EVALUATION OF IRON MESOPARTICLES CORROSION IN OILS

J. Ivanova, T. Melenkova, H. Cesiulis†
Vilnius University, Department of Physical Chemistry, Vilnius, Lithuania

Abstract: The protocol to estimate Fe corrosion in oils was built up. Corrosion estimation was based on the determined concentrations of Fe(II) and Fe(III) that are formed in the corrosive media (e.g. oils) in course of metallic Fe particles corrosion. The spectrophotometric microanalysis technique was adopted to determine Fe(II) and Fe(III) concentrations, and corrosion is expressed as a fraction of Fe(II) and Fe(III) quantity of the initial Fe quantity. The protocol was tested by the experiments on the enforced corrosion of Fe particles in rapeseed and mineral SAE 10 oils containing antioxidants and Fe-particles stabilizing surfactants. The corrosion rates of Fe particles in the rapeseed and SAE 10 mineral oils depend on the particle sizes, as well as on the surfactant and reducing agents used for the synthesis of Fe particles directly in the oil phase by reverse micelles method.

Keywords: iron particles, corrosion, oil, lubrication, spectrophotometry

1. INTRODUCTION

The reliability of machines and mechanisms mainly are defining by the friction processes in the kinematic pairs. For example, in automotive engines it is estimated that about 20-25 % of the generated energy by combustion is lost by the frictional dissipation. The wear defines up to 80-95 % of failures and damages of surfaces [1]. Due to increasing demand for oils and stringent environmental laws the on–going trend in lubricant industry is to explore oils based on the renewable resources, such as various kinds of vegetables. Usually each lubricant contains friction modifiers and anti-wear additives to protect surfaces under the boundary lubrication condition. Nanoparticles as additives shine new properties that differ from the properties of bulk materials, because of size they can penetrate into all places of friction surfaces especially in places where the surface deformations appear due to tribocontacts, local temperature increase or microcracks formation. A wide range of metallic and non-metallic particle additives are described in the literature for lubricants, e.g. [2-7].

Iron nanoparticle technology represents perhaps one of the first generation nanoscale environmental technologies. Over the last few years, various synthetic methods have been developed to produce iron nanoparticles, and nanoscale zero-valent iron particles can be prepared in aqueous solutions via the reduction of ferric iron (Fe(III)) or ferrous iron(II) with appropriate reducing agent such as sodium borohydride [8], hydrazine hydrate [9] or lithium triethylborohydride [10] that yields forming of spherical nanoparticles [11].

A major challenge for environmental applications of reactive nanomaterials is their strong tendency to agglomeration, rapid sedimentation and consequently limited mobility of nanoparticles. For improving nanoparticle stability a steric stabilization using long-chain organic and bioorganic compounds are used [12, 13]. These are caused by the characteristic feature of nanoparticles linked with the extremely high specific area. For example, in the suspension containing typically 1 g/L of Fe-nanoparticles with size ranged from 10 to 100 nm, the specific area exposing to environment is as high as 80-8 m² per 1g of Fe, whereas the specific area of 1 mm thick Fe foil is only 0.0008 m² per 1g of Fe. That results the increasing rate of corrosion even 100000 times only due to the expanded specific area. In addition, reactivity of nano- and meso-particles makes a challenge to prevent them from corrosion. However, information on corrosion of nanoparticles characterization methods has not been documented. Therefore, the aim of this paper is to create a protocol for estimation Fe-particles corrosion in the oils and evaluate it in mineral and rapeseed oils.

† Author for contacts: Prof. Henrikas Cesiulis
E-mail: henrikas.cesiulis@chf.vu.lt
2. EXPERIMENTAL

There were two types of oils used: rapeseed oil (UAB “Naujasis Keilias”, Lithuania), RO, and SAE 10 mineral oil (Orlen Oil, Poland), MO. An antioxidant octadecyl-3-(3',5'-di-t-butyl-4-hydroxyphenyl) propionate, commercial name Irganox 1076 (CAS RN 2082-79-3) from Ciba Chemicals (Tarrytown, NY) was added (0.5 %) to both oils immediately after receiving them from the supplier.

To protect of produced suspensions from sedimentation and agglomeration surfactants were used: glycerol dilaurate GLY G2L (GLY), block copolymer ENB 90R4 (ENB), oxyethylated alcohol OS-20 and lanolin (FVE). The mentioned surfactants were dissolved in the rapeseed and mineral oils at the temperature of 50-60 °C and cooled down before the synthesis of Fe particles. Then synthesis of iron particles was performed at room temperature. To obtain 0.1 wt. % of Fe particles, the corresponding amounts of 1.4M reducing agent and 0.7 M FeSO$_4$ aqueous solutions were added to the oils followed by the vigorous stirring for 30 seconds using Vortex-type mixer, as we described and explained in more details elsewhere [14]. In this way, the amount of water in the final suspension was within 4.4 %. Sizes of iron particles were measured by Dynamic Light Scattering (DLS) under ambient conditions using Zetasizer Nano S equipment (Malvern Instruments).

Corrosion rates of Fe particles in the rapeseed and SAE 10 mineral oils were determined based on the determined concentrations of Fe (II) and Fe (III) in the mixtures. For this purpose the optical density of solutions containing sulfosalicylic acid was measured using a KFK-2MP spectrophotometer. The concentrations range was selected based on the maximal concentration of Fe metallic particles (0.1 wt. %) presenting in the oil phase.

3. RESULTS AND DISCUSSION

Synthesis of Fe particles directly in oil phase. There were two reducing agents used for obtaining iron particles: sodium borohydride NaBH$_4$ and lithium triethylborohydride LiB(C$_2$H$_5$)$_3$H in reverse micelles in oil phase.

The size distributions of obtained Fe particles in rapeseed and SAE 10 mineral oils using NaBH$_4$ as the reducing agent are shown in Fig. 1. It was noticed that in the rapeseed oil with 10 % FVE VO2 lanolin iron particles oxidized shortly at the same rate as in the suspension without surfactant. The smallest size of Fe particles was obtained in the rapeseed oil suspension with 0.5 % OS-20 ethoxylated alcohol. In the rapeseed oil suspensions with 0.5 % ENB 90R4 block copolymer and 10 % GLY G2L glycerol dilaurate surfactants the size distribution ranges of the obtained Fe particles are enough similar.

![Graph](image1.png)

**Figure 1.** The size distribution of Fe-particles obtained using NaBH$_4$ reducing agent in (a) rapeseed oil and (b) SAE 10 mineral oil. Resulting concentration of Fe-particles is 0.1 wt. %.

The size distributions of produced Fe particles in the SAE 10 mineral oil are presented in Fig. 1 b. As it is seen, the size of Fe particles is distributed in a wide range from 50 to 530 nm depending on surfactants used. The smallest iron particles are obtained in the SAE 10 mineral oil suspension with 0.5 % OS-20, the biggest - with 10 % GLY G2L and without surfactant.

The size distributions of obtained Fe particles using LiBET3H reducing agents in rapeseed and SAE 10 mineral oils are shown in Fig. 2. Similarly as using NaBH$_4$ to prepare Fe-containing suspension in
rapeseed oil (Fig. 2a), the same fast oxidation processes of Fe particles were observed using LiBEt₃H too. Ineffective in preparation of Fe particles was 0.5 % OS-20 surfactant.

The size of Fe particles is distributed over a wide range from 105 to 825 nm (see Fig. 2b). The smallest size of Fe particles were produced in SAE 10 mineral oil without additives (105-255 nm). Slightly higher Fe particle sizes obtained with 10 % FVE VO₂ lanolin (140-295 nm). The largest size of Fe particles was obtained in mineral oil with 10 % of GLY G2L (295-825 nm).

**Figure 2.** The size distribution of Fe-particles obtained using reducing agent LiB(C₂H₅)₃H in (a) rapeseed oil and (b) SAE 10 mineral oil. Resulting concentration of Fe-particles is 0.1 wt. %.

**Protocol for the estimation of Fe-particles corrosion in oils.** As the documented procedure for Fe-particles corrosion in oils still does not exist, we made an attempt to create one. In course of corrosion of metallic Fe particles are formed Fe(II) and Fe(III) compounds in the corrosive media (e.g. oils). We adapted microanalysis technique for determination of Fe(II) and Fe(III) concentration, and corrosion is estimating based on the determined concentrations of Fe(II) and Fe(III) in the corrosive media as a fraction of primary concentration of Fe.

It is known that sulfosalicylic acid dissolves Fe(II) and Fe(III) compounds forming coloured complexes with them [15], whereas the metallic Fe remains insoluble. Therefore it is possible to determine concentrations of Fe(II) and Fe(III) by means of photocolorimetry. It was determined separately that maximal absorbance of Fe(II) and Fe(III) complexes with sulfosalicylic acid was obtained at the wavelength λ=490 nm. For calibration the concentrations range was selected based on the typical 0.1 wt. % Fe concentration in the oil phases. Test samples for spectrophotometric analysis were prepared in this way. In a 50 mL flask added a certain amount of standard FeSO₄ solution (18; 36; 72; 144 and 288 µL), then added 1 mL of 20 % sulfosalicylic acid, diluted them with distilled water, and mixed thoroughly. The thickness of cuvettes was selected in a way that the values of optical density would be ranged from 0.1 to 1.0; in this case we used 3 cm cuvettes. At this wavelength the optical density (D) linearly depends on Fe (II/III) concentration in the solution (see Fig. 3).

**Figure 3.** Calibration graph for the determination Fe(II) and Fe(III) concentrations in liquid phase recalculated as percentage of total Fe in the oil phase (λ=490 nm).
Prior determination of Fe(II) and Fe(III) formed during corrosion of Fe particles in the oil, the all amount of the mixture containing metallic Fe and Fe(II) and (III) was precipitated by dilution the oil suspension with heptane. Then a precipitate rinsed by diethyl ether and analysis is performed as described above.

**Testing protocol for corrosion estimation.** Corrosion of synthesized Fe particles was enforced by mixing suspensions in the open tube for fixed period of time from 1 to 5 minutes. Then suspension leaved for 24 hours, and Fe particles/iron oxides were separated from the oil phases and thoroughly washed with heptane.

Fig. 4 shows the fraction of oxidized Fe in the RO and MO suspensions containing surfactants and at various agitation durations. Fe-particles in course of reduction by NaBH₄ are almost completely oxidized in the RO with OS and the MO with FVE, irrespectively of suspension blending duration. In the cases of RO+OS+Fe and MO+FVE+Fe suspensions, the corrosion of Fe rates correlate with particle sizes, i.e. the lower the Fe particle sizes, the larger contact area with the corrosive environment and corrosion of Fe is faster (up to full oxidation). Although the size distribution of Fe particles in the RO with ENB and GLY are sufficiently similar (see Fig. 1 a), the corrosion rates of Fe are totally different (see Fig. 4 a). This can be explained by the composition of produced suspensions; i.e. the combination of RO/MO+surfactant induces or reduces the oxidation rate of Fe particles. The ENB surfactant provides the best protection against corrosion of Fe, but the oxidized amount of Fe significantly increases by the increasing of agitation duration from 1 to 5 minutes. RO+GLY composition maintains a uniform oxidized Fe content, irrespectively of the blending duration.

Corrosion rates of Fe particles in the SAE strongly depend on the suspension blending duration, i.e. the time of exposure to the air (Fig. 4 b). Increase the blending the MO+ENB suspension from 1 to 5 minutes results the slight increase in fraction of oxidized Fe particles from 10 to 30 %. Meanwhile, in the MO+OS suspension corrosion rate of Fe particles significantly depends on a contact time with the air. It should be noted that the OS surfactant provides effective protection against corrosion, mixing in a minute, but by increasing the blending duration from 1 to 5 minutes the preservation mechanism of adsorbed OS film becomes ineffective. As it is seen in Fig. 1 b, the size distribution ranges of Fe particles in the MO with GLY and without surfactant are sufficiently similar. However, the fraction of oxidized Fe particles in the MO is lower than that in the suspension with GLY. It is obvious that MO+GLY G2L composition is chemically affects Fe particles and increases their oxidation.

![Figure 4](image-url)

**Figure 4.** The fraction of corroded Fe (%) in: (a) rapeseed and (b) SAE 10 mineral oils with different surfactants and agitation duration. NaBH₄ reducing agent was used for preparation of Fe particles.

Fig. 5 shows the fractions of oxidized Fe particles in the RO and MO suspensions with different surfactants and agitation duration. In RO or MO suspensions containing ENB the corrosion rate of Fe significantly increases with the increase of blending duration. The results presented in Fig. 5 a show that the corrosion rate of Fe correlates not only with the Fe particle sizes, but with the overall
composition of suspensions.

The study of Fe corrosion in the RO with OS demonstrates that this composite system enhances the corrosion rate of Fe particles irrespective on their sizes and the blending duration. The fraction of oxidized Fe particles in RO+GLY suspension is within ~23 %, irrespectively of Fe particle sizes and the blending duration. The corrosion rates of Fe associated with the range of Fe particle sizes and stabilization mechanism of GLY surfactant.

![Figure 5](image1.png)  
**Figure 5.** Oxidized fraction of Fe (%) in: (a) rapeseed and (b) SAE 10 mineral oils with different surfactants and agitation duration. LiBEt₃H reducing agent is used for preparation of Fe particles.

The results presented in Figure 5 b shows that in MO+GLY suspension the fraction of oxidized Fe particles remains within 15 %, whereas in MO+FVE suspension the fraction of oxidized Fe remains uniform (~38 %), independently of blending duration and sizes of Fe particles.

Summarizing, the corrosion rate should be correlated with the Fe particle size. However, it is emphasized that in some cases the stabilization mechanism of surfactant becomes the most important. As it is shown in Fig. 4 and 5, the fraction of oxidized (corroded) Fe increases with increasing blending duration (contact with air duration) and decreasing sizes of Fe particles.

It is noted that using NaBH₄ and LiBEt₃H for the synthesis of Fe-particles, the fractions of oxidized Fe particles in the rapeseed oil are quite similar. Meanwhile, in case of reduction by LiBEt₃H in the MO suspensions the fraction of oxidized Fe particles is lower, than in case of reduction by NaBH₄. In addition, in most cases, irrespective of used oil medium, but depending on the blending duration, the OS surfactant is not effective for protection of Fe particles against corrosion.

3. CONCLUSIONS

1. Nano and meso-particles possess high specific area exposing to environment, therefore heterogeneous reactions, including corrosion occurs faster. The protocol for the estimation of Fe particles corrosion in the oils was created. Corrosion is estimating based on the determined by means of spectrophotometry Fe(II) and Fe(III) concentrations in the corrosive media (e.g. lubricating oils) as a fraction of primary concentration of Fe particles.

2. The protocol was approved by the evaluation of provoked Fe particles corrosion in rapeseed and mineral SAE 10 oils containing antioxidants and Fe-particles stabilizing surfactants. The corrosion rates of Fe particles in the rapeseed and SAE 10 mineral oils depend on the particle sizes, as well as on the surfactant and reducing agents used for the synthesis of Fe particles directly in the oil phase by reverse micelles method.
ACKNOWLEDGMENT

The authors acknowledge funding from FP7 Oil&Sugar project (295202). Also, partial funding was granted by the Research Council of Lithuania (MIP-031/2014). Authors are grateful to dr. S. Asadauskas (Centre for Physical Sciences and Technology, Vilnius) for delivery of some surfactants and antioxidants, and to JSC “Thermofisher Scientific Baltic” for opportunity to use Zetasizer for the determination the size of Fe particles.

REFERENCES