

Biodegradability and other chemical properties of vegetable oil based Ekosata recycling mould oil

1. Background and the Aim

According to the present European Union strategy on waste materials they must be utilised primarily as material (reuse, recycling), secondary as energy and if neither of those is possible, they can be disposed by ecologically beneficial methods. Until now however different waste vegetable oils have been utilised in Finland mainly as energy. Thus the activity of Suomen Kasviöljykiekerrätys Ltd and Ekosata Ltd is to manufacture recycling oil products from waste vegetable oils for many different uses. This represents globally the present top goal of waste hierarchy (<http://ekooil.com/etusivu.php>).

The aim of this research was to determine important physico-chemical properties of vegetable oil based Ekosata recycling mould oil. From environmental point of view the biodegradability determined by BOD OxiTop method (see chapter 4) was the most important evaluated property in this research. The determinations were carried out for two different oil samples.

2. Experimental

The research methods and the equipments used for the determinations and calculations of the physico-chemical properties of Ekosata recycling mould oils are presented here shortly but they are described in details in the scientific publications of docent Toivo Kuokkanen or in the practice work handout of Physical Chemistry, University of Oulu.

The density [kg/dm³] of two oil samples were measured at 25 °C by the common procedure using Anton Paar DMA densitometer. Correspondingly, the values of *surface tension* [dyne/cm] were determined by common du Nouy's ring method using Kruss torsion balance. The values of *dynamic viscosity* [cP] were measured at 25 °C by Brookfield DV-II+ rotation viscometer by ASTM-D-2983 standard method. *Water contents* of mould oil samples [mg/kg] (or ppm) were determined by Karl Fisher method using Mettler DL 36 KF Coulometer automation titrator. The calorimetric heat measurements and calculation of the *calorific heat values* (called for liquids also as the specific heat values) in the unit [MJ/kg] or [kJ/g] were performed according to DIN 51900, ISO 1928, and ASTM D240. In our studies, calorific heat was determined with an IKA C200 calorimeter. *The contents of harmful heavy metals* [mg/kg] (Cd, Co, Cr, Cu, Ni, Pb, V, Zn, Fe, As, Ba, Mg, Sn, Sb) were determined by ICP-OES method (inductively coupled plasma optical emission spectrometer) using Philips PU 7000 ICP-OES equipment.

The values of biodegradability BOD_n (n in [days]) were determined in OECD 301F standard conditions (here BOD₂₈ values) by respirometric manometric BOD OxiTop method using the equipment shown in (1), Figure 1. This method is based on the very accurate automatic pressure measurements (360 BOD values are given in every experiment) in closed bottles under constant temperature (here 20.0 ± 0.2 °C). The instrument calculates the BOD value in the desired unit [mg/L] using the equation:

$$\text{BOD}[\text{mg/L}] = M(\text{O}_2)/RT_m \times [(V_{tot} - V_l)/V_l + \alpha T_m / T_0] \times \Delta p(\text{O}_2)$$

where $M(\text{O}_2)$ is the molecular weight of oxygen (32,00 g/mol), R is a gas constant (83.144 l hPa mol⁻¹ K⁻¹), T_m is the measurement temperature (K), T_0 is 273.15 K, V_{tot} is the bottle volume (ml), V_l is the liquid phase volume (ml), α is a Bunsen absorption coefficient, (0.03103) and $\Delta p(\text{O}_2)$ is the difference in partial oxygen pressure [hPa] as given by WTW.

3. Results and Discussion

The values of chemical properties of two different Ekosata recycling mould oil samples are presented in Table 1 where for comparison also the corresponding values for water are presented. Correspondingly, the development of their biodegradation percent BOD/ThOD [%] where BOD is the determined oxygen demand and ThOD is the theoretic oxygen demand, is show in Figure 2. The results show that the values of the density, surface tension and biodegradation percent for two samples are rather similar, the values of calorimetric heat and water content differ slightly but the viscosities differ clearly.

Table 1. Chemical properties of two Ekosata recycling mould oils.

Sample	Density [kg/dm ³]	Surface tension [dyne/cm]	Viscosity [cP]	Water content [mg/kg]	Calorimetric heat value [MJ/kg]	Cd, Co, Cr, Cu, Ni, Pb, V, Zn, Fe, As, Ba, Mg, Sn, Sb metal content
sample 1	0.9045	34.4	56.3	173	40.3	all < 20 [mg/kg]
sample 2	0.9049	34.2	34.3	378	39.6	all < 20 [mg/kg]
Water	0.9978	70.5	1.4	---	---	---

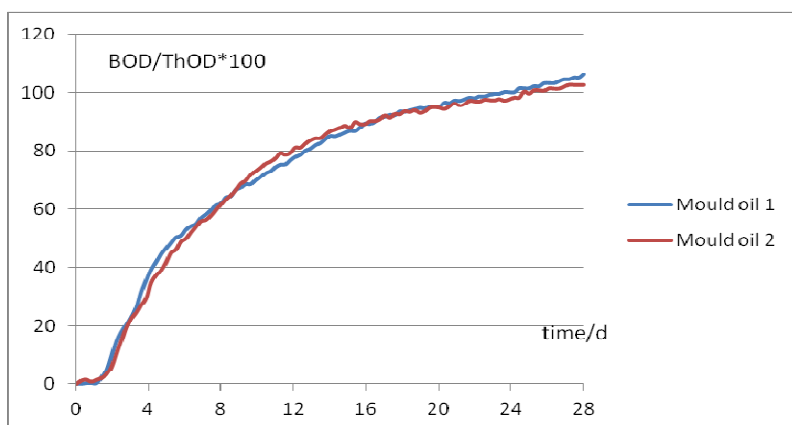


Figure 2. Biodegradation of Ekosata mould oil determined in OECD 301F standard conditions.

4. Conclusions

The following conclusions can be presented:

1. The studied two vegetable based Ekosata recycling mould oils *don't contain harmful heavy metals*.
2. Their general *physical properties are typical for lubricants*.
3. Ekosata recycling mould oil contains only small amount of water and being thus an *excellent fuel*. The heat value is dependent slightly on the water content.
4. According to the OECD Guideline for testing of chemicals the pass levels for ready biodegradability are 70% removal of DOC and 60% of ThOD or ThCO₂ production for respirometric methods. Thus the vegetable based Ekosata recycling mould oil is *ready biodegradable*.
5. The studied Ekosata mould oil is *fully biodegradable* and this value was reached in OECD 301F conditions at 20 °C as early as in about a month.
6. As final conclusion it can be presented that the manufacturing of fully biodegradable recycling oils from waste vegetable oils represent the present top goal of waste hierarchy and their use can be considered as “eco-action”.

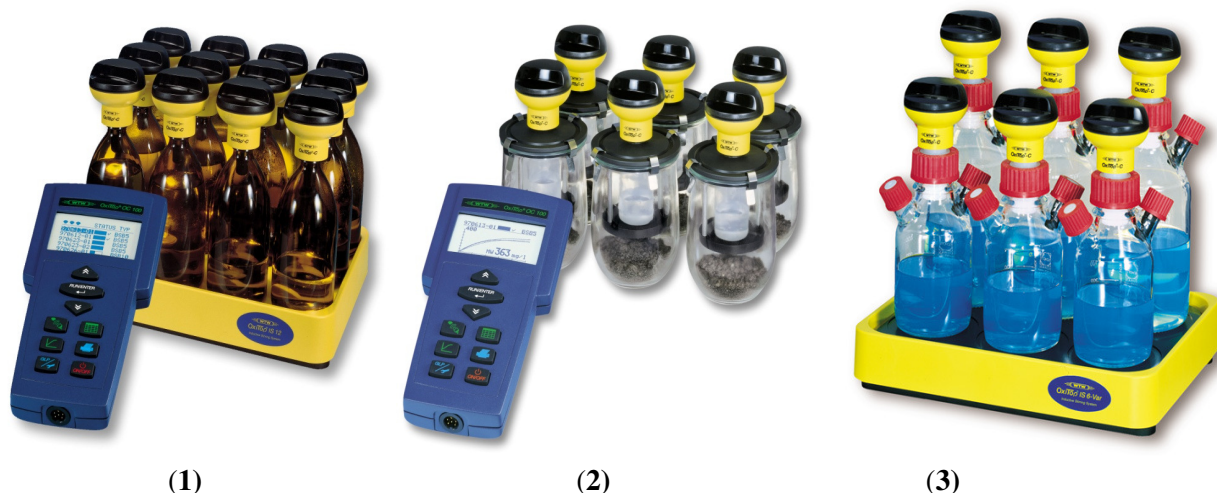


Figure 1. BOD Oxitop apparatus for respirometric manometric measurements in solution (1), in solid phase or soil (2), and in solution in desired atmosphere (possibility also for sampling).

4. Reference BOD publications *(study of oil products are marked with red number)*

I. PhD Theses

1. P. Vähäoja: Oil analysis in machine diagnostics. PhD thesis. Acta Universitatis Ouluensis, 2006.
2. K. Roppola: Environmental Applications of Manometric Respirometric Methods. PhD thesis. Acta Universitatis Ouluensis, 2009.

II. International publications

3. T. Kuokkanen, P. Vähäoja, I. Välimäki and R. Lauhanen: Suitability of the Respirometric BOD Oxitop Method for Determination the Biodegradability of Oils in Ground Water Using Forestry Hydraulic Oils as Model Compounds. - *Int. J. Environ. Anal. Chem.*, 84, 2004, 677-689.
4. P. Vähäoja, T. Kuokkanen*, I. Välimäki, S. Vuoti and P. Perämäki: Biodegradabilities of Some Chain Oils in Groundwater as Determined by the Respirometric BOD OxiTop Method. - *Anal. and Bioanal. Chem.*, 381, 2005, 445-450.
5. P. Vähäoja, P. Piltonen, A. Hyvönen, J. Niinimäki, J. Jalonen and T. Kuokkanen*: Biodegradability of Certain Wood Preservatives in Groundwater as Determined by the Respirometric BOD Oxitop Method, - *Water, Air and Soil Pollution*, 165, 2005, 313-324.
6. P. Vähäoja, K. Roppola, Ilkka Välimäki and T. Kuokkanen: Studies of Biodegradability of Certain Oils in Forest Soil as Determined by the Respirometric BOD Oxitop Method. - *Int. J. Environ. Anal. Chem.*, 85, 2005, 1065-1073.
7. K. Roppola, T. Kuokkanen, H. Nurmesniemi, J. Rämö, R. Pöykiö and H. Prokkola: Comparison Study of Manometric Respirometric Test and Common Chemical Methods in the Determination of BOD₇ in a Pulp and Paper Mill's Wastewaters. - *J. Autom. Meth. and Manage. Chem.*, 2006, 1-5.
8. K. Roppola, T. Kuokkanen, J. Rämö, H. Prokkola and E. Heiska: Comparison Study of Different BOD Tests in the Determination of BOD₇ in Domestic Sewage. - *J. Autom. Meth. and Manage. Chem.*, 2007, ID 39761, 1-4.
9. J. Kaakinen, P. Vähäoja, T. Kuokkanen* and K. Roppola: Studies on the Effects of Certain Soil Properties on the Biodegradation of Oils Determined by Respirometric Method. - *J. Autom. Meth. and Manage. Chem.*, 2007, ID 34601, 1-7.
10. K. Roppola, T. Kuokkanen, K. Kujala and M. Kuokkanen: Utilization Potential of Peats - a Study on Peat biodegradability Determined by Respirometric Method. - *Water, Air and Soil Pollution*, 2008, 59-66.

11. M. Karhu, J. Kaakinen, T. Kuokkanen and J. Rämö: Biodegradation of Light Fuel Oils in Water and Soil as Determined by the Manometric Respirometric Method. - *Water, Air and Soil Pollution*, 2008, the proof available, 12 pp.
12. K. Roppola, T. Kuokkanen, J. Rämö, H. Prokkola and J. Ruotsalainen: Characterisation of organic fractions of pulp and paper mill wastewater with a manometric respirometric BOD method and automatic COD analyses. - *Chemical Speciation and Bioavailability*, 21, 2009, 121-130.
13. Partly, T. Leiviskä, H. Nurmesniemi, R. Pöykiö, J. Rämö, T. Kuokkanen and J. Pellinen: The Effect of Biological Wastewater Treatment on Molecular Weight Distribution of soluble Organic Compounds and on the Reduction of BOD, COD and P in the Pulp and Paper Mill Effluent. - *Water Research*, 42, 2008, 1-9, 3952-3960.
14. Partly, T. Kuokkanen, H. Nurmesniemi, R. Pöykiö, K. Kujala, J. Kaakinen and M. Kuokkanen: Chemical and Leaching Properties of Paper Mill Sludge. - *Chemical Speciation and Bioavailability*, 20 (2), 2008, 111-122.
15. Partly, R. Pöykiö, K. Kujala, T. Kuokkanen, H. Nurmesniemi and M. Kuokkanen: Utilization of Paper Mill Sludge as a Landfill Hydraulic Barrier Material in Finland. - ICSW 2008, *The 23rd International Conference on Solid Waste Technology and Management, Philadelphia, PA, U.S.A.*, 30.3.-2.4.2008, 639-645 and a poster.
16. V. Vauhkonen, R. Lauhanen, S. Ventelä, J. Suojäranta, A. Pasila, T. Kuokkanen, H. Prokkola and S. Syväjärvi : The phytotoxic effects and biodegradability of stored rapeseed oil and rapeseed oil methyl ester. - accepted for publication in *Agricultural and Food Science*, 2010, 21 pp.
17. H. Prokkola, T. Kuokkanen, P. Vähäoja and J. Rämö: Biodegradability studies of tall oil soaps in different water and soil environments. – The publication under writing.

III. Other scientific publications

18. K. Saarela, T. Kuokkanen, H. Nurmesniemi, J. Rämö, R. Pöykiö and H. Prokkola: Comparison between the Respirometric Oxitop Test and Conventional Chemical Methods in the Determination of BOD of Waste Water from a Pulp and Paper Mill. - *Kemian Päivät 2005*, 26.–28.4.2005, Poster and Abstract 2P4, pp. 18-19.
19. T. Kuokkanen, J. Rämö, H. Nurmesniemi, R. Pöykiö and H. Prokkola: Chemical Studies of Paper Mill Sludge for Material Efficient Utilization. - *Kemian Päivät 2007*, 27.–29.4.2007, Helsinki, Poster and Abstract 3.5, 2007, p. 24.
20. H. Prokkola and T. Kuokkanen: Biohajoavuuden määrittäminen vedessä, HighBio, Projekti Info 40, 4 s.
21. H. Prokkola T. Kuokkanen and M. Kuokkanen: Biohajoavuuden määrittäminen kiinteässä faasissa BOD Oxitop -menetelmällä, *HighBio, Projekti Info 62*, 2010, 3 pp.
22. A. Heponiemi, L. Rahikkala, T. Kuokkanen and U. Lassi: Catalytic oxidation of wastewaters under mild conditions. – Poster presented in *14th Nordic Symposium on Catalysis*, 29 – 31 August 2010 Marienlyst, Denmark; publication accepted for publication in *Topics in Catalysis*, 18 pp.
23. M. Kuokkanen, T. Vilppo, T. Kuokkanen, T. Stoor and J. Niinimäki: Chemical and technological studies of binding agent containing wood pellet production. - *Bioresources*, 2011, 22 pp, in press.

Oulu, May 1, 2011

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