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Preliminary Study of Ten Randomly Selected Metalworking Fluids Biodegradability

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***Abstract* – There have been studied 10 different metalworking fluids of emulsion, semi-synthetic and synthetic types, according to their availability to biodegradation. As the microbial inoculum was used the activated sludge becoming from the sewage treatment plant treating the municipal sewage waste waters and obtained results were compared. It was find out that only one of tested fluids has the biodegradability lower than 20 % after 21 days of cultivation. Six samples have the biodegradations rate in the range 39-55 % and two had their biodegradability above 60 %. As the most biodegradable tested samples of metalworking fluids were evaluated synthetics with their biodegradability above 44 %. Two of them achieved the biodegradability 50-55% and one reached the level 68 %. Than followemulsions; their biodegradabilitywas 39-40% in three cases of four tested samples. One sample achieved the biodegradations rate 65%, but it has to be note that this sample had lower addition of organic carbon input – this was 141 mg C in opposite 252-281 mgC. One sample of semi-synthetics has the lowest reached ultimate biodegradation – 19.5%.**

***Keywords* – Biodegradability, Metalworking Fluids, Cutting Fluids, Carbon Dioxide, Microorganisms.**

I. INTRODUCTION

Modern metalworking fluids (MWFs) used in many machining operationsare formulated from a range of base fluids and chemical additives. Straight oils which usually didn´t contain any water, soluble oils (usually called emulsion or macro-emulsions), semi-synthetic fluids (semi-chemical fluids, semi-synthetic soluble oils or micro-emulsions) and synthetic fluids (which usually didn´t contain any mineral oil). Whether the cooling or lubricating the cutting zone is desired; different MWF is chosen. Typical advantages and disadvantages of different MWFs provide Table2; while the typical composition is shown in the Table 1. Straight oils are excellent in the lubricating; while synthetic fluids are the choice when the cooling is required. Emulsions are in the middle, but in some of shaping operations may be unstable, e.g. when the ultrasound during the machining is utilized. Emulsions, semisynthetic and synthetic fluids are diluted with water prior to use to obtain the proper concentration; which ensures the desired properties during the machining. The lubricant base stock may differ from one to other, but primarily it may be mineral base derived from the crude oil, vegetable or animal base and synthetic base fluids. The use of mineral oil base fluids is on the decline due to their high toxicity and low biodegradability. Synthetic base fluids may include mostly synthetic hydrocarbons, synthetic esters orpolyalkene glycols [1], [2], [3], [4].

For environmentally adapted lubricants were identified criteria such as: high biodegradability, low toxicity, relative content of renewable raw material, functional performance during use phase and favorable environmental performance over the whole life cycle (from raw material production through MWF blending and use to recycling or disposal) [2].

Biodegradability is the main aspect with respect to environmentally friendly. Biodegradable substance is susceptible to biochemical breakdown by the action of microorganism. The original molecule of a recyclable substance will disappear in the primary degradation. Then, carbon dioxide, hydrogen, and biomass will form in the ultimate degradation. Ultimate biodegradability is important as it ensures the safe reintegration of the organic material in the natural carbon cycle [5].

Table 1 Composition of different MWFs [1].

Type of Additive	**A***	**B***	**C***	**D***
Mineral oil	60-90	40 - 85	<40	
Synthetic lube			40	40-80
Lubricity/ oiliness agents	< 40	< 10	< 20	< 10
EP-additives	< 15	< 30	< 10	< 45
Emulsifiers		< 30	< 35	
Corrosion inhibitors		< 10	< 5	< 10
Coupling agents		< 5	< 8	< 5
Biocides		< 2	< 2	< 2

A Straight oils, B * Emulsion, C* Semi-synthetics, D * Synthetics.*

The biodegradability of synthetic hydrocarbons such as polyalphaolefines may vary from 20-95% depends on their viscosity. Synthetic esters have excellent biodegradability properties and very low toxicity. Polyalkene glycols exhibit low toxicity, and while they are biodegradable, the degradations rate is slow. The bioresistance leads to longer sump life. Anyway while the final composition of any MWFs may consist of 15-20 ingredients together with some changes which undergoes during the span life; the final biodegradability may be different to those of used base fluids and additives. Many hundreds of combination of the different ingredients is possible. Emulsifiers (e.g.

sulfonates, fatty alcohol ethoxylates, quarternary ammonium salts etc.) are added to assist in the formation and stabilization of emulsions (they put together the oil droplets to water phase). Corrosion inhibitors (e.g. sulfonathes, amine, zink alkyl dithiophosphate etc.) are added to protect the metal part from contact with the oxygen to limit rust and corrosion of ferrous and non-ferrous metals. Biocides (e.g. phenol derivatives, formaldehyde releasers, isothiazolinones etc.) are added to control the bacterial contamination which may cause the degradation of the fluid. While the lifespan of the fluid is reduced the costs for the machining are increased. Anyway many microorganisms may be also harmful for the operator’s health and may cause some skin irritations (occupational dermatitis) or respiratory problems (chronic bronchitis, asthma etc.). Other common additives are anti-wear additives, extreme pressure additives, foam inhibitors etc. [1], [2], [4]-[6].

The main purpose of this study was to evaluate and compare the ultimate degradability’s of 10 different metalworking fluids of emulsion, semisynthetic and synthetic types randomly selected from the market.

II. MATERIAL AND METHODS

All chemicals were analytically graded and employed without any further purification. List of chemicals used for the preparation of mineral medium for the biodegradability test is defined in [14].

For the biodegradability experiment there were selected 10 different MWFs from emulsion, semisynthetic to synthetic types randomly selected from the market. Concentrates were diluted with the tap water prior to use. The composition of hazardous substances as they are listed in the material safety data sheet is shown in the Table 3. MSDS of the sample 10 was not available.

TOC (total organic carbon) measurements were determined by direct injection of the diluted sample (1:2) into a Shimadzu TOC-VCPN analyzer, calibrated with standard solutions of potassium phthalate. The starting concentration of the TOC for samples was set up to 381-375 mg/l (one sample has the concentration 188 mg/l TOC), while the total volume of the solution was 750 ml.

Ultimate biodegradability of the samples were performed as it was previously described in [15] and [16] by the utilization of modified test. In a closed system of bottles (simple schema is shown in the Fig. 1), there were recorded the change in the conductivity of absorption solution after reaction of evolved carbon dioxide by the inoculum placed separately in the reaction bottle together with the tested sample and mineral medium. The biodegradability was calculated from the amount of produced carbon dioxide according to (1):

$$D = 100.\left(m_{CO_2\,test} - m_{CO_2\,blank}\right) / ThOC \qquad (1)$$

Where, *ThOC* is the carbon input by the application of the test substance in mg C and m_{CO_2} is the amount of evolved carbon dioxide (in mg C), calculated from the calibration curve according to recorded conductivity of absorption solution.

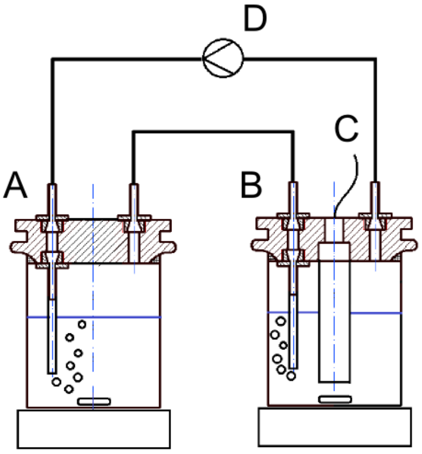

Fig.1. Schema of the apparatus for the indirect biodegradability measurement.
A – reaction bottle, B – carbon dioxide absorption bottle, C – Conductivity probes, D – peristaltic pump.

III. RESULTS

At the Fig. 2, 4 and 6 there are displayed recorded amounts of evolved carbon dioxides and at the Fig. 3, 5 and 7 there are shown the ultimate biodegradation curves for tested emulsion, semi-synthetic and synthetic types of metalworking fluids. The amount carbon dioxide produces in the blank was in the limits of standardized test (below 50 mg C). The production of carbon dioxide in the blank is usually explained by the endogenous respiration; while there was no addition of organic carbon. The degradation of the standard chemical (glucose) was carried out as expected and was above 60 % of theoretical carbon dioxide production in 10-day window. Tested emulsions had similar degradability (39.6 – 40.6 %) except Sample 4 which achieve 65.7 %, while the carbon input was only 141 mg C. Semi-synthetics had degradability very different (sample 5 achieved 19.5 %; and sample 6 achieved the biodegradability over twice – 43.5 %). As the mostly degradable metalworking fluids were investigated samples of synthetics where the degradation levels reached 44.1 % (Sample 8), 50.5 % (Sample 10), 54.7 % (Sample 9) and 68.3 % (Sample 7). Results are summarized in the Table 4.

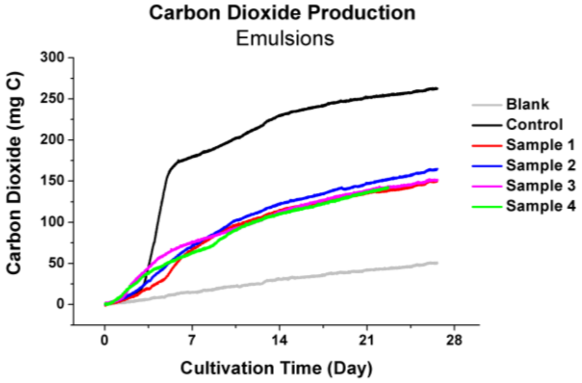

Fig.2. Carbon dioxide production – Emulsions.

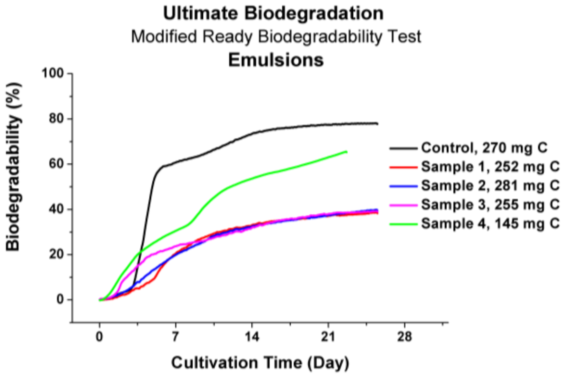

Fig.3. Degradation curves – Emulsions.

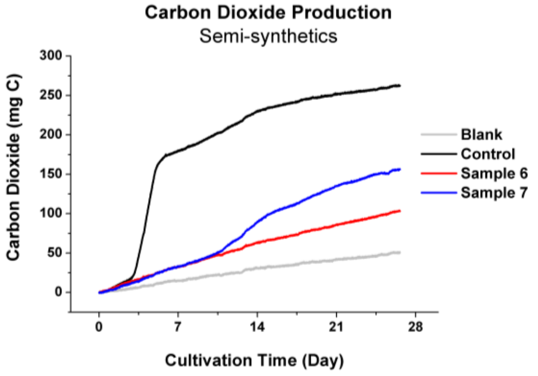

Fig. 4 Carbon dioxide production – Semi-synthetics.

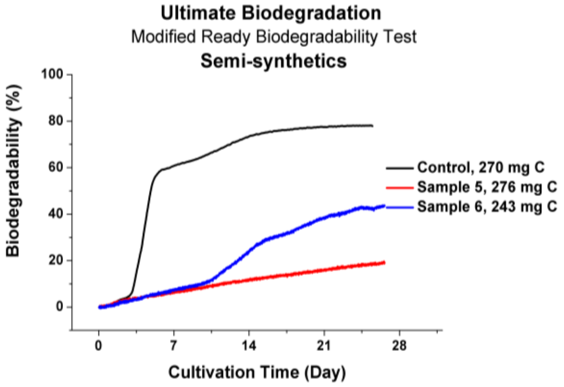

Fig.5. Degradation curves – Semi-synthetics.

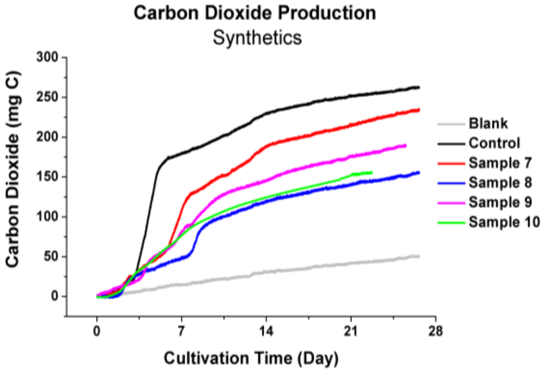

Fig.6. Carbon dioxide production – Synthetics.

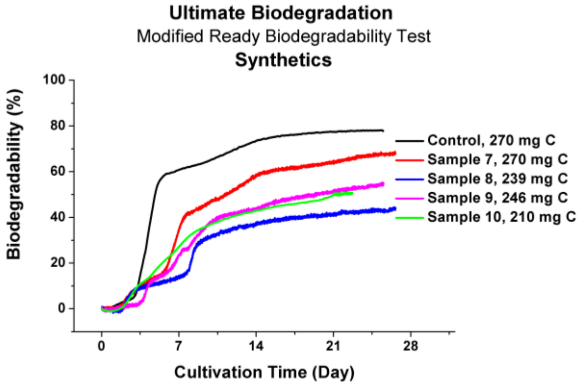

Fig. 7 Degradation curves – Synthetics.

Table 4: Ultimate biodegradability of tested samples.

	Carbon input [mg C]	**Biodegradability [%]**
Emulsions		
Sample 1	**252**	**39.6**
Sample 2	**281**	**40.6**
Sample 3	**255**	**39.7**
Sample 4	**141**	**65.7**
Semi-synthetics		
Sample 5	**276**	**19.5**
Sample 6	**243**	**43.5**
Synthetics		
Sample 7	**270**	**68.3**
Sample 8	**239**	**44.1**
Sample 9	**246**	**54.7**
Sample 10	**281**	**50.5**

IV. CONCLUSION

Followed research will focus on the application of different advanced oxidation methods (AOP´s) to the same samples with the expectation of biodegradability enhancements.

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Table 2: Advantages and disadvantage of different kinds of MWFs [5], [7] – [13].

Type of MWFs	Advantages	Disadvantages
Straight oils	• excellent lubricity • they are relatively easy to maintain • bacterial activity is minimal • once the useful life of the straight-oil MWF is over, the used product can be burned for fuel value or recycled	• low cooling properties • high fire hazards • create mists or smoke
Emulsions	• great reduction of heat because of water's excellent cooling properties • economy resulting from dilution with water, • better operator acceptance and improved health and safety benefits	• they are prone to intensive microbial deterioration • evaporation losses • rust control problems • softening of hard water may be required (salts react with the emulsifier in the soluble oil to form an insoluble scum which floats on the surface)
Semi-synthetics	• semi-synthetic fluids have better lubricating properties than do synthetic fluids • good cooling properties • good microbial control • better rust and rancidity control than emulsifiable oils	• foam easily • softening of hard water may be required
Synthetics	• excellent cooling properties, • good lubricity, • longer service life • more environmental friendly then soluble oils • easiest MWFs to maintain • more resistant to biological attack than soluble oils.	• higher the initial cost • poor lubricity

Table 3 – Hazardous components of tested metalworking fluids according to their available MSDS.

CAS Number	Hazardous Components	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7	Sample 8	Sample 9
		Content [%]								
10043-35-3	Boric acid (neutralized) and its salts - **corrosion inhibitors**	<5.5					<5.5			
107-66-4	Dibutyl phosphate (organic phosphorus compounds) - **lubricity improvers**								1-5	
112-34-5	Diethylene glycol n-butyl ether (ethers and esters of polyhydric alcohols) - **solvents/coupling agents/lubricity improvers**				1-5	1-5				
122-99-6	2-phenoxyethanol (ethers and esters of polyhydric alcohols) - **solvents/coupling agents/lubricity improvers**					7-10				
1623-15-0	Mono-n-butyl phosphate (organic phosphorus compounds) - **lubricity improvers**								1-5	
141-43-5	Monoethanolamine (MEA) - aliphatic amines - **neutralizing agents**								1-5	
68608-26-4	Na salts (Petroleum sulfonates obtained by sulfonation of lubricating oil fractions) - **anionic surfactants, corrosion inhibitors**			1-5						
27458-92-0	Isotridecanol (monohydric alcohols) - **solvents/coupling agents**						<1			
31075-24-8/ 31512-74-0	1,2-Bis(dimethylamino)ethane-bis(2-chloroethyl) ether copolymer / Polixetonium chloride - **biocides**							0.01-1	0.01-1	0.01-1
55406-53-6	3-iodopropynyl butylcarbamate (carbamates) - **fungicides**				<1		0.1-1	0.01-1		
5625-90-1	Methylene-bistetrahydro-1,4-oxazine (bismorpholinomethane) - aldehyde derivatives - **biocides**				1-5		<5			
64741-97-5	Distillates (petroleum), solvent-refined light naphthenic				25-50					
68131-39-5	Alcohols, C12-15, ethoxylated			1-5						
68412-55-5	Poly(oxy-1,2-ethanediyl), .alpha.-(carboxymethyl)-.omega.-(tridecyloxy)-, branched				<1					
68425-15-0	Tert-dodecyl polysulfide						<25			
68920-66-1	Ethoxylated C16-C18 fatty alcohols	5-10	5-10							
70955-07-6	Alcohols, tallow, propoxylated					5-10				
96690-34-5	Amines, C12-14-tert-alkyl, mixed sec-Bu and iso-Bu phosphates						5-10			