



Environmental implications of crude glycerin used in special products for the metalworking industry and in biodegradable mulching films



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ABSTRACT

Crude glycerin from biodiesel supply chain can replace synthetic glycerol or other chemicals in industrial applications. To improve sustainability according to the biorefinery perspective, a purification phase will be carried out only if it is really necessary to reach standards for industrial processes or final products. In metal working, the use of crude glycerin-based hydraulic fluids, replacing mineral oil-based and glycol-based ones, has fulfilled industrial requirements and made it possible to increase (i) worker safety because of its non-flammability; (ii) biodegradability and (iii) time-life of the product due to anti-wear properties; in addition, post-use waste management will be simplified, due to the possibility to declassify fluids as special waste. In biodegradable mulching films, the replacement of synthetic glycerol was successful because it made it possible both to maintain the same compounding conditions and to obtain the same yields and film biodegradation in an agronomic trial on muskmelon. The benefits compared with conventional polyethylene films are the same as conventional readily biodegradable films. The key parameters in the analytical composition of glycerin concerning specific industrial applications are discussed; the environmental benefits in metal working fluid formulation and in mulching film compounding are then assessed.

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1. Introduction

Crude glycerin (CG) is a byproduct of the biodiesel chain, every ton of methyl-ester produced generating approximately 0.1 tons of CG. According to the International Renewable Energy Agency, total biodiesel production in 2012 was more than 2 million tons of CG. 1,2,3-propanetriol (aka glycerol) is the main component of CG. Synthetic glycerol, which the carbon is generally fossil-based, is a high-value and commercial chemical with thousands of different applications; global demand was 1.99 mega tons in 2011 and this is expected to reach 3.06 mega tons by 2018 (Transparency Market Research, 2014). For these reasons, the industrial valorization of CG from biodiesel production is gaining interest in order to recoup part of the production cost of biodiesel and therefore to promote biodiesel industrialization on a large scale (Yang et al., 2012).

CG composition varies with the type of catalyst used to produce biodiesel, the transesterification efficiency, the recovery efficiency of the biodiesel, the presence of other impurities in the feedstock, and the recovery processes, if any. Hansen et al. (2009) studied the chemical compositions of 11 CG collected from seven Australian biodiesel producers and indicated that the glycerol content ranged between 38% and 96%, with some samples including more than 14% methanol and 29% ash. Salt content in CG obtained with homogeneous alkaline catalyst generally ranged from 5 to 7% (Lancrenon and Fedders, 2008), and also in heterogeneous transesterification processes, impurities existing in the natural raw feedstock tend to accumulate in the CG phase.

Pure glycerol is an extremely reactive molecule and for this characteristic is widely applied in many different applications, as confirmed by around three thousand patent applications, but CG has also been proposed as an excellent source of carbon in different fields starting from feed, i.e. calories for broilers, laying hens and pigs, although glycerol in excess may affect metabolism (Yang et al., 2012). In addition, fermentative industrial applications of CG

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produce propylene glycol, 1,3-propanediol (Mu et al., 2008), citric acid from *Yarrowia lipolytica* (Papanikolaou and Aggelis, 2009), poly(3-hydroxybutyrate) (PHB) (Ibrahim and Steinbüchel, 2009), docosahexaenoic and eicosapentaenoic acid from algae or fungi as ingredients for fortified foods or feeds (Athalye et al., 2009; Ethier et al., 2011), lipids with a high concentration of monounsaturated fatty acids (Liang et al., 2010), and succinic acid (Vlysidis et al., 2011). CG (without any purification) could also be used directly to produce methane by anaerobic digestion (López et al., 2009), acrolein by vaporization (Sereshki et al., 2010), and as a green solvent for some organic reactions (Wolfson et al., 2009).

This work focused on the environmental implications of CG applications in two industrial fields which exemplify the potential of the industrial use of CG as a replacement for polluting chemicals or synthetic glycerol: in metal working fluids (MWFs) as safety hydraulic fluids and as a component of biodegradable mulching films (BMFs). MWFs, also called suds, coolants or slurry, are widely used in various manufacturing processes viz during the machining of metals to reduce friction and cooling and to help carry away debris such as swarf and fine metal particles. Over the last 10–15 years, globalization and the current economic and financial crisis have strongly changed the global lubricants industry structure. A majority of the MWFs used worldwide are based on non-renewable mineral oils. In 2010, about 5.3% of the worldwide lubricant consumption was used to formulate MWFs, which are about 197 million tons (Gosalia, 2010). The potential hazard towards human health and the environmental impact is a critical factor in the use of mineral oil-based MWFs (Dettmer, 2004).

The application of CG as a main MWF component can be advantageous: since CG is produced from renewable resources, and it turns by- and surplus products into an innovative raw material for mineral oil replacement, also making it possible to achieve environmental certification as a biolubricant, e.g. European “ecolabel” or American “USDA biobased”. However, the possibility of using a lubricant from renewable carbon sources becomes interesting for the industry only when its technical performances are similar (or better) if compared to conventional mineral oils. In particular, not only lubrication, but also hydrolysis stability and oxidation stability via transesterification should be taken into account. A biolubricant containing natural source components (such as vegetal oil and/or CG), viz biobased lubricant, could ensure better lubrication and at the same time it could increase workers' health and safety and reduce the environmental impact due to potentially better biodegradability (Lazzeri et al., 2006). For these reasons, it can be more easily disposed of than a product based on mineral oil, or after its disposal it could be a source of organic acids, useful as a domestic cleaning product or in the paint industry (Mannan, 2012).

The second industrial application of CG investigated in this paper is mulching films; traditionally made of low density polyethylene (LDPE), these accounted for 25% of the 2.9 million tons of agricultural plastic films consumed worldwide in 2011, and in Europe alone 545,000 tons of plastic mulches per year (AMI, 2011). Conventional plastic mulching films are commodity products and therefore produced by the main converters active in the plastic agro-market. BMFs, excluding oxo-photo or other fragmentable mulches, are estimated to be applied several thousand tons per year in Europe, mainly in the horticultural areas. Biodegradable mulches can be laid on the same crops as traditional plastic mulches, but also on other crops where the harvesting requirements, the lack of herbicides or the agronomical techniques in general require a material with different performances in terms of end of life (e.g. raspberry and blueberry, processing tomato or vine).

A BMF has mechanical properties and characteristics similar to traditional plastic mulches: good soil coverage until the end of the crop cycle with proper weed control, using the same laying machines and irrigation system, and guaranteeing similar crop

yield and quality (Scarascia-Mugnozza et al., 2006; Briassoulis, 2006, 2007). Differences mainly regard lower thickness (BMF is generally 12–15 μm depending on crop and climate condition), that allows a lower consumption of material per square meter and full biodegradability in soil, which is the key characteristic of these materials. In fact, they do not need to be removed from the field after their use and can be incorporated in the soil at the end of their life cycle and degraded by soil microorganisms, significantly reducing post-harvest plastic waste.

On the contrary, in Europe, according to EC Directive n°31 (1999)EC (1999) and EC Directive n°76 (2000)EC (2000), conventional plastic mulch films must be removed from the field at the end of their use and properly disposed of, involving high costs due to contamination and degradation characteristics, including the contamination of the films with pesticides (Briassoulis et al., 2012, 2013). These difficulties can explain the low percentage of recovery of traditional plastic films and the illegal practices for disposal (burning in the field, uncontrolled landfilling, film incorporation in the soil at the end of the crop cycle) that involve environmental concerns (Garthe, 2004). These procedures, in fact, cause the release of dangerous substances in the soil, with a negative environmental impact (Kyricou and Briassoulis, 2007), but also in the air, through the burning that releases air pollutants, such as polycyclic aromatic hydrocarbons (Font et al., 2004). A valuable solution to this problem is provided by BMF. A mulching film can be considered “biodegradable” if it complies with the requirements of the norms on biodegradability (e.g. ISO 17556, 2012; ISO 14855-1, 2012; CEN 13432, 2005). There are different national standards that indicate how to assess the biodegradability in soil of a mulching film, e.g. NF U52-001 (2005) in France or UNI 11495 (2013) in Italy. In general, it is possible to summarize the various standards in a few main points: (i) absence of eco-toxicity effects on the soil and on the crops; (ii) no release of hazardous substances (i.e. heavy metals above certain thresholds) both in composting conditions and in soil; (iii) disintegration of the film; (iv) biodegradation (90% at soil temperature within 12 or 24 months) in standard condition and in comparison with a reference (crystalline cellulose).

In this paper, the investigations and results covering the functional and chemical aspects of a new MWF based on CG derived from the biodiesel chain are presented, together with a systematic analysis of the performance of a new CG-based BMF. The type of formulation of the new products has to be considered as confidential information and it will not be reported in detail.

The aims of this paper were to identify the environmental key issues in the use of CG in industrial applications in which the environmental cost of purification is not necessary and environmental benefits could be optimized.

2. Materials and methods

2.1. Materials

CG derived from a biodiesel chain was purchased from Cerealdoks S.p.A. (Vicenza, Italy). Pure industrial glycerin, oil derived and used as a reference, was kindly provided by Foundry Chem (Torino, Italy).

2.2. Characterization of crude glycerin

Glycerin density was measured by gravimetric analysis. Water, methanol and glycerol contents were determined by using, Karl Fischer colorimetric titration, UNI, (1996), GLC analysis, and HPLC determination, respectively. An HP1100 (Hewlett Packard, Waldbronn, Germany) system equipped with a HP1047A refractive index detector and an Aminex HPX-87H column (7.8 mm $\times$ 300 mm, Bio-

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