Efficiency of Steel Corrosion Inhibitors in an Environment of Ethanol–Gasoline Blends

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ABSTRACT: Ethanol produced from renewable sources (i.e., bioethanol) is a first-generation biofuel that is currently being added as a biocomponent into gasolines. Mixtures of ethanol and gasoline are designated as ethanol–gasoline blends (EGBs). Ethanol has high polarity and moisture affinity, which considerably influence the properties of the resulting EGBs including their aggressiveness to many metallic and nonmetallic materials. The corrosion aggressiveness of EGBs can be minimized by suitable corrosion inhibitors. In this study, we tested three different corrosion inhibitors on mild steel in the environment of aggressive E10, E25, E60, and E85 fuels. The inhibitors tested were diethylene triamine (DETA) and two mixed inhibitors containing propargyl alcohol, dibenzyl sulfoxide, and octadecyl amine. To study the efficiency of the corrosion inhibitors, we used static and dynamic corrosion tests and electrochemical measurements including impedance spectroscopy and potentiodynamic polarization. The highest corrosion aggressiveness on mild steel was observed for the E60 fuel. The highest inhibitory efficiency was, for all the fuels tested, observed for the DETA inhibitor. For the DETA concentration of 100 mg·L⁻¹, the inhibitory efficiency in the E60 fuel was determined to be around 98%.

1. INTRODUCTION

Modern society is significantly dependent on energy from fossil fuels, which are limited and exhaustible. Thus, the threat of energy shortage is becoming more serious considering the ever-increasing energy consumption of mankind. This and other (especially environmental) factors lead toward renewable and more environmentally friendly alternative energy sources, especially in mobile transportation.

There are a number of potentially available biofuels. Among them, bioethanol produced by biomass fermentation seems to be the most attractive substitute of fossil gasolines. In 1970, Brazil introduced the first large bioethanol program called ProAlcool with a vision to replace part of the gasoline production, and the main sources are wheat and sugar beet. The European Union accounts for about 3% of the worldwide bioethanol production, and the main sources are wheat and sugar beet. The majority of bioethanol is used in Brazil. About 20% of cars in Brazil use pure bioethanol (E100) and the rest burn E22 or E85 fuels.

In the European Union, the bioethanol content in conventional fuels is limited by legislation that sets the oxygen content to 2.7 wt % and the bioethanol content to 5 vol %; an increase in the bioethanol content to 10 vol % is being considered. In the Czech Republic, an obligatory blending of conventional gasolines with 4.1 vol % of ethanol has been set by legislation since June 2010. Fuels with an ethanol content of up to 5 vol % have to meet the requirements of the ČSN EN 228 standard and fuels with higher ethanol contents (E85) have to meet the requirements of the ČSN P CEN/TS 15293 standard.

Ethanol intended to be used as a gasoline component must be pure, without haze, anhydrous (absolute), and denatured. The ethanol content before and after the denaturation must be higher than 99.7 and 95.6 vol %, respectively.

The blending of gasolines with bioethanol is related to several different problems that are caused by the different chemical nature of bioethanol and hydrocarbon-based gasolines. Besides some other problems, material compatibility of metallic or nonmetallic construction materials with ethanol can be very problematic, especially for fuels with higher ethanol contents. Conversely, fuels containing less than 10 vol % of ethanol should not exhibit such problems. The problematic material compatibility can be caused by the corrosion aggressiveness of the ethanol–gasoline blends.
(EGBs), which is related to the higher polarity of ethanol and its ability to increase the solubility of water in the EGBs. The corrosion aggressiveness of the EGBs can be promoted by chlorides that can be dissolved in water because of water contamination caused by the failure to comply with good transportation and storage conditions; alternatively, ethanol itself can be a source of undesirable chlorides also. Also, the solubility of oxygen in EGBs can have a negative impact on the corrosion aggressiveness of the EGBs as oxygen can be a part of the corrosion reactions as a depolarizer. The dissolved oxygen can help to oxidize some unsaturated gasoline compounds to peroxides and acidic substances that are corrosion agents for some metallic materials.[8−10]

The corrosion effects of EGBs are mostly exhibited on the metallic part of fuel systems and on internal engine components. Corrosion in fuel systems can be inhibited using corrosion inhibitors.11,12 This kind of anticorrosion protection has been widely applied to study corrosion processes in metal–fuel systems.33−35 Also, electrochemical methods have been used to study the inhibitory effects of ethanol amine in the EGBs.35,40

Furthermore, the action mechanism of many steel corrosion inhibitors in the aqueous solutions of hydrochloric acid or sodium chloride was studied; chitosan,[20,41] Schiff bases,[25] bis-(benzimidazole) derivatives,26−28 porphyrin,29 pyrazine,16 and glucosamine-based, pyrimidine-fused heterocycles,30,31 and so forth were used as steel corrosion inhibitors in these studies. In many cases, environmentally friendly, the so-called “green corrosion inhibitors” are being sought.32 Such corrosion inhibitors have low ecotoxicity and could also be applicable for crude oil extraction.

Also, the influence of the addition of TiO$_2$ nanoparticles on the inhibition of the natural steel corrosion inhibitor based on the extracts[40,49] in an environment of EGBs was tested.49 The study demonstrated the beneficial effect of these nanoparticles on inhibition.49

The aim of this work was to test the efficiency of the selected steel corrosion inhibitors. Steel corrosion inhibition is of utmost importance as steel is the most common construction material in the automotive industry and is also used for the construction of fuel systems that come into contact with fuels containing different amounts of corrosive ethanol. Three different inhibitors were tested: (i + ii) two mixed inhibitors (MIs) containing propargyl alcohol, dibenzyl sulfoxide, and octadecyl amine and the (iii) diethylenetriamine (DETA) inhibitor. The MIs were chosen as they have been used as corrosion inhibitors for the transportation, storage, and processing of crude oils. The choice of the DETA inhibitor is justified by the fact that it is known as an efficient inhibitor for aqueous environments and is cost-effective and relatively easily available. Different gravimetric methods (static and dynamic) and electrochemical methods were applied for testing and all of them clearly revealed that the DETA

Figure 1. Time dependence of the weight losses related to the sample area (left) and the corrosion rate of mild steel (right) in the contaminated E10 (red), E25 (gray), E60 (green), and E85 (blue) fuels without the inhibitors.

be used in concentration ranges of 50−200 mg·kg$^{-1}$.26 For crude oil transportation and storage, inhibitors containing propargyl alcohol can be used. For the protection of equipment for the atmospheric distillation of crude oils, inhibitors containing dibenzyl sulfoxide, heterocyclic nitrogen bases, and low-molecular-weight amines seem to be the most efficient.

There are a number of publications in which the protective effects of different corrosion inhibitors on different materials in aqueous or nonaqueous environments were demonstrated.27−31 The efficiency of the corrosion inhibitors and mechanisms of their action can be studied in different laboratory flow apparatuses that simulate the corrosion of metallic materials in different environments.32 Electrochemical methods have widely been applied to study corrosion processes in metal–fuel systems.33−35 Also, electrochemical methods have been used to study the inhibitory effects of ethanol amine in the EGBs.35,40

For the effective use of corrosion inhibitors, it is important to know their action mechanism as there is no versatile inhibitor that would be efficient for all corrosion environments or for all materials. To choose an efficient inhibitor, it is necessary to consider several factors including environment properties, inhibitory properties, the potential presence of corrosion agents, and so forth.22

There is no versatile classification of inhibitors. Thus, to achieve an easier orientation in a huge number of applicable inhibitors, it is suitable to characterize the type of industry and the type of corrosion environments. Corrosion environments can be divided into aqueous and nonaqueous as the nature and the intensity of corrosion processes significantly differ in such environments. In aqueous environments, electrochemical corrosion occurs, whereas electrochemical and chemical corrosion occur in nonaqueous environments.23

In the crude oil refining industry, anticorrosion protection is very important, and significant attention is paid to the upstream to downstream processes. Here, corrosion processes are inhibited by a combination of suitable materials, anticorrosion coatings, electrochemical protection, corrosion inhibitors, and so forth. Corrosion inhibitors protect metal surfaces either by sorbing on the metal surface or by reacting with the corrosion-active compounds.24 Another action mechanism of the corrosion inhibitors includes the formation of a thin protective polymeric layer on the surface.25 For the crude oil industry, the inhibitors composed of amines with long chains or fatty amides or imidazolines or fatty acids, and their salts seem to be the most efficient. These inhibitors can
inhibitor was the most efficient one in the environments of EGBs with the inhibitory efficiency of up to 98%.

2. RESULTS AND DISCUSSION

2.1. Dynamic Test. In the apparatus with the fuel circulation for dynamic testing (see Figure 1), the contaminated fuels without inhibitors were tested. The obtained results were used as the reference data for the calculation of the efficiency of the corrosion inhibitors. The experiments without the inhibitors were performed for the same time as the experiments with the inhibitors. The stabilization of the (corrosion) weight losses and the corrosion rates of mild steel in time is presented in Figure 1.

The lowest weight losses for mild steel were observed for the E10 fuel (see Figure 1). Conversely, the highest weight losses were observed for the E60 fuel—especially for the first 96 h. With the increasing time, the weight loss of mild steel in the E60 fuel gradually stabilized, and only small weight changes were observed. The contaminated E60 fuel showed the highest aggressiveness to mild steel in comparison with the other fuels tested. This is very well in accordance with the findings presented in our previous publications.30,51 The testing period of 340 hours was found to be sufficient enough to achieve a metal—fuel balance.

The efficiency of the individual inhibitors in the environment of the E10, E25, E60, and E85 fuels is evident from the course of the time dependences of the weight losses shown in Figure 2 and Table 1. In all the fuels tested, the high efficiency of the DETA inhibitor was clearly demonstrated. In the presence of the DETA inhibitor, no significant weight losses of mild steel were observed during the entire test (see Figure 2). A slight weight loss of mild steel was observed only after the pickling of the surface of the mild steel, as evidenced by the results of the corrosion rates (see Table 1). However, the corrosion rate observed did not exceed the value of 3 μm·year⁻¹. This value was neither exceeded in the most aggressive E60 fuel, for which the DETA inhibitor showed an efficiency higher than 98.9%. Very surprisingly, the inhibitor efficiency increased with the increasing aggressiveness of the fuels, as demonstrated in Table 1.

Table 1. Corrosion Rate of Mild Steel (after Pickling in Chelaton III) in an Environment of EGBs and the Inhibitor Efficiencies after 340 h in the Apparatus with Fuel Circulation (Dynamic Test)

| fuel | corrosion rate (μm·year⁻¹) | inhibitor/efficiency (%) |
|------|---------------------------|-------------------------|
|      | no inhibitor | MI 1 | MI 2 | DETA |
| E10  |       13.5   | 13.1 | 3.0  | 9.5  | 29.6 | 0.5  | 96.3 |
| E25  |    150.5    | 93.5 | 37.9 | 17.6 | 88.3 | 1.9  | 98.7 |
| E60  |   245.7     | 205.9| 16.2 | 48.7 | 80.2 | 2.7  | 98.9 |
| E85  |     57.2    | 34.2 | 40.2 | 17.4 | 69.6 | 1.4  | 97.6 |

The MIs (MI 1 and MI 2) exhibited a mild effect on the reduction of the corrosion aggressiveness for the E10 fuel, for which a gradual increase in the weight loss of mild steel was observed. For the contaminated E25 fuel, the effect of the MIs was like that for the E10 fuel, but (unlike the E10 fuel) the measurable corrosion rate was already recorded after 48 h and the corrosion rate stabilized at values of 2 orders of magnitude higher. According to the weight losses, the MI 2 inhibitor seems to have an efficiency of about 88.3%. Because of the high aggressiveness of the contaminated E60 fuel (twice as much as for E25), the MI 1 inhibitor was found to be practically ineffective. The MI 2 inhibitor exhibited an efficiency of the corrosion inhibition of mild steel in the E60 fuel of about 80%. The contaminated E85 fuel had a noticeably lower aggressiveness in comparison with the E25 and E60 fuels. The efficiency of the MI 1 inhibitor in the E85 fuel was comparable with that of the E25 fuel. Despite this, it was demonstrated that the MI 1 inhibitor was not as effective to be applicable for real EGBs and its efficiency decreased with an increasing fuel aggressiveness. Very good results were achieved for the MI 2 inhibitor in the E25 and E60 fuels. This inhibitor contains octadecyl amine that can increase the inhibitor efficiency by its alkalizing ability, that is, it can neutralize undesirable acidic substances. Satisfactory results were achieved for the MI 2 inhibitor in the E10 and E85 fuels. For these fuels, this inhibitor could be suitable because of their considerably lower aggressiveness.
The corrosion effects of the tested fuels were also confirmed by the comparison of the surfaces of mild steel from the experiments with and without the inhibitors (see Figure 3). For the surfaces of mild steel from the experiments without the inhibitors, we observed substantial defects caused by pitting and surface corrosion and their combination depending on the ethanol content in the EGBs used. This is because with the increasing ethanol content in the fuels, the fuels can absorb higher amounts of water with ions that increase the corrosion aggressiveness.

When comparing the surface of mild steel in the environment of the fuels with and without the inhibitors, the least changes were observed for the MI 1 inhibitor. This inhibitor did not exhibit any significant anticorrosive effects, and the appearance of the mild steel surface did not differ significantly in comparison with the experiment with no inhibitor. In case of the MI 2 inhibitor containing octadecyl amine with alkalizing effects, significant anticorrosive effects were observed, and the surface of mild steel after the corrosion experiments differed significantly in comparison with the experiment with no inhibitor. For the experiment with this inhibitor in the contaminated E60 fuel, for instance, much less extensive pitting corrosion was observed than for the MI 1 experiment or the no inhibitor experiment (see Figure 3). For the DETA inhibitor, the appearance of the mild steel surface did not change in comparison with the no inhibitor experiment, that is, this inhibitor exhibited the most significant anticorrosive effects in comparison with the MIs.

2.2. Static Test. During the static tests, the metal–fuel balance was achieved at different times, but in all the cases before the test finished (i.e., before 890 h), when the corrosion rate increase was significantly slowed down. This indicates that the test period of 890 h was sufficient enough for the static test (see Figure 4. In this figure, the E10 fuel was not included, as no weight loss of mild steel was observed during the test. Also, the dependence of the weight losses and corrosion rates for the experiments with the DETA inhibitor is not presented in the figure, as no weight losses were observed. The resulting corrosion rates after pickling and the calculated corrosion efficiencies of the inhibitors are presented in Table 2.

In the contaminated E25 fuel, it was discovered that the anticorrosive effect of the MI 1 inhibitor was much worse in comparison with the MI 2 inhibitor, for which an efficiency of 78% was observed. A comparable result was observed for the
contaminated E60 and E10 fuels also. For the E10 fuel, it was only possible to calculate the corrosion rate and efficiency after pickling in Chelaton III.

For the MI 2 inhibitor, it was not possible to measure the weight losses of mild steel in the E85 fuel during the static test, despite the fact that significant surface changes occurred. The surface of mild steel was covered by a layer of corrosion products of such an oxide structure that partially protected the metal and avoided further corrosion progress. Despite this, a significant weight loss was observed after the test and pickling in Chelaton III. The efficiency of both MI was similar for the E85 fuel (see Table 2). For the first 48 h, an initial very slow increase in the corrosion rate was observed for the E85 fuel in the experiments with no inhibitor with the MI 1; then, the corrosion rate sharply increased up to 264 h of the test. This effect could be caused by the initial passivation of mild steel and by a gradual progress of corrosion as a result of an increasing concentration of the released corrosion products that can inhibit the metal fuel balance and catalyze the corrosion processes. Such a catalytic effect was not observed for the MI 2 inhibitor containing octadecyl amine. From the comparison of the curves of the time dependences of the weight losses and corrosion rates, the information about the environment (resistivity and permittivity) as well as the corrosion data (the polarization resistance and capacitance of the electrical double layer). The response of the environment had an ideal capacitance character. Conversely, the phase interface response was modeled by a constant phase element (CPE) denoted as $Q_{dl}$ in Figure 6.

All the evaluated spectral parameters (impedance and polarization characteristics) are presented in Tables 3 and 4.

Table 2. Corrosion Rate of Mild Steel (after Pickling in Chelaton III) in an Environment of EGBs and the Inhibitor Efficiencies after the Static Test

| fuel   | no inhibitor (μm·year$^{-1}$) | MI 1 (μm·year$^{-1}$) | MI 2 (μm·year$^{-1}$) | DETA (μm·year$^{-1}$) |
|--------|-------------------------------|------------------------|------------------------|-------------------------|
| E10    | 19.7                          | 7.7                    | 60.9                   | 4.6                      |
| E25    | 25.3                          | 18.5                   | 26.9                   | 5.6                      |
| E60    | 34.6                          | 26.7                   | 22.8                   | 7.7                      |
| E85    | 25.1                          | 14.7                   | 41.4                   | 12.2                     |

For the static test, these values were significantly lower as the metal–fuel systems are much less loaded than those during the dynamic test.

The corrosion aggressiveness of the tested fuels is demonstrated by the comparison of the surfaces of mild steel also (see Figure 5. During the test, no weight losses were observed for the E10 fuel, but a visual evaluation of the surface of mild steel revealed a mild pitting corrosion. The visual evaluation also revealed a moderate positive effect of the MI 1 inhibitor. Despite this, a strong pitting corrosion was observed for the E25 and E60 fuels. The high efficiency of the DETA inhibitor is demonstrated by the surface of the mild steel tested in the E60 fuel, where the steel retained a clean surface with a bright metallic gloss throughout the entire experiment.

2.3. Electrochemical Methods—Testing of the DETA Inhibitor. All the impedance spectra of mild steel measured in the contaminated E60 and E85 fuels were formed by a high-frequency and a low-frequency part that were clearly separated (see Figures 7 and 8). From the impedance spectra, it was possible (using an equivalent circuit; see Figure 6) to evaluate the information about the environment (resistivity and permittivity) as well as the corrosion data (the polarization resistance and capacitance of the electrical double layer). The response of the environment had an ideal capacitance character. Conversely, the phase interface response was modeled by a constant phase element (CPE) denoted as $Q_{dl}$ in Figure 6.

All the evaluated spectral parameters (impedance and polarization characteristics) are presented in Tables 3 and 4.

![Figure 5. Detailed pictures of the selected steel samples after the static test in the individual fuels with and without the inhibitors, zoomed in 6.3 times.](image-url)
Table 3. Impedance Parameters as Estimated by the Impedance Spectra Approximation

| fuel         | $R_1$ (kΩ·cm$^2$) | $C_1$ (nF·cm$^{-2}$) | $R_2$ (kΩ·cm$^2$) | $C_2$ (nF·cm$^{-2}$) | $R_p$ (kΩ·cm$^2$) | $Q_d$ (μΩ$^{-1}$·s$^{-1}$·cm$^{-2}$) | $n$ | $C_{dl}$ (μF·cm$^{-2}$) |
|--------------|--------------------|----------------------|-------------------|----------------------|-------------------|-------------------------------------|     |-------------------------|
| E60          | 60.7               | 0.17                 | –                 | –                    | 24.0              | 29.5                                | 0.766| 24.0                    |
| E60 + DETA   | 49.3               | 0.37                 | –                 | –                    | 16 900            | 7.20                                | 0.865| 6.12                    |
| E85          | 69.4               | 0.11                 | 55.6              | 0.87                 | 44.5              | 33.4                                | 0.722| 31.0                    |
| E85 + DETA   | 17.3               | 0.49                 | –                 | –                    | 3100              | 27.9                                | 0.913| 26.1                    |

Table 4. Tafel Parameters, the Corrosion Potentials and Currents, and the Inhibition Efficiency

| fuel         | $\beta_1$ (V/dec) | $\beta_2$ (V/dec) | $E_{corr}$ (V vs Ag/AgCl) | $i_{corr}$ (μA·cm$^{-2}$) | $E_i$ (%) |
|--------------|-------------------|-------------------|--------------------------|----------------------------|-----------|
| E60          | 0.56              | 0.24              | –                        | –                          | –         |
| E60 + DETA   | 0.22              | 0.40              | 0.190                    | 3.6 × 10$^{-3}$             | 99.8      |
| E85          | 0.32              | 0.38              | –                        | –                          | –         |
| E85 + DETA   | 0.32              | 0.38              | –0.055                   | 2.4 × 10$^{-2}$             | 98.8      |

During the measurement, it was determined that the shape of the high-frequency part of the spectra was dependent on the type of the reference electrode used. When a pseudoreference platinum electrode was used, the impedance response at high frequencies was always formed by one capacitance loop starting from the beginning of the coordinate axis in a complex plane. The loop was very well approximated by the impedance of a parallel combination of resistance and capacitance. When a silver chloride electrode with a salt bridge was used, two capacitance loops appeared in some cases (see Figure 7 and Figure 8). This is a combination of the spatial impedance (the resistivity and capacitance of the environment) and the serial resistance, especially the porous frit of the bridge.

Figure 7 compares the spectra in the environment of the contaminated fuels without the DETA inhibitor. A smaller radius of a half circle of the low-frequency spectrum part for the E60 fuel is evident in this figure. The smaller radius corresponds to the evaluated lower value of the polarization resistance in Table 3. Almost 2 times the higher value of the polarization resistance observed in the E85 fuel corresponds to the evaluated lower value of the polarization resistance (see Table 4 and Figure 8). This deviation is associated with the inhomogeneity on the electrode surface, especially the porous frit of the bridge.

Table 4). This is a combination of the spatial impedance (the resistivity and capacitance of the environment) and the response associated with the impedance of the reference electrode surface, especially the porous frit of the bridge.

Figure 7 compares the spectra in the environment of the contaminated fuels without the DETA inhibitor. A smaller radius of a half circle of the low-frequency spectrum part for the E60 fuel is evident in this figure. The smaller radius corresponds to the evaluated lower value of the polarization resistance in Table 3. Almost 2 times the higher value of the polarization resistance observed in the E85 fuel corresponds to the lower corrosion rate of mild steel. The contaminated E60 fuel without the inhibitor showed a higher corrosion aggressiveness in comparison with the E85 fuel.

Unlike the fuels without the inhibitors, enormously high polarization resistances (see Table 4 and Figure 8) were observed for the fuels containing the DETA inhibitor. These high values demonstrate the high ability of DETA to inhibit the corrosion of mild steel in the EGBs. The intensity of the inhibition was significant, especially in the E60 fuel. As it can be seen in Table 3, the value of polarization resistance in this environment was about 5 times higher than that for the E85 fuel. Also, a significant decrease of the capacitance of the double layer in the E60 fuel is clearly related to the higher adsorption of the DETA inhibitor on the surface of mild steel. From the measured data presented in Table 3, an increasing inhibitory activity of DETA with an increasing fuel aggressiveness is evident.

The values of $n$ presented in Table 3 are the important parameters describing the properties on the steel—electrolyte interface. The $n$ values lower than 1 ($n < 1$) represent the deviation of the measured capacity from the ideal capacity ($n = 1$) that is presented as the effective capacity $C_{eff}$ in Table 3. This deviation is associated with the inhomogeneity on the electrode surface or with the steel surface roughness. In general, the deviation of the measured capacity from the ideal value (capacity) increases with the decreasing $n$ values. In the Nyquist diagram, this fact can be exhibited by the shifting of the semicircle. 44,52,53 As a result of the high serial resistance $R_s$ (high-frequency response) that is associated with the low conductivity of an environment and the geometric arrangement of a measuring cell, it was necessary to calculate the $C_{eff}$ values from eq 1, where $R_s$ is the serial resistance, $Q_d$ is the double-layer response, and $R_p$ is the polarization resistance.

$$C_{eff} = Q_d^{1/n} \left( \frac{R_p R_s}{R_s + R_p} \right)^{1-1/n}$$ (1)
The Tafel curves measured on mild steel in the tested fuels with and without DETA are compared in Figures 9 and 10.

![Figure 9. Potentiodynamic polarization curves of mild steel in the E85 fuel with no inhibitor and in the E85 fuel with 100 mg·L⁻¹ of DETA.](image)

![Figure 10. Potentiodynamic polarization curves of mild steel in the E60 fuel with no inhibitor and in the E60 fuel with 100 mg·L⁻¹ of DETA.](image)

From the evaluated polarization characteristics presented in Table 4, the current densities were calculated according to the Stern–Geary equation. From the obtained current densities, the efficiency of the DETA inhibitor was determined for the E60 and E85 fuels.

For both fuels, the DETA inhibitor caused a substantial shift in the corrosion potentials toward positive values, and the corrosion current densities were also decreased. The shift in the corrosion potentials and the decrease in the corrosion current densities indicate that DETA acts as an anodic inhibitor that actively helps to effectively suppress the anodic partial corrosion process in the EGBs. Considering an overall moderate decrease in the polarization curves into lower current densities, it can be concluded that the adsorbed inhibitor influences the cathodic reaction (predominantly a reduction in the dissolved oxygen) also.

As shown in Table 5, the DETA inhibitor also has a strong alkalizing ability, which is already exhibited at a concentration of 100 mg·L⁻¹ by a pH increase. The inhibitor, by its alkalizing ability, initially neutralizes acidic substances that can act corrosively to mild steel. The alkalizing ability of DETA is associated with a decrease in the corrosion potential. Despite this, such a decrease was not observed, as the shift toward positive values was predominant.

The measured polarization data also demonstrate the higher efficiency of DETA in the E60 fuel, in which a higher increase in the corrosion potential (up to 0.39 V) and 1 order of magnitude decrease in the current density were observed in comparison with the E85 fuel. In the E60 fuel, the efficiency of the DETA inhibitor was measured and calculated to be 99.8%. This result agrees with the results of the static and the dynamic tests.

### 3. CONCLUSIONS

In this study, we have presented the testing of the efficiency of three corrosion inhibitors on mild steel in an environment of aggressive EGBs that were contaminated by water and trace amounts of sulfates and chlorides. The aggressiveness of the E10, E25, and E60 fuels increased with the ethanol content, that is, the E60 fuel was the most aggressive fuel for mild steel. The aggressiveness of the E85 fuel was lower than that of the E25 fuel. The MI 1 inhibitor containing propargyl alcohol and dibenzyl sulfide (originally designed for corrosion inhibition for the transportation, storage, and processing of crude oils) was found not to be sufficiently efficient to be applied for real EGBs. In the concentration in which the MI 1 inhibitor was applied in this study, its efficiency decreased with the increasing aggressiveness of the EGBs applied. For the E60 fuel in the dynamic test, the efficiency of this inhibitor was about 16%. The highest efficiencies (∼40%) of this inhibitor were recorded for the E25 and E80 fuels. The MI 2 inhibitor containing propargyl alcohol, mercaptobenzothiazole, and octadecyl amine gave acceptable inhibition efficiencies for the E25 and E60 fuels. Satisfactory results of this inhibitor were observed for the E85 fuel also. In the static and dynamic tests, the efficiency of the MI 2 inhibitor in the E60 fuel was about 75–80%. The DETA inhibitor was found to be the most efficient among all the inhibitors tested. Its efficiency was about 96–99% depending on the content of ethanol in the EGBs tested. For this inhibitor, an increasing efficiency was observed with the increasing fuel aggressiveness, that is, the highest efficiency was observed for the E60 fuel. The efficiency of this inhibitor was proven by the electrochemical methods also. The efficiency determined by the electrochemical methods was about 99.8%. The polarization measurements revealed that this inhibitor had characteristics of an anodic inhibitor with a high adsorption ability that was proven by the results of impedance spectroscopy also. By the pH measurements, the alkalizing ability of the DETA inhibitor was demonstrated. The measurements proved the DETA inhibitor to be a sufficient corrosion inhibitor for mild steel in the real EGBs. For all the inhibitors tested, the static and dynamic tests showed good results that correlated well with each other. These results suitably complemented the data obtained using electrochemical methods.

### Table 5. pH Values of the Contaminated E60 and E85 Fuels before and after the Additivation with DETA

| fuel   | no additives | with additives |
|--------|--------------|----------------|
| E60    | 7.09         | 9.85           |
| E85    | 6.76         | 9.72           |

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4. EXPERIMENTAL SECTION

4.1. Preparation of Contaminated EGBs. Contaminated EGBs were prepared from (i) a gasoline base and (ii) fermented, absolutized ethanol (≥99.99%, Sigma-Aldrich, p.a.) with water content up to 650 mg·kg⁻¹. The gasoline base was prepared from five different petroleum fractions: reformate, isomerate, and FCC gasolines (light, middle, and heavy). The petroleum fractions were mixed in such a volume ratio that the contents of the saturated, unsaturated, and aromatic hydrocarbons met the requirements of the CSN EN 228 standard. The group-type composition of the gasoline base (53.9 vol % of the saturated, 10.6 vol % of the unsaturated, and 35.5 vol % of the aromatic hydrocarbons) was verified by gas chromatography.⁵⁰,⁵¹

To increase their aggressiveness, the EGBs were purposely contaminated by a solution containing sodium chloride (99.9%), sodium sulfate anhydrous (99%), 96% sulfuric acid, and 100% acetic acid (all p.a. chemicals purchased from Penta Chemicals, the Czech Republic). The solution was added into the EGBs in an amount of 0.5 vol % so that the resulting fuel contained (after adding demineralized water to the desired amount) 3 mg·L⁻¹ of sodium chloride, 2.5 mg·L⁻¹ of sodium sulfate, 2.5 mg·L⁻¹ of sulfuric acid, and 47.8 mg·L⁻¹ of acetic acid. The desired water content in the model contaminated EGBs was 0.5 vol % for the E10 fuel, 1.75 vol % for the E25 fuel, and 6 vol % for the E60 and E85 fuels.

4.1.1. Corrosion Inhibitors. Three different inhibitors were tested, and all of them were added into each of the prepared EGBs (see Table 6. The first two (mixed) inhibitors were originally designed as corrosion inhibitors for the transportation, storage, and processing of crude oils. DETA, which was supposed to be a promising corrosion inhibitor for mild steel, was the third inhibitor.

As the MIs contain sulfur-containing compounds (dibenzyl sulfoxide with 14 wt % of sulfur and the sodium salt of mercaptobenzothiazole, with 35 wt % of sulfur), their concentration in the fuels was chosen such that the sulfur content met the requirements of the CSN EN 228 standard (<10 mg·kg⁻¹). The resulting sulfur content after additivization by the inhibitors was verified according to ASTM D 5453 using the elemental analyzer Mitsubishi TS 100/TN (Cosa Instrument Corporation, USA). The sulfur content after the additivization was measured for the E60 fuel only, and the obtained values were as follows: 9.4 and 8.5 mg·kg⁻¹ for the MI 1 and the MI 2 inhibitor, respectively.

Table 6. Tested Inhibitors and Their Concentrations in the EGBs⁴⁴,⁵⁵

| inhibitors                 | manufacturer, purity | amount (mg·L⁻¹) |
|----------------------------|----------------------|----------------|
| MI 1 propargyl alcohol     | Sigma-Aldrich, p.a.  | 100            |
| dibenzyl sulfoxide         | Merck Millipore, p.a.| 65             |
| MI 2 propargyl alcohol     | Sigma-Aldrich, p.a.  | 100            |
| octadecyl amine            | Merck Millipore, p.a.| 70             |
| mercaptobenzothiazole, sodium salt | Merck Millipore, p.a. | 25             |
| DETA diethylenetriamine    | Sigma-Aldrich, p.a.  | 100            |

4.2. Metallic Materials for Corrosion Studies. Corrosion studies were performed on carbon steel 11375 (in this manuscript, designated as “mild steel”) containing 0.16 wt % of carbon, 0.032 wt % of phosphorus, and 0.028 wt % of sulfur. From a 1 mm thick steel sheet, 10 × 40 mm plates were prepared. For the electrochemical measurements, a cylindrical electrode with a surface area of 2.6 cm² was prepared from mild steel. Prior to the experiment, the steel surface was adjusted by grinding using sandpaper (1200 mesh) and polishing under running water so that the surface was adjusted evenly. Then, the sample surface was degreased with acetone and ethanol and then dried freely or using a pulp tissue.⁶⁶

4.3. Testing of the Corrosion Inhibitors. Several tests were applied to study the corrosion inhibitors including a dynamic test, a static test, and electrochemical measurements. These tests are briefly described in the following subsections. They are all described in deep detail elsewhere.⁵⁶

4.3.1. Dynamic Test. The apparatus with the fuel circulation for the dynamic test is presented in Figure 11. Although the apparatus is more complicated in comparison with the apparatus for the static test, this is compensated by much shorter testing periods, as the testing is performed with circulating fuel during the thermal stress. This testing method is suitable for several applications including (i) the fast prediction of fuel aging, (ii) testing the changes in fuel quality, and (iii) testing the fuel influence on metallic and nonmetallic materials.⁵⁶

The main part of the apparatus is the tempered flask in which a direct contact between the tested fuel and the sample hung on a hook occurs. The reservoir of the tested fuel is equipped by a reflux cooler that ensures the connection of the entire apparatus to the atmosphere. Also, the cooler is used to freeze the volatile compounds (at −40 °C) to avoid possible
fuel losses. The fuel circulation in a closed circuit (made from chemically resistant, inert material, e.g., Teflon, Viton, Tygon, etc.) is ensured by a peristaltic pump that transfers the fuel from the storage flask back to the tempered flask.

In the apparatus, 400 mL of fuel at a flow rate of 0.5 L·h⁻¹ was tested. The fuel was heated in the tempered part to 40 °C and bubbled with air at a flow rate of about 20–30 mL·min⁻¹. The testing was performed on two metallic plates (see Section 4.2) that were removed from the apparatus and weighed at regular time intervals. Prior to weighing, the surface layer of the corrosion products was removed using a pulp tissue and the sample was rinsed with acetone and dried. From the time-dependent weight losses, the corrosion rate in mm·year⁻¹ (νₜₚ) was calculated according to eqs 2 and 3.

\[
νₜₚ = 8.76 \frac{ν_{pm}}{ρ}
\]  

(2)

\[
ν_{pm} = \frac{Δm}{t·S}
\]  

(3)

where \(ν_{pm}\) is the corrosion rate in g·m⁻²·h⁻¹, \(ρ\) is the density of the metallic material in g·cm⁻³, \(Δm\) is the average weight loss in g, \(S\) is the surface area of the metallic material in m², and \(t\) is the time of exposure (in hours).50

After the test, the tested samples were pickled in a 10 wt % solution of disodium salt of ethylenediaminetetraacetic acid (EDTA). From the overall weight loss of steel, the ultimate corrosion rate was calculated.

4.3.2. Static Immersion Test. The static test was designed according to the methods described in the ČSN 03 8452 and ASTM D130-04 standards. This test is based on the exposure of metallic materials for a certain time in the tested samples (corrosion environment) at a given ratio between the sample volume and the area of the metallic material. In our study, the ratio was chosen to be 10 mL of the EGB (corrosion environment) to 1 cm² of the metallic material so that the corrosion rate was not stabilized too soon. The static test was performed as a long-term test at room temperature without air entrance in a closed 250 mL GL45 bottle that contained 160 mL of the fuel and two metallic plates with a total surface area of 16 cm². The metallic samples were removed from the bottle and weighed at certain time periods. The corrosion rate was calculated from the obtained weight losses (see Section 4.3.1).56

After the test, the tested samples were pickled in a 10 wt % solution of disodium EDTA. From the overall weight loss of steel, the ultimate corrosion rate was calculated.

4.3.3. Electrochemical Measurements. Electrochemical measurements were performed on the FRA Solartron 1250 (Schlumberger, UK) and potentiostat SI 1287 (Schlumberger, UK) devices at a laboratory temperature in a three-electrode arrangement in a cell containing 100 mL of fuel.50,51,56

The cell was placed in a Faraday cage. The electrode system consisted of (i) a working electrode from mild steel, (ii) an auxiliary platinum electrode, and (iii) a reference silver chloride electrode with a bridge containing 1 mol·L⁻¹ solution of lithium chloride in ethanol for measurements in nonaqueous environments. For long-term measurements, a pseudoreference platinum electrode was used to avoid environmental contamination by leaking from the bridge of the reference electrode.

At the beginning of each measurement, the corrosion potential was measured during its stabilization for 1 h. Then, the electrochemical impedance and polarization characteristics were measured. The electrochemical impedance was measured at an amplitude of 5 mV in a frequency range of 60 kHz to 1 mHz. From the electrochemical impedance spectrum, the environmental resistance (resistivity) and polarization resistance were evaluated. Polarization curves were measured in a range of ±300 mV relative to the corrosion potential. Resistivities determined by EIS were used to obtain the \(iR\) drop from the polarization curves. The evaluation of the linear cathodic and anodic parts of the polarization curves allowed one to obtain the Tafel coefficients \(β\), for a given metal–fuel system. The Tafel coefficients, as well as the polarization resistance \(R_p\), were used for the calculation of the corrosion current density \(i_{corr}\) according to the Stern–Geary equation (see eq 4).

\[
i_{corr} = \frac{β_1β_2}{2·(β_1 + β_2)·R_p}
\]  

(4)

4.3.4. Calculation of the Inhibitor Efficiencies. The effect is specific, especially in relation to the metal composition, metal properties, and environment properties. The inhibitor efficiency can be evaluated according to the following equations (see eqs 5a–5c)

\[
E_i = \frac{R_{p,i} - R_{p,0}}{R_{p,i}}·100
\]  

(5a)

\[
E_i = \frac{ν_{pm,0} - ν_{pm,i}}{ν_{pm,0}}·100
\]  

(5b)

\[
E_i = \frac{i_{corr,0} - i_{corr,i}}{i_{corr,0}}·100
\]  

(5c)

where \(E_i\) is the inhibitor efficiency in %, \(R_p\) is the polarization resistance of the material, and \(ν_{pm}\) is the corrosion rate of the material in a metal–fuel system; \(i_{corr}\) see eq 4; \(β\) the indices i and 0 describe the system with and without the inhibitor, respectively.56

4.4. Total Acid Number. Total acid number (TAN) measurements were performed according to IP 177/96 and ASTM D664-89 on an automatic DMS TITRINO 716 (Metrohm) with a potentiometric detection of the point of equivalence. The obtained results are presented in Table 7.

| fuel          | TAN (mg KOH·g⁻¹) |
|---------------|------------------|
| E10 + 0.5% H₂O | 0.0155           |
| E25 + 2.0% H₂O | 0.0196           |
| E60 + 6% H₂O  | 0.0210           |
| E85 + 6% H₂O  | 0.0312           |

4.5. pH Measurement. The pH measurements were performed on an inoLab pH/Cond Level 1 instrument at a laboratory temperature. These measurements were performed for the contaminated E60 and E85 fuels before and after the additivation with the DETA inhibitor (100 mg·L⁻¹).

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the implications of allocation.

of bioethanol and bio-ethyl tertiary butyl ether (bioETBE): assessing 115
Available online: https://www.sae.org/publications/technical-papers/
powertrains in the European context. SAE Technical Paper 2004.

1991.
gasoline blended fuels.
performance and pollutant emission of an SI engine using ethanol-
Fuel Reference Work 1
■
EDTA ethylenediaminetetraacetic acid
■
ABBREVIATIONS
CPE constant phase element
DETA diethylene triamine
EDTA ethylenediaminetetraacetic acid
EGBs ethanol–gasoline blends
EIS electron impedance spectroscopy
EU European Union
MI mixed inhibitor

■ REFERENCES
(1) Edwards, R.; Mahieu, V.; Griesemann, J.-C.; Larivé, J.-F.; Rickeard, D. J. Well-to-wheels analysis of future automotive fuels and powertrains in the European context. SAE Technical Paper 2004. Available online: https://www.sae.org/publications/technical-papers/content/2004-01-1924/ (accessed Oct 10, 2018).
(2) Rosillo-Calles, F.; Cortez, L. A. B. Towards ProAlcool II—a review of the Brazilian bioethanol programme. Biomass Bioenergy 1998, 14, 115–124.
(3) Malča, J.; Freire, F. Renewability and life-cycle energy efficiency of bioethanol and bio-ethyl tertiobutyl ether (bioETBE): assessing the implications of allocation. Energy 2006, 31, 3362–3380.
(4) Australia, Environment Australia. Setting the Ethanol Limit in Petrol: An Issues Paper; Department of the Environment and Heritage: Canberra, Australia, 2002.
(5) European Union. Directive 2009/28/EC of the European Parliament and of the Council of 23 April 2009 on the promotion of the use of energy from renewable sources and amending and subsequently repealing Directives 2001/77/EC and 2003/30/EC, in Official Journal of the European Union, 2009. Available online: https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32009L0028&from=EN (accessed Oct 10, 2018).
(6) Agarwal, A. K. Biofuels (alcohols and biodiesel) applications as fuels for internal combustion engines. Prog. Energy Combust. Sci. 2007, 33, 233–271.
(7) Zákon, č. 201/2012 Sb., o ochraně ovzduší—sídlákovi povinnosti průvozovatele zdrojů znečistování ovzduší (Law No 201/2012 on air protection—the basic obligations of operators of air pollution sources, Czech Republic), in Czech, 2013. Available online: https://www.zakonypridodi.cz/cs/2012-201#cast1 (accessed Oct 10, 2018).
(8) Tshiteya, R. Properties of Alcohol Transportation Fuels. Alcohol Fuel Reference Work 1; Meridian Corporation: Alexandria, VA, USA, 1991.
(9) Hsieh, W.-D.; Chen, R.-H.; Wu, T.-L.; Lin, T.-H. Engine performance and pollutant emission of an SI engine using ethanol-gasoline blended fuels. Atmos. Environ. 2002, 36, 403–410.
(10) Pereira, R.; Pasa, V. Effect of mono-olefins and diolefins on the stability of automotive gasoline. Fuel 2006, 85, 1860–1865.
(11) Jones, D. A. Principles and Prevention of Corrosion, 2nd ed.; Prentice Hall: Upper Saddle River, NJ, USA, 1996.
(12) Munger, C. G. Corrosion Prevention by Protective Coatings; NACE International: Houston, TX, USA, 1985.
(13) Dariva, G. G.; Galio, A. F. Corrosion Inhibitors—Principles, Mechanisms and Applications. In Developments in Corrosion Protection; Alidkhazraei, M., Ed.; IntechOpen: London, United Kingdom, 2014. Available online: https://www.intechopen.com/books/developments-in-corrosion-protection/corrosion-inhibitors-principles-mechanisms-and-applications (accessed Oct 10, 2018).
(14) Sasti, V. S. Corrosion Inhibitors: Principles and Applications; Wiley: Chichester, NY, USA, 1998.
(15) Dutta, A.; Saha, S. K.; Banerjee, P.; Patra, A. K.; Sukul, D. Evaluating corrosion inhibition property of some Schiff bases for mild steel in 1 M HCl: competitive effect of the heteroatom and stereochemical conformation of the molecule. RSC Adv. 2016, 6, 74833–74844.
(16) Obot, I. B.; Umoren, S. A.; Ankah, N. K. Pyrazine derivatives as green oil field corrosion inhibitors for steel. J. Mol. Liq. 2019, 277, 749–761.
(17) Saha, S. K.; Banerjee, P. Introduction of newly synthesized Schiff base molecules as efficient corrosion inhibitors for mild steel in 1 M HCl medium: an experimental, density functional theory and molecular dynamics simulation study. Mater. Chem. Front. 2018, 2, 1674–1691.
(18) Verma, C.; Quraishi, M. A.; Ebenso, E. E. Microwave and ultrasonus irradiations for the synthesis of environmentally sustainable corrosion inhibitors: An overview. Sustainable Chem. Pharm. 2018, 10, 134–147.
(19) Verma, C.; Haque, J.; Quraishi, M.; Ebenso, E. E. Aqueous phase environmental friendly organic corrosion inhibitors derived from one step multicomponent reactions: A review. J. Mol. Liq. 2018, 275, 18–40.
(20) Macedo, R. G. M. d. A.; Marques, N. d. N.; Tonholo, J.; Balaban, R. d. C. Water-soluble carboxymethylchitosan used as corrosion inhibitor for carbon steel in saline medium. Carbohydr. Polym. 2019, 205, 371–376.
(21) Askari, M.; Alidkhazraei, M.; Ghafari, S.; Hajizadeh, A. Film former corrosion inhibitors for oil and gas pipelines - A technical review. J. Nat. Gas Sci. Eng. 2018, 58, 92–114.
(22) Finisgar, M.; Jackson, J. Application of corrosion inhibitors for steels in acidic media for the oil and gas industry: a review. Corros. Sci. 2014, 86, 17–41.
(23) Migahed, M. A.; Al-Sabagh, A. M. Beneficial role of surfactants as corrosion inhibitors in petroleum industry: a review article. Chem. Eng. Commun. 2009, 196, 1054–1075.
(24) Rajeev, P.; Surendranathan, A.; Murthy, C. S. Corrosion inhibiting potential of the oil well steels using organic inhibitors—a review. J. Mater. Environ. Sci. 2012, 3, 856–869.
(25) Quraishi, M. A.; Jamal, D. Corrosion inhibition by fatty acid oxadiazoles for oil well steel (N-80) and mild steel. Mater. Chem. Phys. 2001, 71, 202–205.
(26) Miksic, B. M.; Furman, A. Y.; Kharshan, M. A. Effectiveness of the Corrosion Inhibitors for the Petroleum Industry Under Various Flow Conditions. Proceedings of Corrosion Conference & Expo, Atlanta (Georgia), USA, 2009. Available online: https://www.onepetro.org/conference-paper/NACE-09573 (accessed Oct 10, 2018).
(27) de Souza, F. S.; Spinelli, A. Caffeic acid as a green corrosion inhibitor for mild steel. Corros. Sci. 2009, 51, 642–649.
(28) Penninger, J. Corrosion inhibitors for aluminum. U.S. Patent 4,647,429, 1987.
(29) Shefr, E. M.; Park, S.-M. 2-Amino-5-ethyl-1, 3, 4-thiadiazole as a corrosion inhibitor for copper in 3.0% NaCl solutions. Corros. Sci. 2006, 48, 4065–4079.
(30) Cotton, J. B.; Scholes, I. R. Benzotriazole and related compounds as corrosion inhibitors for copper. Br. Corros. J. 1967, 2, 1–5.
(31) Mansfeld, F.; Smith, T.; Parry, E. P. Benzotriazole as corrosion inhibitor for copper. Corrosion 1971, 27, 289–294.
(32) Nesci, S.; Schubert, A.; Brown, B. Thin channel corrosion flow cell. WO Patent 015318A1, 2009.
(33) Yoo, Y. H.; Park, I. J.; Kim, J. G.; Kwak, D. H.; Ji, W. S. Corrosion characteristics of aluminum alloy in bio-ethanol blended
gasoline fuel: Part I. The corrosion properties of aluminum alloy in high temperature fuels. Fuel 2011, 90, 1208–1214.

(34) Bhola, S. M.; Bhola, R.; Jain, L.; Mishra, B.; Olson, D. L. Corrosion behavior of mild carbon steel in ethanolic solutions. J. Mater. Eng. Perform. 2011, 20, 409–416.

(35) Jafari, H.; Idris, M. H.; Ourdjini, A.; Rahimi, H.; Ghobadian, B. EIS study of corrosion behavior of metallic materials in ethanol blended gasoline containing water as a contaminant. Fuel 2011, 90, 1181–1187.

(36) Traldi, S. M.; Costa, I.; Rossi, J. L. Corrosion of spray formed Al-Si-Cu alloys in ethanol automobile fuel. Key Eng. Mater. 2001, 189–191, 352–357.

(37) Sridhar, N.; Price, K.; Buckingham, J.; Dante, J. Stress corrosion cracking of carbon steel in ethanol. Corrosion 2006, 62, 687–702.

(38) Nie, X.; Li, X.; Northwood, D. O. Corrosion Behavior of metallic materials in ethanol-gasoline alternative fuels. Mater. Sci. Forum. 2007, 546, 1093–1100.

(39) Baena, L. M.; Gomez, M.; Calderon, J. Aggressiveness of a 20% bioethanol~80% gasoline mixture on auto-parts: I behavior of metallic materials and evaluation of their electrochemical properties. Fuel 2012, 95, 320–328.

(40) De Souza, J. P.; Mattos, O. R.; Sathler, L.; Takenouti, H. Impedance measurements of corroding mild steel in an automotive fuel ethanol with and without inhibitor in a two and three electrode cell. Corros. Sci. 1987, 27, 1351–1364.

(41) Rabizadeh, T.; Khameneh Asl, S. Chitosan as a green inhibitor for mild steel corrosion: Thermodynamic and electrochemical evaluations. Mater. Corros. 2019, 70, 738.

(42) Saha, S. K.; Dutta, A.; Ghosh, P.; Sukul, D.; Banerjee, P. Adsorption and corrosion inhibition effect of Schiff base molecules on the mild steel surface in 1 M HCl medium: a combined experimental and theoretical approach. Phys. Chem. Chem. Phys. 2015, 17, 5679–5690.

(43) Murmu, M.; Saha, S. K.; Murmu, N. C.; Banerjee, P. Amine cured double Schiff base epoxy as efficient anticorrosive coating materials for protection of mild steel in 3.5% NaCl medium. J. Mol. Liq. 2019, 278, 521–535.

(44) Murmu, M.; Saha, S. K.; Murmu, N. C.; Banerjee, P. Effect of stereochemical conformation into the corrosion inhibitive behaviour of double azomethine based Schiff bases on mild steel surface in 1 mol L−1 HCl medium: An experimental, density functional theory and molecular dynamics simulation study. Corros. Sci. 2019, 146, 134–151.

(45) Dutta, A.; Saha, S. K.; Banerjee, P.; Sukul, D. Correlating electronic structure with corrosion inhibition potentiality of some benzenimidaizole derivatives for mild steel in hydrochloric acid: combined experimental and theoretical studies. Corros. Sci. 2015, 98, 541–550.

(46) Singh, A.; Lin, Y.; Ansari, K. R.; Quraishi, M. A.; Ebenso, E. E.; Chen, S.; Liu, W. Electrochemical and surface studies of some Porphines as corrosion inhibitor for J55 steel in sweet corrosion environment. Appl. Surf. Sci. 2015, 359, 331–339.

(47) Verma, C.; Olasunkami, L. O.; Ebenso, E. E.; Quraishi, M. A.; Obot, I. B. Adsorption behavior of glucosamine-based, pyrimidine-fused heterocycles as green corrosion inhibitors for mild steel: experimental and theoretical studies. J. Phys. Chem. C 2016, 120, 11598–11611.

(48) Vu, N.; Hien, P. V.; Man, T. V.; Hanh Thu, V. T.; Tri, M. D.; Nam, N. D. A Study on Corrosion Inhibitor for Mild Steel in Ethanol Fuel Blend. Materials 2017, 11, 59.

(49) Hoai Vu, N. S.; Hien, P. V.; Mathesh, M.; Hanh Thu, V. T.; Nam, N. D. Improved Corrosion Resistance of Steel in Ethanol Fuel Blend by Titania Nanoparticles and Aganonerion polymorphum Leaf Extract. ACS Omega 2019, 4, 146–158.

(50) Matějovský, L.; Macák, J.; Pospíšil, M.; Baroš, P.; Staš, M.; Krausová, A. Study of Corrosion of Metallic Materials in Ethanol–Gasoline Blends: Application of Electrochemical Methods. Energy Fuels 2017, 31, 10880–10889.