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THE IMPACT OF AN IRON-BASED MODIFIER FOR LIQUID FUELS ON HUMAN HEALTH AND THE ENVIRONMENT

WPŁYW NA ŚRODOWISKO I ZDROWIE CZŁOWIEKA MODYFIKATORA ŻELAZOWEGO SPALANIA PALIW CIEKŁYCH

Abstract: It is necessary to use specific modifiers in order to reduce harmful emissions arising in the combustion of liquid fuels into the atmosphere. Such modifiers include organic metal salts which are soluble in fuels and tend to form metal oxides under combustion process conditions, improving the oxidizing properties of fuels. The modifier, described in this paper was used in liquid fuel combustion tests, showing a desirable effect of reducing CO, NO_x and hydrocarbon emissions. For such modifiers to be approved for use, examination of their physico-chemical, toxicological and ecotoxicological properties is required according to REACH Regulation. REACH is intended, first of all, to provide appropriate protection to the environment and human health, while striving to maintain competitiveness of European enterprises in the global market. Discussed in this paper is the effect of an iron-based modifier for liquid fuels on human health and on the land and air and the aquatic environment. The modifier was subjected to physico-chemical analyses, and toxicological and ecotoxicological tests in accordance with good laboratory practice and OECD guidelines. The test results indicate that the modifier is a safe substance, posing no hazard to human health or the environment.

Keywords: fuel modifiers, toxicology, ecotoxicology, combustion, liquid fuels

Introduction

Fuel combustion processes generate harmful emissions into the atmosphere. Specific additives are used commercially in the power industry to reduce such emissions. Such additives include modifiers based on organic metal salts, dispersed in organic solvents, which are soluble without limitations in the combusted liquid fuels. Testing of the product is required, to determine its toxicological and ecotoxicological properties in connection with the intended launching of a facility producing 100 Mg per year of the modifier [1].

The toxicological tests are intended to assess any undesirable or harmful effect of chemical substances or other factors on living organisms, and to perform a probability analysis for their occurrence in various exposure conditions. Living organisms are exposed to the combined positive and negative effect of chemical substances and environmental conditions during their growth and development. The observed impact is the response of such living organisms to their exposure to all biologically active components [2, 3].

Ecotoxicological properties are established in examinations of organisms, populations, communities, biocenoses, and ecosystems in the aspect of their exposure to chemical factors, their penetration from the environment into the organisms, as well as any toxic effect that may occur. Ecotoxicology as a science deals with the impact of toxic substances on the biocenosis, especially on the parameters of the life cycle of organisms in natural conditions. Such life cycle parameters include: reproduction, lethality, life span, and maturing time [4].

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Discussed in this paper is the effect on human health and the environment of an iron-based modifier for liquid fuels. The necessary tests, enabling the assessment of risks to human health and the environment, were carried out, in accordance with Good Laboratory Practices, at the Institute of Industrial Organic Chemistry, Pszczyna, Poland.

Methodology

Assessment of environmental risks

Ecotoxicological tests were carried out on the example of respiration inhibition of micro-organisms in activated sludge according to OECD Guideline No. 209 (Method C.11) [5, 6]. The test was intended to assess the toxic effect of an iron-based modifier on micro-organisms in activated sludge. The test system was a mixture comprising water, a synthetic sewage feed, activated sludge, and a reference material solution.

Two sets of test samples were prepared in the initial experiment: one set comprising a nitrification inhibitor. A N-allylthiourea (ATU) solution at a concentration of 2.32 g/dm^3 was used for inhibiting nitrification.

Every test system included an abiotic control (sample F_A), experimental control (samples F_{B1}-F_{B2}), samples containing the test material (F_{T1}-F_{T5}) and samples containing the reference material (F_{R1}-F_{R5}). Activated sludge from a biological waste-water treatment plant was used as a microbial inoculum.

The respective amounts of the test material components are shown in Table 1.

Table 1

Amounts of components in the respective mixtures (test material: iron-based modifier)

Components of mixtures	**Amounts in test vessels**				
	F_{T1}	F_{T2}	F_{T3-5}	F_{B1-2}	F_A
Test material [mg]	5	50	500	0	500
Synthetic sewage feed [dm^3]	0.016	0.016	0.016	0.016	0.016
Activated sludge [dm^3]	0.25	0.25	0.25	0.25	0
Water [dm^3]	A volume of water was added to obtain a total of 0.5 dm^3 in every test vessel				
Total volume of mixture [dm^3]	0.5	0.5	0.5	0.5	0.5
Concentrations in the mixtures:					
of test material [mg/dm^3]	10	100	1000	0	1000
of activated sludge (suspended solids) [g/dm^3]	1.5	1.5	1.5	1.5	0

All mixtures were aerated intensely and incubated for three hours. The test material was used in the following concentrations: 10.0; 100.0; 1000.0 mg/dm^3. The reference material was used at the following concentrations: 0.5; 5.0; 10.0; 20.0; 50.0 mg/dm^3. Each sample was transferred into a BOD bottle after 3 hours and the concentration of oxygen was measured within 10 minutes using an oxygen electrode.

Oxygen consumption rate (R), as expressed in milligrams per liter per hour [mg/dm^3·hr], and specific respiration rate (R_S), as expressed by the amount of oxygen consumed by 1 gram of dry weight of the microbial activated sludge per hour [mg/g·hr], were calculated using the following formula:

$$R = (Q_1 - Q_2) / \Delta t \cdot 60 \tag{1}$$

where Q_1 is the oxygen concentration at the beginning of measurement [mg/dm^3], Q_2 is the oxygen concentration at the end of measurement [mg/dm^3], Δt is the duration of measurement:

$$R_S = R / SS \qquad (2)$$

where SS - suspended solids concentration, as found at the beginning of the experiment [g/dm^3].

Based on the data obtained from Equations (1) and (2), the inhibitory effect of the test material on micro-organisms in the activated sludge was measured. This enables the calculation of the value of EC_{50}, defined as the statistical effective concentration, which induces in the environmental sewage feed a respiration inhibition of 50% [2]. The value of EC_{50} was calculated using the software ToxRat Professional 2.10

$$I = \left[1 - \frac{(R - R_A)}{R_B}\right] \times 100 \ [\%] \qquad (3)$$

where I is the percentage of respiration inhibition, R is the oxygen consumption by the test sample [mg/dm^3·hr], R_A is the oxygen consumption by the abiotic control [mg/dm^3·hr], R_B is the oxygen consumption by the experimental control [mg/dm^3·hr].

Assessment of risks to human health

Toxicological tests were carried out according to OECD Guideline No. 405 (Method B.5) for the acute irritation/corrosion of the eye in rabbit [7, 8]. It was the objective of the test to provide information about the potential health risks, caused by the impact of the iron-based modifier on the eye.

Table 2

Grading of ocular lesions [6, 7]

Cornea (opacity: degree of density)	
No ulceration or opacity	0
Scattered or diffuse areas of opacity, details of iris clearly visible	1
Easily discernible translucent area, details of iris slightly obscured	2
Nacrous area; no details of iris visible, size of pupil barely discernible	3
Opaque cornea, iris is not discernible through the opacity	4
Iris	
Normal	0
Markedly deepened rugae, congestion, swelling, moderate hyperaemia or injection; iris is reactive to light	1
Hemorrhage, gross destruction, or no reaction to light	2
Conjunctiva - redness (refers to palpebral or bulbar conjunctiva; excluding cornea and iris)	
Normal	0
Some blood vessels hyperaemic	1
Diffuse, crimson color; individual vessels not easily discernible	2
Diffuse, beefy red	3
Conjunctiva - swelling (refers to eye lids and/or nictitating membranes)	
Normal	0
Some swelling above normal	1
Obvious swelling, with partial eversion of lids	2
Swelling, with lids about half closed	3
Swelling, with lids more than half closed	4

In the experiment, 0.1 cm^3 of the test material (iron-based modifier) was applied into the conjunctival sac of one eye of a test animal; the other eye, which remained untreated, served as a control. The test was carried out in three animals to confirm the actual irritant effect or absence of irritation.

For the duration of the experiment, the animals were subjected to daily general clinical observation in respect of disease incidence and lethality. Detailed clinical observations for any lesions in the cornea, iris and conjunctiva were assessed after the lapse of 1, 24, 48 and 72 hours from the application of the test material.

The scoring of acute irritation/corrosion of the eye was defined using the grading of ocular lesions (Table 2). The grading concerns lesions in the cornea, iris and conjunctiva.

Results

Assessment of environmental risks

After the experiment, the following calculations were made for every sample: oxygen consumption (R), specific respiration rate (R_S) and percentage of respiration inhibition (I) in micro-organisms from activated sludge by the test material (iron-based modifier). The test results are shown in Table 3.

Table 3

Results of tests for various concentrations of the iron-based modifier

	Oxygen consumption [mg/dm³·hr]	**Specific respiration rate [mg/g·hr]**	**Percentage of respiration inhibition in micro-organisms from activated sludge [%]**
Control	32.46	21.64	-
Test material concentration: 10 mg/dm³	32.70	21.80	0.74
Test material concentration: 100 mg/dm³	32.28	21.52	2.03
Test material concentration: 1000 mg/dm³	31.94	21.29	3.08

It was established that the concentration of the iron-based modifier, causing 50% percentage of respiration inhibition in micro-organisms from the activated sludge (EC_{50}) was higher than 1000 mg/dm^3.

Assessment of risks to human health

Ocular lesions were observed in the conjunctiva in rabbits after application of the test material (iron-based modifier), although such changes were not detected in the iris or cornea. Clinical observation 1 hr after the test substance application detected diffuse crimson redness in the conjunctiva in three rabbits, accompanied by congestion of the nictitating membrane and circumcorneal injection. Moreover, minor conjunctival swelling and swelling of the nictitating membrane was found in rabbits 2 and 3, while swelling of the nictitating membrane alone was observed in rabbit 1.

24 hours after the test substance application, rabbits 1 and 3 showed hyperaemia of some blood vessels and of the nictitating membrane, while rabbit 2 showed diffuse crimson

redness, hyperaemia of the nictitating membrane and circumcorneal injection. In addition, swelling of the nictitating membrane was observed in rabbits 1 and 2.

Clinical observation 48 hours after the test substance application showed hyperaemia of some blood vessels and of the nictitating membrane in the conjunctiva in the three rabbits. 72 hours after the test substance application, no ocular lesions were found in the conjunctiva in rabbits 1 and 3 while only rabbit 2 continued to have hyperaemia of some of its blood vessels and of the nictitating membrane.

Table 4 shows grading of acute eye irritation/corrosion based on the grading scale referred to in Table 2, pursuant to OECD Guideline 405 (Method B.5). The effect of acute eye irritation/corrosion in rabbit was assessed based on average results observed after 24, 48 and 72 hours. Pursuant to the OECD Guideline, results observed 1 hour after the application of the iron-based modifier are omitted from such grading.

Table 4

Grading of acute eye irritation/corrosion

Rabbit	**Eye part**	**After**				**Average results after 24, 48 and 72 hours**
		1 hr	**24 hrs**	**48 hrs**	**72 hrs**	
1	Cornea	0	**0**	**0**	**0**	0.0
	Iris	0	**0**	**0**	**0**	0.0
	Conjunctiva - redness	2	**1**	**1**	**0**	0.7
	Conjunctiva - swelling	1	**1**	**0**	**0**	0.3
2	Cornea	0	**0**	**0**	**0**	0.0
	Iris	0	**0**	**0**	**0**	0.0
	Conjunctiva - redness	2	**2**	**1**	**1**	1,3
	Conjunctiva - swelling	1	**1**	**0**	**0**	0.3
3	Cornea	0	**0**	**0**	**0**	0.0
	Iris	0	**0**	**0**	**0**	0.0
	Conjunctiva - redness	2	**1**	**1**	**0**	0.7
	Conjunctiva - swelling	1	**0**	**0**	**0**	0.0

Analysis of the test results

Assessment of environmental risks

The results of tests of the iron-based modifier indicate that, in experimental conditions in a test concentration range from 100 to 1000 mg/dm^3, the test material shows an inhibitory effect on respiration of micro-organisms in activated sludge. The test material concentration for which 50% respiration inhibition of micro-organisms in the activated sludge was observed (EC_{50}) is higher than 1000 mg/dm^3.

Respiration rate in the control was R_S = 21.64 mg/g·hr (Table 3), which seems a reliable result because it is higher than the limiting result of 20 mg of oxygen per gram of activated sludge per hour.

Assessment of risk to human health

After application of the test material (iron-based modifier), no ocular lesions were detected in the cornea and iris while the conjunctiva of the test animals showed only temporary lesions. Average results after 24, 48 and 72 for the conjunctiva (in three rabbits) were 0.9 for the redness and 0.2 for the swelling.

Based on the above results, it was found, pursuant to Annex to the Regulation of the Minister of Health of 10 August 2012 on the criteria and methods for the classification of chemical substances and mixtures, that the iron-based modifier for liquid fuels has no irritant effect on the eye in rabbit [9].

Moreover, pursuant to Regulation of the European Parliament and of the Council (WE) No. 1272/2008 of 16 December 2008 on the Classification, Labelling and Packaging of Substances and Mixtures (CLP), the iron-based modifier for liquid fuels is not categorized which means, it is not a hazardous substance and poses no risk to human health [10].

Summary and conclusions

This paper presents the results of toxicological and ecotoxicological tests on two selected examples. The toxicological results are discussed using the example of acute eye irritation/corrosion test in rabbit. No ocular lesions were observed in the cornea or in the iris while only temporary lesions were detected in the conjunctiva.

Ecotoxicological tests are discussed on the basis of the percentage of respiration inhibition in activated sludge. The test results indicate that the modifier's concentration causing 50% respiration inhibition in micro-organisms in activated sludge is higher than 1000 mg/dm^3.

Other results of toxicological and ecotoxicological tests indicate that the test iron-based modifier for liquid fuels is a safe substance, posing no risk to human health or the environment. Such tests, although not discussed in this paper, are going to be used for preparing registration documents for the product under REACH.

Based on the test results and pursuant to the Annex to the Regulation of the Minister of Health of 10 August 2012 on the criteria and methods for the classification of chemical substances and mixtures [9], the iron-based modifier for liquid fuels is found to be a safe substance, posing no risk to human health and to the land and air and the aquatic environment.

References

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[7] OECD Guideline 405 for the Testing of Chemicals: Acute Eye Irritation/Corrosion; 2012.

[8] EU Method B.5.: Acute Toxicity: Eye Irritation/Corrosion. Regulation of the Commission (EC); No. 440/2008 of 30 May 2008.

[9] Regulation of the Minister of Health of 10 August 2012 on the criteria and methods for the classification of chemical substances and mixtures. DzU 2012, item 1018.

[10] Regulation of the European Parliament and of the Council (EC) on the Classification, Labelling and Packaging of Substances and Mixtures (CLP); No. 1272/2008 of 16 December 2008.

WPŁYW NA ŚRODOWISKO I ZDROWIE CZŁOWIEKA MODYFIKATORA ŻELAZOWEGO SPALANIA PALIW CIEKŁYCH

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Abstrakt: W celu ograniczenia emisji szkodliwych produktów spalania paliw ciekłych do atmosfery występuje konieczność stosowania specyficznych modyfikatorów. Jednym z nich są rozpuszczalne w paliwie organiczne sole metali, które w warunkach procesu spalania tworzą tlenki metali poprawiające własności utleniające paliw. Opisany modyfikator zastosowany został w testach spalania paliwa ciekłego, gdzie wykazał korzystny wpływ w ograniczeniu emisji węglowodorów, CO i NO_x. Dopuszczenie do stosowania wyżej wymienionych modyfikatorów wymaga określenia ich własności fizykochemicznych, toksykologicznych i ekotoksykologicznych w ramach rozporządzenia REACH. Najważniejszym celem tego rozporządzenia jest zapewnienie właściwej ochrony zdrowia ludzkiego i środowiska przy jednoczesnym dążeniu do zachowania konkurencyjności europejskich przedsiębiorstw na światowym rynku. W pracy przedstawiono wpływ na zdrowie człowieka oraz na środowisko wodne, lądowe i powietrzne modyfikatora żelazowego do paliw ciekłych. Badania fizykochemiczne, toksykologiczne i ekotoksykologiczne tego dodatku wykonane zostały zgodnie z dobrą praktyką laboratoryjną oraz wytycznymi OECD. Na podstawie uzyskanych wyników badań stwierdzono, iż badany modyfikator jest substancją bezpieczną i niestanowiącą zagrożenia dla zdrowia człowieka oraz środowiska.

Słowa kluczowe: modyfikatory paliw, toksykologia, ekotoksykologia, spalanie, paliwa ciekłe