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Material Compatibility in Renewable Fuels and Characterization Methods

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Abstract: Renewable fuels can make a significant contribution to achieving climate protection targets. In addition to 2nd generation biogenic fuels, synthetic fuels such as OME and DMC show in particular great potential. With respect to metallic materials, however, there are special challenges with regard to the material compatibility. Investigations with oxygenates such as ethanol or OME have shown that in some cases significant corrosion attack can occur on fuel-carrying components. Besides the respective fuel blend, the input of water and ions in particular increases the corrosiveness. Knowledge of material compatibility is therefore of utmost importance for a successful market acceptance. In this contribution, established and highly innovative test methods to characterize the corrosion behavior in regenerative fuels are illustrated. In addition to the specific experimental setup, a statistical-based test design enables to investigate the influence of corrosion-stimulating components in ethanol-blended gasoline on the material resistance of fuel-carrying aluminum components. The abstraction of the specific results into a ternary system allows a general transferability for other future-oriented oxygenate fuels such as OME.

Key words: regenerative fuel, oxygenate, ethanol, gasoline, corrosion, aluminum

1. Introduction

The use of regenerative fuels shows a significant potential to reduce climate-relevant greenhouse gas emissions (GHG). Oxygenates such as oxymethylene ether (OME), methyl formate (MeFo), or second-generation ethanol from biomass and sugarcane are regarded to have a positive CO_2-bilance [1] and additionally enable almost particle-free combustion. The latter is particularly advantageous with regard to urban fine-particles emissions. In comparison to pure-electric and hydrogen-based drive concepts, those fuels allow a rapid implementation despite the strong legal restrictions [2, 3] using the existing infrastructure and requiring only a slight adaption of the motor process parameters. Renewable fuels are proving to be particularly promising for long-haul transport, heavy goods vehicles, and aviation. However, in contact with metallic materials such as aluminum (e.g., in fuel-carrying components, fuel tanks, etc.) an increased risk for local corrosion attack and a significant material degradation is already known [4-5]. For example, the corrosion behavior in ethanol-containing gasoline fuels fundamentally differs from the behavior known in aqueous electrolytes. Compared to corrosion in seawater, already small amounts of corrosion-stimulating components can lead to a considerable electrochemical corrosion attack. This degradation behavior cannot be explained by the ion concentration itself. Own studies have shown that the degradation mainly depends on the respective fuel composition.

Objective of this contribution is to establish a cross-fuel method to evaluate the material compatibility, based on a physico-chemical approach. Therefore, the degradation behavior of pure aluminum (passive metallic material) was investigated, using the

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example of an ethanol-based fuel (as a representative of oxygenates). By means of a statistical description approach, the main effects and interactions of the respective fuel components on relevant corrosion characteristics were quantitatively characterized. In addition, a physico-chemical analysis of the solubility behavior at the level of intermolecular interactions provides an understanding of the fuel-specific corrosion phenomena. The implementation of the results into a ternary system approach allows the transferability of the results to other oxygenates in principle.

2. Material and Methods

2.1 Material

To avoid superimposed effects caused by precipitations of alloying elements, the pure aluminum EN AW-1050A (composition according to DIN EN 573-3) was chosen for all investigations. The samples were cut from a rolled aluminum sheet and polished with 1000 grid SiC paper in ethanol. The dimensions of the samples are 100 mm x 10 mm x 4 mm (length x width x thickness).

2.2 Fuel Composition

Commercially available gasoline consists of a variety of components. In order to ensure the repeatability of the results, simplified test fuels with a defined composition were used. These are composed of a fossil reference fuel, pure ethanol (99.8% V/V), and corrosion-stimulating contaminants. As a reference fuel, the corrosion-inert “fuel C” (composition: isooctane and toluene, each 50% V/V) in accordance to ASTM D 471 was selected. Ethanol, water, sodium chloride, and acetic acid were added into the reference fuel in various concentrations (refer to section “experimental design”), oriented towards common European field gasoline formulations.

2.3 Immersion Tests

The investigations were carried out as immersion tests in pressure-tight reactors. To increase the reliability of the results, four samples have been placed in each reactor. The samples were positioned approximately half in the liquid phase and half in the vapor phase. A cage-like sample holder made of polytetrafluoroethylene (PTFE) separated the samples from each other as well as from the reactor material in order to avoid superimposed galvanic corrosion. The test temperature was cycled between 21°C (100 hours exposure time including heating phase) and 60°C (68 hours exposure time including cooling phase) in accordance to the guideline VDA 230-207. The total test duration was 12 weeks and the medium was replaced every second week. At this occasion, the samples were evaluated visually, microscopically and gravimetrically.

2.4 Experimental Design (DoE)

In order to provide a sufficient data basis for a robust, exponential approach and to establish a multivariate regression model, a central composite design (CCD) was chosen. Each of the four corrosion-relevant factors *ethanol, water, chloride, and acetic acid* were varied at five levels. The factor setting of the boundary points of the orthogonal experimental space were based on critical field formulations and were coded with the step values “-1” (min) and “+1” (max). The coded step value “0” represents the mean value between “+1” and “-1”. The so-called star points of the experimental space were obtained by multiplying the level values “+1” and “-1” with a factor of α = 1.483. Refer to Table 1 for the respective setting.

Table 1 Experimental setup.

Level	Ethanol [% V/V]	Water [mg/kg]	Chloride [mg/kg]	Acetic Acid [mg/kg]
-α	25	3.102	3.1	7.9
-1	30	6.000	6	20
0	40	12.000	12	45
+1	50	18.000	18	70
+α	55	20.898	20.9	82.1

As corrosion-describing quality criteria, the parameter *corrosion degree* (percentage of the attacked surface in the liquid phase) and *average corrosion depth* were selected. The evaluation of the corrosion degree was based on high resolution sample photos. Microscopic pictures were taken by confocal interferometry. The depth of the corrosion pits was determined by the microscopic focus method. The analysis of main effects and interactions was based on the contrast method; statistical significance was determined by means of ANOVA.

3. Results and Discussion

The results of this contribution focus the quality criteria *corrosion degree* and *corrosion morphology*. Comprehensive results are available in source [6]. Within the investigated experimental matrix, the quality criterion *corrosion degree* is mainly determined by the content of ethanol and water, Fig. 1. Both the main effects of ethanol and water are classified as highly significant ($p < 0.01\%$). An increase of the ethanol content leads to a disproportionate decrease of the corrosion degree. The main effect of water is opposite and much less pronounced: Increasing the amount of water leads to an approximately linear increase in the corrosion degree. The main effects of the factors *chloride* and *acetic acid* are comparatively low and therefore not content of this paper.

Statistically high significant interactions are also found for the factors “ethanol” and “water” ($p = 0.5\%$), Fig. 2. This interaction is in particular pronounced for high concentration of water at low ethanol contents.

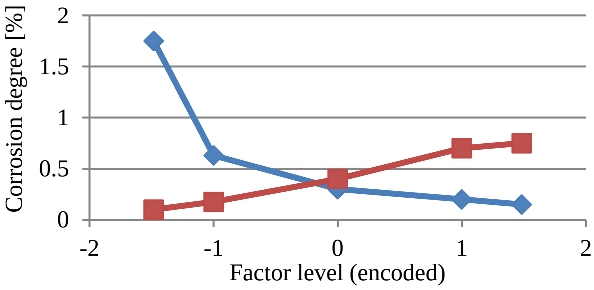

Fig. 1 Main effects of the factors ethanol (blue curve) and water (red curve) on the corrosion degree.

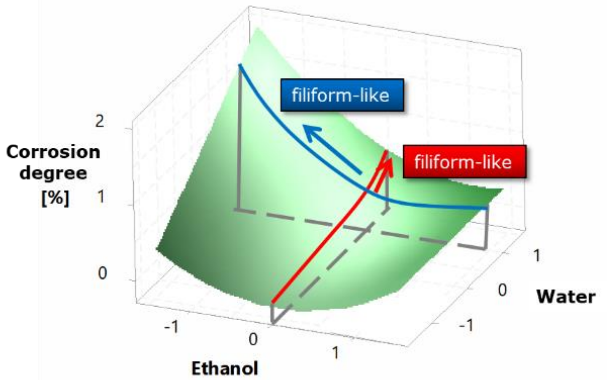

Fig. 2 Interaction effects of the factors ethanol and water on the corrosion degree.

With an increasing amount of ethanol, the water-induced interaction decreases rapidly.

Significant interactions can also be observed with regard to the attack morphology. Basically, two different corrosion morphological structures can be distinguished: filiform-like (local areal) and pitting-like (local), Fig. 3. The morphological structure depends significantly on the respective concentration of the ethanol and water. At low water contents, the morphological structure of the attack changes only slightly (picture A) when varying the ethanol content (picture B).

Especially for lower ethanol amounts, the attack gets a distinctive filiform-like character as the proportion of water increases (picture D). Note that a significant influence of chloride and acetic acid is not discussed in this contribution. This phenomenon corresponds to the average depth of the local attack. Ethanol shows the greatest effect ($p < 0.01\%$) on the quality criterion *corrosion depth*, Fig. 4. Increasing contents of ethanol leads to an almost linear expansion of the corrosion depth. A statistically high significance influence can be documented for the factor water. With increasing water content (> 6,000 mg/kg), a decrease of the corrosion depth can be observed. Remark: Chloride also has a statistically highly significant main effect, which, however, is significantly lower compared to the influence of ethanol. This finding is of fundamental importance, since chloride ions should actually be the most stimulating component in an electrolyte.

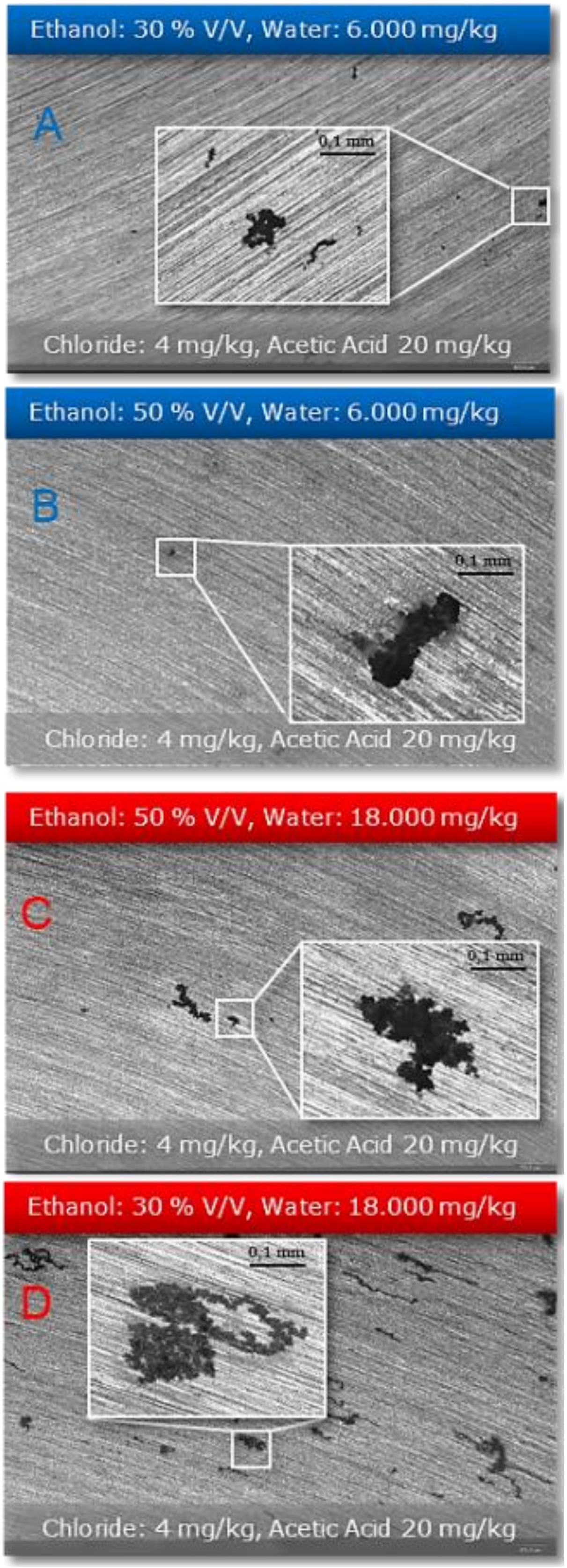

Fig. 3 Corrosion morphological structure, depending on the respective ethanol and water content.

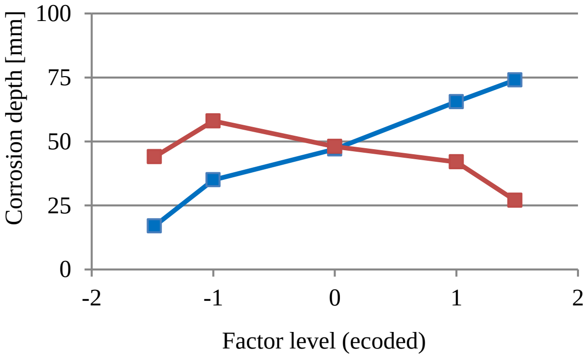

Fig. 4 Main effects of the factors ethanol (blue curve) and water (red curve) on the corrosion depth.

4. Conclusion

Presuming an unchanged ion concentration, the corrosion behavior in ethanol-blended gasoline is mainly affected by the respective ethanol and water content. The corrosion degree decreases significantly with rising ethanol contents and disproportionally increases with higher water concentration. The latter also means that the local attack tends to become a more filiform-like character and shows only slight corrosion depths.

An understanding of this corrosion behavior can be derived by a physico-chemical approach of the molecular structure of the fuel. Basically, the fuel consists of the immiscible components “fuel C” and “water” (including dissociated salts). Adding ethanol as an amphiphilic molecule, however, these two mentioned immiscible components will be “solved” as a micro emulsion. The respective micro-phase solubility depends on the particular blending ratios. It can be assumed that the proximity to the limit of maximum water solubility at a given ethanol content has an influence on the morphological structure of the corrosion attack. For an appropriate visualization, the respective phase position in a ternary phase diagram was correlated with the corrosion characteristics, Fig. 5.

It is noticeable that the distance between the phase position in relation to the binodal curve increases disproportionately with increasing ethanol content. For example, a small distance to the binodal curve (E30)

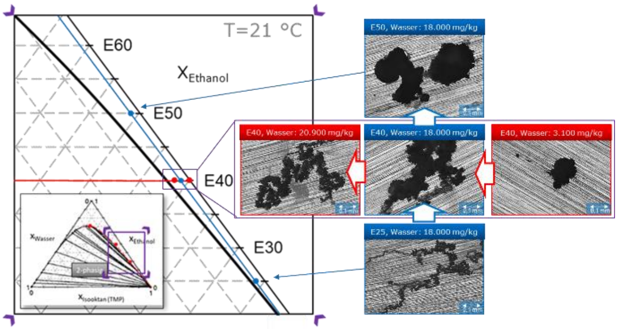

Fig. 5 Correlation between the corrosion morphology and the ternary phase position.

leads to a more filiform-like attack, while the morphological structure tends to get a pitting-like character with increasing ethanol content. Modeling the fuel as a microphase emulsion also explains locally enriched concentrations of chloride. An indirect characterization of the phase size based on the electrical conductivity as an indicator for the micro phase mobility could be achieved in own studies [6]. The mobility of ions depends on the size of such microstructures as well as on intermolecular forces.

Outlook: The modelling of the fuel as a stable micro emulsion and the correlation between the phenomenological results and the phase position in a ternary phase diagram allows a comprehensive understanding of the physico-chemical relationships of corrosion. In addition, a transferability of the results to next generation renewable fuels (oygenates such as OME) is basically possible and implemented in current research activities.

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