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Dihydroxyacetone crystallization: Process, environmental, health and safety criteria application for solvent selection

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HIGHLIGHTS

- A novel crystallization solvent selection procedure is described.
- Selection criteria include process, cost, environmental, health and safety issues.
- Dihydroxyacetone crystallization solvent selection is presented as a case study.
- Methanol was the overall best choice among the solvents assessed.
- The methodology described proved to be suitable, simple and flexible.

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ABSTRACT

Dihydroxyacetone is a good candidate to valorize the excess glycerol obtained as byproduct in biodiesel production. Crystallization is likely the key unit operation to obtain a high quality and pure dihydroxyacetone. The selection of an appropriate solvent for crystallization is not trivial and depends on multiple factors. At the present work a new solvent selection methodology, based on solvents relative comparisons, is described and applied to dihydroxyacetone crystallization as a case study. The procedure accounts not only for process factors such as solubility and yield, but also for cost, recycling, disposal, environmental, health and safety issues. Solubility and theoretical yield data for dihydroxyacetone in methanol, ethanol and 2-propanol were experimentally determined, while cost, life-cycle assessment, environmental, health and safety data of solvents were gathered from different bibliographic sources, software and databases. Among the solvents assessed, methanol resulted as the best overall choice for DHA crystallization. The methodology proved to be a suitable, simple and flexible procedure for solvent selection at the initial stages of the crystallization operation design, being able to be upgraded for advanced stages of the crystallization process development.

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1. Introduction

Nowadays, the necessity of replacing fossil fuels has boosted the search for renewable alternative energy sources and so the development of biofuels such as biodiesel. Nevertheless, the continuous increasing demand for biodiesel has resulted in an excess of glycerol production, obtained as byproduct (10% w/w), causing a significant devaluation in its price (da Silva et al., 2009; Katryniok et al., 2011; Kenar, 2007). Glycerol has a large amount of well-known applications in food, pharmaceuticals, personal care, cosmetics and other industrial applications; however these classical uses are not adequate to absorb the surplus of glycerol and research efforts are being dedicated towards its valorization (da Silva et al., 2009; Katryniok et al., 2011; Kenar, 2007). Moreover, the production of high value-added compounds from glycerol will not only beneficiate its own market but also the biodiesel industry as its economic viability is closely linked to glycerol (Kenar, 2007). In this context the 1,3-dihydroxy-2-propanone, commonly known as dihydroxyacetone (DHA), stands out from other compounds that can be obtained from glycerol, and not only for its relative high price with respect to glycerol, within a 250–500-fold value (Katryniok et al., 2011), but also because, as estimated by the American Chemical Society, the demand of DHA will meaningfully increase in the next years (Ma et al., 2010). The DHA can be used for the organic synthesis of various fine chemicals, but it most remarkable application is in cosmetic formulations as a self-tanning agent, which is based on the Maillard reaction with amino groups of human skin (Bauer et al., 2005; Hekmat et al., 2003; Katryniok et al., 2011; Kenar, 2007).

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DHA can be obtained from glycerol via catalytic chemical or biotechnological oxidation processes, but at industrial scale it is generally produced by oxidative fermentation due to economic, safety and quality requirements (Hekmat et al., 2003; Katryniok et al., 2011). *Gluconobacter oxydans* is the most widely used microorganism for this bioprocess (Hekmat et al., 2003, 2007; Ma et al., 2010). Many studies deal with the glycerol-DHA fermentation improvement and optimization (Bauer et al., 2005; Hekmat et al., 2003, 2007; Hu and Zheng, 2011; Hu et al., 2011, 2012; Li et al., 2010; Ma et al., 2010) but the downstream separation and purification process have received less attention. The downstream process will include several unit operations but crystallization is most likely the key separation/purification step to obtain a pure and high quality DHA.

The selection of an appropriate solvent for crystallization is a critical point in order to achieve optimal process performance. Solute solubility is probably the most important process factor when selecting a solvent, as it will determine the crystallization method and yield; thus, strategies of solvent selection for organic compounds crystallization based on solute solubility prediction have been proposed (Frank et al., 1999; Nass, 1994).

In the last two decades there has been a growing concern about chemistry sustainability and so green chemistry has become a requirement for industrial processes development and chemical compounds obtained or used thereof. The Globally Harmonized System of Classification and Labelling of Chemicals (GHS), created by the United Nations (United Nations, 2003), was the starting point for a global system of information and classification of chemical substances based on their health, physical and environmental hazards. The European Union (EU) has implemented the GHS into the CLP regulation (Regulation on classification, labelling and packaging of substances and mixtures of the European Union) (European Union, 2008), which is complementary to the REACH regulation (Regulation concerning the Registration, Evaluation, Authorization, and Restriction of Chemicals) (European Union, 2006), that addresses chemicals production and use in ways that lead to the minimization of significant adverse effects on human health and the environment. Therefore, in addition to process parameters such as solubility, crystallization solvent selection methodologies need also to include criteria based on environmental, health and safety (EHS) issues. Following this trend, in the last years different pharmaceutical companies such as GlaxoSmithKline (GSK), SANOFI, Pfizer, Astra Zeneca and the American Chemical Society Green Chemistry Institute Pharmaceutical Roundtable (ACS GCIPR) have developed their own proprietary general guides for solvent selection based on EHS assessment combined with factors relative to their industrial processes (Curzons et al., 1999; Dunn, 2012; Henderson et al., 2011; Prat et al., 2013). These guides are only fully available for internal use within the companies, and although the final rating or solvent classifications have been published, the methodology followed and assessment tools used are completely private. Apart from these proprietary guides other works have proposed different general solvent selection methods (Capello et al., 2007; Slater and Savelski, 2007), intended for fine chemical and pharmaceutical industries, which have considered environmental, health and/or safety issues, but lack of considerations relative to the crystallization process such as solubility, yield or solvent cost.

Therefore, based on a case study for DHA crystallization, the present work aims to propose a new methodology for crystallization solvent selection that joints together the assessment of fundamental process and economic factors, such as solute solubility, crystallization yield, solvent cost and life-cycle assessment, and EHS hazards inherent to solvents. This methodology will establish a relative comparison between the solvents assessed that will help to select the most appropriate one or ones among the feasible candidates at the initial stages of the crystallization process development, but also will allow for solvent selection improvement as design process advances by upgrading the method. This methodology is a valuable tool that can be applied at any scale of process design: laboratory, pilot and industrial plant.

2. Materials and methods

2.1. Solubility measurement

DHA solubility was measured in three different alcohols: methanol, ethanol and 2-propanol. This initial set of solvents was selected following the well-known rule of thumb "like dissolves like", and considering that these three alcohols are commonly used as solvents in industrial processes; their assessment provided an appropriate framework to develop, evaluate and explain the novel solvent selection method proposed.

Dihydroxyacetone dimer was purchased from Sigma-Aldrich (lot number: MKBJ4156V), and high purity methanol, absolute ethanol and 2-propanol were purchased from Fisher Chemical.

40 mL of solvent was added to a 45 mL septum screw-capped test tube. The test tube was submerged in a bath and brought to the desire temperature within −8 to 30 °C. Higher temperatures were not assayed as DHA have been found to decompose above 40 °C (Zhu et al., 2003). The temperature of the bath was controlled with a recirculation cryothermostat Frigiterm-10 (J.P. Selecta). Excess DHA was then added and left to dissolve with magnetic stirring, the dissolved concentration being checked over time; stirring was stopped 10 min before sampling and afterwards a 2.5 mL sample was withdrawn using a glass syringe with 0.45 μm PTFE filter; the DHA concentration was then determined by HPLC analysis. The DHA concentration was measured until saturation was achieved; saturation time ranged within 96–288 h depending on temperature and solvent. Then, the saturated solution density was measured, at the same temperature of the saturated solution, with a 5 mL pycnometer, the sample being withdrawn as described before. The saturated solution density was used to express the DHA solubility as grams of DHA per kilogram of solvent. The temperature of all materials and equipment used was controlled throughout the process. Experiments were done by triplicate, the standard deviation being always below 5%.

2.2. DHA HPLC analysis

The DHA concentration HPLC analysis was based on that published by Hekmat et al. (2003) with some modifications. A HPLC Shimadzu VP series, equipped with degasser, auto sampler, pump, column oven, PDA detector and communications bus modules, was used. Chromatograms were analyzed with the LabSolutions LCsolution software. The HPLC column was a Rezex RCM-Monosaccharide Ca+2 (8%) 300 × 7.8 mm (Phenomenex). The operation mode was isocratic, MilliQ water being the eluent. The flow rate, temperature and injection volume were 0.6 mL/min, 40 °C and 10 μL, respectively. DHA concentration was measured with the PDA detector at 271 nm. A calibration curve with DHA aqueous solutions was constructed, the concentration range being within 0–10 g/L.

2.3. DHA X-ray powder diffraction analysis

Four crystalline forms, one monomeric and three dimeric polymorphs (α, β and γ), are known for DHA (Slepokura and Lis, 2004); their crystallographic data are available from the Cambridge Crystallographic Data Center: CCDC 231363, CCDC 231358, CCDC 231359 and CCDC 231360, respectively. Thus, analyses by

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