

ESTIMATION OF CORROSION RATE IN BIOFUELS

1. Corrosivity of biofuels

Ethanol may be used as biofuel in several variants. It can be used as fuel for gasoline engines either directly as pure bioethanol fuel (E100), or mixed with gasoline (E5 - E85). It can also serve as the source material for production of other fuels – by reacting ethanol with isobutene, it can be converted to ethyl tertiary-butyl ether (ETBE), or it may be used to produce fatty acid ethyl esters, which are the basis of the biodiesel.

Ethanol is miscible with hydrocarbons in any ratio. The most used mixture in the world of ethanol and gasoline are listed in Table I.

Table I: Common mixtures of ethanol and gasoline

Designation	E5	E10	E22	E85	E100
Ethanol content (in vol.%)	max. 5	max. 10	20-24	70-85	100

Furthermore, ethanol is a polar compound that is easily soluble in water. The solubility of water in ethanol therefore increases significantly also in the mixtures of ethanol and gasoline. Ethanol added to gasoline also affects the properties of the resulting mixture due to its different physical and chemical properties. Ethanol in gasoline increases the octane number, water solubility, polarity, increases vapor heat, affects vapor pressure, reduces calorific value, CO and hydrocarbon emissions, but on the other hand, increases aldehyde emissions and slightly increases the total volume when mixed with hydrocarbons.

The biggest issue with gasoline mixtures is their increased corrosivity, which is caused by the increased solubility of water. Higher polarity further leads to an increase in the solubility of polar contaminants (salts, acids), which further increase corrosivity. Corrosivity is also increased by the significantly higher solubility of oxygen in gasoline mixtures than in water. Corrosive effects are manifested on the metal components of the fuel system and internal engine components (fuel tank, fuel pipes, fuel pump, cylinder walls). Additionally, burning ethanol produces acidic organic products that can be corrosive in the cylinder and exhaust pipes.

2. Electrochemical methods of estimation of corrosion rate

Due to the polar character of ethanol, corrosion in biofuels with high ethanol content (E60-E100) has an electrochemical character, and hence, electrochemical methods can be used to determine the corrosion rate of materials in these environments. The advantage of these methods is the short measurement time and the ability to determine even relatively low corrosion rates. On the other hand, the measurements are complicated by the high resistivity of the environment. This can be overcome by addition of small amounts of conductive additives (typically, tetraalkylammonium tetrafluoroborates or perchlorates are used). This allows to increase the conductivity of the fuel without significantly affecting the corrosion rate.

2.1 Electrode potential measurement

Electrode potential is the potential difference that develops at the interface of the metal immersed in an electrolyte. It is measured as the voltage that develops in an electrochemical cell, which is composed of the studied material (in electrochemistry designated as the working electrode) and a reference electrode. The electrode potential is also directly related to the Gibbs energy, and therefore

provides information about the driving force of the processes that take place on the electrode. The electrode potential of a metal immersed in a corrosive electrolyte is called the corrosion potential. The corrosion potential (also called free potential, OCP - open circuit potential) is then defined as the potential of the electrode without the presence of polarization from an external source.

2.2 Electrochemical Impedance Spectroscopy (EIS)

The basic kinetic corrosion parameter is the corrosion current density (current per unit surface area). It can be determined in several ways (measurement of polarization resistance, Tafel extrapolation). In environments with high resistivity, the most convenient method of measuring the polarization resistance is the electrochemical impedance spectroscopy, which during a single measurement enables the determination of both the resistivity of the environment and the polarization resistance, which is related to the corrosion current density as expressed by the Stern-Geary equation:

$$i_{corr} = \frac{B}{R_p}$$

where the constant B is defined as follows:

$$B = \frac{\beta_a \cdot \beta_c}{2.303 \cdot (\beta_a + \beta_c)}$$

where i_{corr} is the corrosion current density, β_a and β_c are the anodic and cathodic Tafel slopes (see Chap. 2.3), and R_p the polarization resistance.

Electrochemical impedance spectroscopy is based on the perturbation of the measured electrochemical system with an AC sinusoidal voltage signal of small amplitude and varying frequency. The response of the system is expressed as impedance $Z(\omega)$, which is a complex number and has a real and an imaginary part as follows:

$$Z(\omega) = Z_{real} + Z_{imag} = |Z| \cdot (\cos \varphi + j \cdot \sin \varphi)$$

where ω is the angular frequency, φ is the phase angle between voltage and current, Z_{real} represents the real part of impedance and Z_{imag} the imaginary part of impedance and j the imaginary unit.



Figure 1: Nyquist plot of the Randles circuit (left) and the Randles circuit (right).

By measuring impedance of the studied system at varying frequency, an impedance spectrum is obtained, which may be plotted in the complex plane, called the Nyquist diagram. The impedance spectrum is then approximated (fitted) by the impedance of an equivalent circuit in a dedicated software, whereby individual elements of the circuit are assigned a physical meaning. The simplest equivalent circuit (model) of a metal corroding in an electrolyte is the Randles circuit shown in Fig. 1.

This model is composed of electrolyte resistance R_s in series with a parallel combination of polarization resistance (charge transfer resistance) R_p and electrical double layer capacitance C_{dl} .

2.3 Potentiodynamic polarization

Potentiodynamic polarization is based on varying the potential of the studied sample (working electrode) and detecting the current response. The output of the measurement is the polarization curve.

In semi-logarithmic coordinates, the experimentally measured curve is curved near the corrosion potential, and linear at higher potentials. The linear region on the curve is called the Tafel region (Fig. 2).

By extrapolating the Tafel regions, the slopes of the Tafel regions (Tafel constants) β_a and β_c can be obtained and used to calculate the corrosion current density using the Stern-Geary equation. The length of the linear Tafel region on the cathodic curve is usually limited to approximately one decade of current. A higher concentration of ionically dissolved species increases the conductivity of the environment and expands the Tafel region.

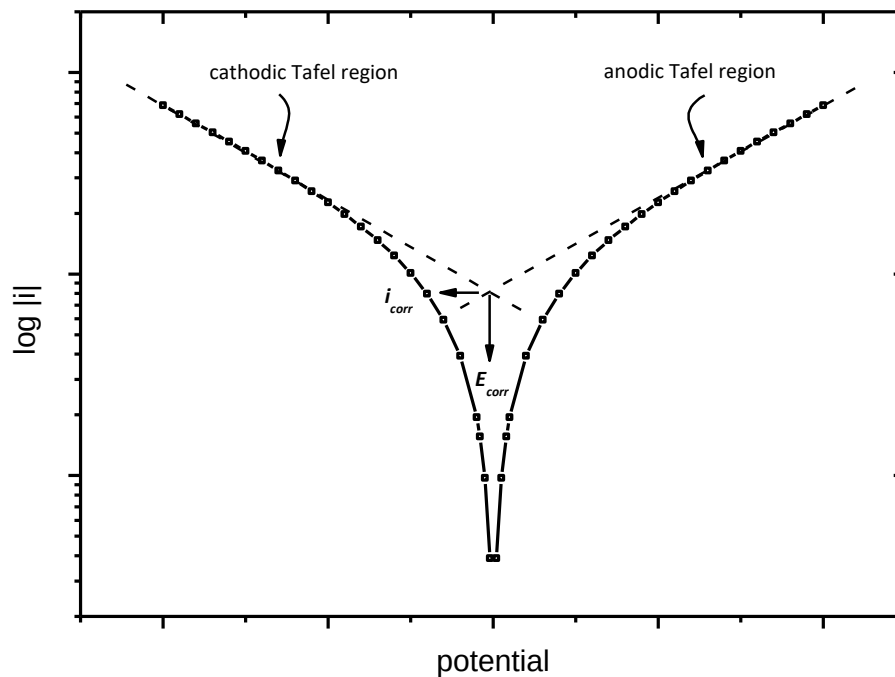


Figure 2: Experimental polarization curve of iron with Tafel regions marked

3. WORK PROCEDURE

3.1 Preparation of measuring equipment

Carefully grind the working electrode (steel sample) with 240 emery paper before each measurement. Rinse with distilled water, ethanol and dry with a blow dryer. Inspect the surface for stains (surface should be free of corrosion products). Rinse the measuring cell and fill it with the appropriate electrolyte. Connect the working, auxiliary and reference electrodes according to the teacher's instructions (see Fig. 3). An integrated Gamry electrochemical multisystem, controlled by the Gamry Framework program, is used for measurement.

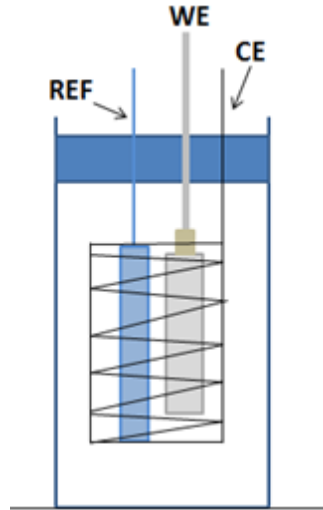


Figure 3: Electrochemical cell circuit diagram: REF – reference electrode (Ag/AgCl/LiOH in ethanol), WE - working electrode, CE - auxiliary electrode (304 steel wire)

2.2 Tasks

1. In the Gamry Framework, measure the corrosion potential, impedance spectrum and polarization curves of a steel sample in two environments: ethanol and model biofuel E85. Measure the impedance spectrum in the frequency range 1 kHz - 1 mHz with an amplitude of 20 mV. Using the ZSimpWin software, evaluate the impedance spectra. The resistance value obtained at low frequencies corresponds to the polarization resistance R_p . Deduct the constants of the Tafel regions β_a and β_c from the polarization curves.
2. From the obtained values of the polarization resistance and the Tafel constants, calculate the corrosion current density in $A \cdot cm^{-2}$ (divide the current by the surface area of the sample) according to the Stern-Geary equation.
3. Calculate the corrosion rate as penetration rate in $mm \cdot year^{-1}$ from the corrosion current density according to Faraday's law.

$$v_{kor} = \frac{i_{corr} \cdot M \cdot t}{Z \cdot F \cdot \rho}$$

4. Compare and comment on the corrosion rates of individual measurements.