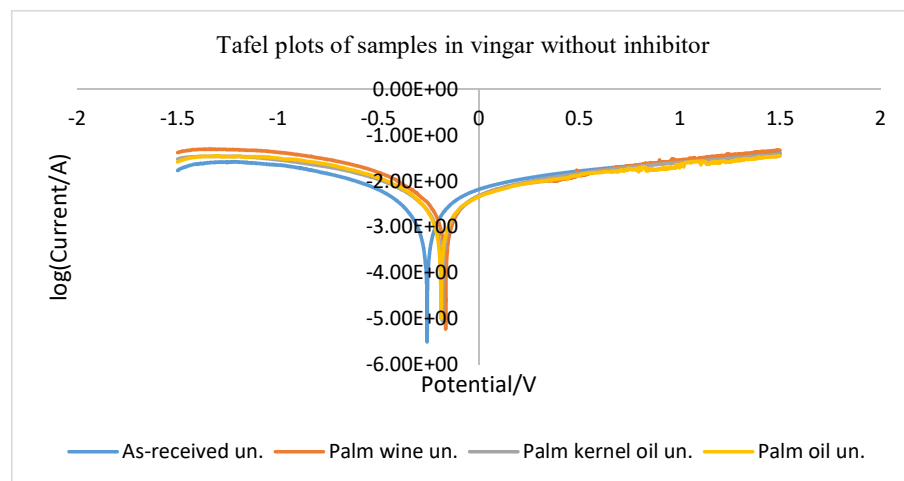Figure 2. The representative Tafel polarization plots of samples in 1 M of HCl.

Figure 3. The representative Tafel polarization plots of samples in homemade vinegar.

Figures 2 and 3 showcases the comparative results between the Tafel plots of the tempered samples in 1 M of HCl and those of homemade vinegar media. Figure 3 as graphically represented on the Tafel diagram of the homemade vinegar replicated the opposite behaviours as recorded on the Figure 2 Tafel plot. This suggests that the corrosion media reacted differently on samples in the respective solutions.
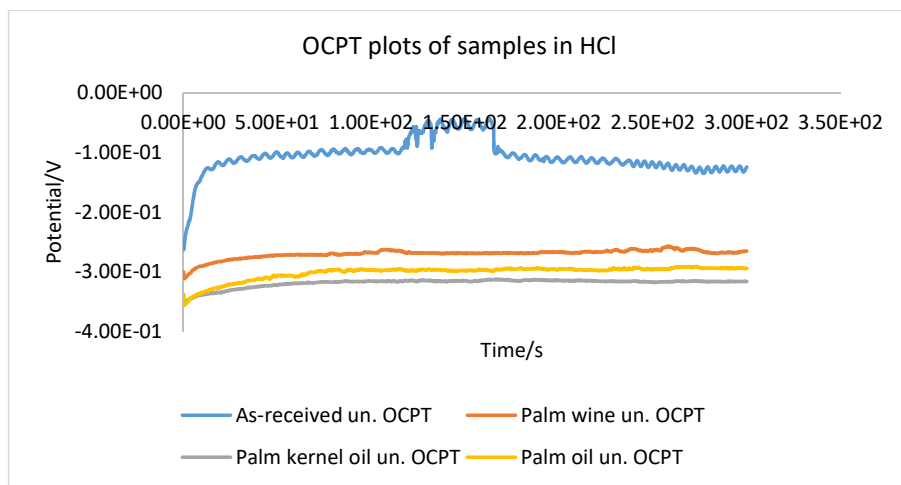

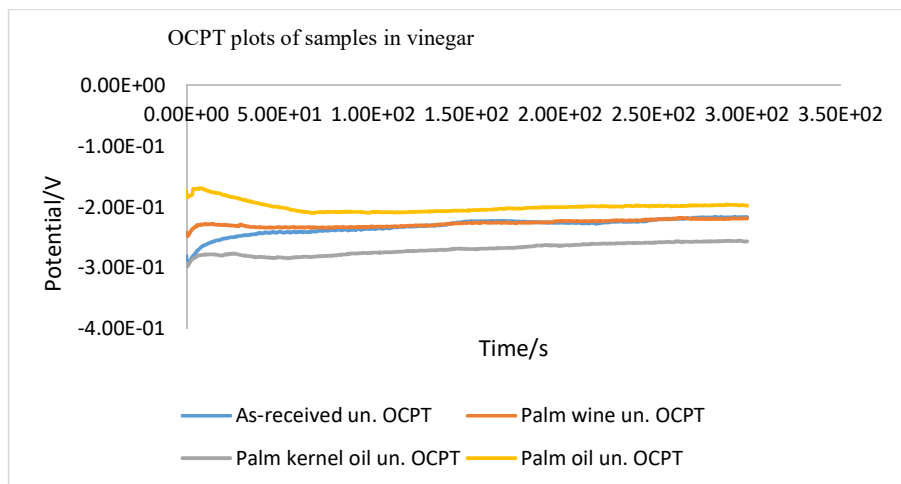Figure 4. OCPT plots of samples in 1.0 M of HCl

Figure 5. OCPT plots of samples in homemade vinegar with inhibitor.

Open circuit potential (OCP) is a passive experiment that represents the measured voltage when no current is flowing in the cell. Recording this potential over time can supply important information about the condition of the metal surface and the changes that can occur on it [16]. Figure 4 to 5 shows the OCP variation with time as measured to determine the voltage difference

between the samples immersed in 1.0 M of HCl and vinegar, and the reference electrode (mainly, the standard calomel electrode). Measurement of OCP changes over time is very important to assess the influence of depolarizers on corrosion reactions in the system. The plots of current potential against time are used to detect the initiation or an accelerated attack of the electrolytes on the samples [17, 18]. An increase in OCP means cathode depolarization   and increased corrosion, a decrease in potential is an indication of reduced corrosion [16]. In general, lower corrosion potential was recorded on OCPTs of all the samples as observed on Figure 4 to 5 irrespective of the corrosion environments. In all cases, the OCP value varies over time to less negative potentials. The maximum recorded OCP potential in 1.0 M of HCl medium was seen on the as-received sample with approximate value of $-1.10e^{-01}$ V, while the maximum OCP in the vinegar solution was observed on the palm wine tempered sample with approximate value of $-1.97e^{-01}$ V.
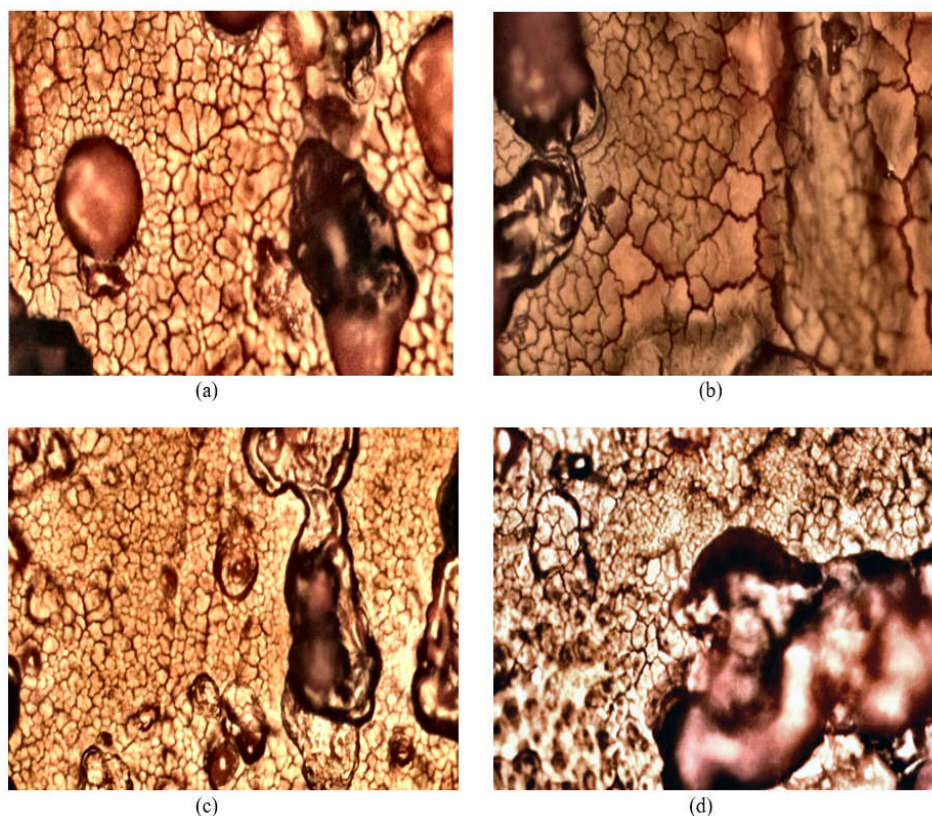

Figure 6. Optical micrographs of samples, (a) for as-received, (b) palm kernel quench solution, (c) palm oil quench solution, and (d) palm wine quench solution.

Preparation of coupons for optical metallography

Coupons were prepared and analyzed at the Materials and Metallurgy laboratory, Federal University of Technology, Owerri, Imo state, Nigeria. The instrument used for the investigation of the microstructures of the coupons was Keyence Digital Microscope, model VH-Z450 with

high magnification lens. A sample from the as-received was mounted and ground with different grades of emery paper sizes in the order of 220, 400, and 600-grits under running water till a smooth surface was obtained, and thereafter, they were polished with cloth covered with a solution of silicon carbide until a mirror-like smooth surface was obtained. Finally, etching was done with 2% nitric acid and after which the surfaces were immediately observed with the metallurgical microscope.

The micrographs in Figure 6 clearly shows that the grain size of the sample quenched in palm wine has the smallest size, followed by the sample quenched in palm oil, and the sample quenched in palm kernel, and finally the sample from the as-received in that incremental order.

CONCLUSIONS

Looking at previous published literatures, it can be concluded that most of these studies have focused mainly on acidic environments. Therefore, it is important to note that mild acids like vinegar has received almost no consideration as corrosion medium, and neither has consumable palm wine been used as a quenchant. Also, fewer studies have been carried out on using all aspects of palm produce to test their quenching capabilities on the hardness of medium carbon steel. The results revealed a hardness value of 265, 351, 359 and 431 HB for the as-received, palm kernel oil, palm wine and palm oil respectively, while those of palm oil tempered, palm wine tempered and palm kernel oil tempered were found to be 292, 377, and 405 HB, respectively. It was further discovered that the novel palm wine quenchant provided the best hardness and quenching medium in the as-quenched state, while the palm kernel oil sample that was quenched and tempered produced a better hardening effect on the test sample after tempering.

Finally, it was determined on the average, that the corrosion rate of palm oil tempered samples showed more susceptibility to corrosion in HCl solutions having values of $2.261e^{+003}$ mil/year. Vinegar offers the highest corrosion rate value of $4.017e^{+002}$ mil/year for palm wine tempered. The corrosion rate of the as-received samples pulled the lowest values while on the treated samples, palm kernel oil showed the least corrosion rate values and is therefore recommended as the best palm tree produce for heat treatment of medium carbon steel. It is believed that the results obtained will be of industrial relevance in the processing and applications of medium carbon steel.

ACKNOWLEDGEMENTS

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