

available at www.sciencedirect.comjournal homepage: www.elsevier.com/locate/chnjc

Article

Kinetic study and kinetic parameters of lipase-catalyzed glycerolysis of sardine oil in a homogeneous medium



Ángela García Solaesa, María Teresa Sanz*, Sagrario Beltrán, Rodrigo Melgosa

Department of Biotechnology and Food Science (Chemical Engineering Section), University of Burgos, Burgos 09001, Spain

ARTICLE INFO

Article history:

Received 18 November 2015

Accepted 4 January 2016

Published 5 April 2016

Keywords:

Lipase

Glycerolysis

Tert-butanol

Mass transfer

Kinetic model

ABSTRACT

The production of polyunsaturated fatty acids (PUFAs) concentrates by enzymatic catalysis has gained interest due to their stereospecificity and the milder conditions employed compared to the use of inorganic catalysts. The enzymatic glycerolysis of sardine oil by Lipozyme® 435 to get PUFA concentrates in the forms of di- and monoacylglycerols (DAGs, MAGs) in an optimized amount of tert-butanol as the organic solvent was studied. First, mass transfer limitation of the reaction system was analyzed. The effects of different operating variables such as lipase loading, temperature and feed composition were investigated. A semi-empirical kinetic model based on the reversible elementary reactions of glycerolysis and hydrolysis of the glycerides was employed to correlate the experimental kinetic data. A molar ratio glycerol:oil of 3:1 was the optimum, which produced more than 84 wt% of MAG at 323 K. A comparison with other glycerolysis systems was performed using MAG yield, reaction rate and significance of kinetic parameters.

© 2016, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

1. Introduction

Fish oil is rich in omega-3 (n-3) polyunsaturated fatty acids (PUFAs) such as eicosapentaenoic acid (EPA) and docosahexaenoic acid. The health benefits of n-3 fatty acids have been widely established in the literature [1–3]. Among the different types of lipid derivatives containing PUFA concentrates, MAG and DAG have good bioavailability [4,5]. In addition, MAG or its mixtures with DAG account for 75% of worldwide emulsifier production [6]. The process currently used in industry to obtain MAG is glycerolysis using an inorganic alkaline catalyst at high temperature (493–533 K). This method has several disadvantages such as it gives a dark color and burnt taste as well as high energy consumption. Furthermore, chemical glycerolysis is not suitable for producing MAG rich in PUFA due to oxidation problems. Enzymatic glycerolysis is an attractive al-

ternative for the production of MAG rich in PUFA since the reaction can be carried out under mild conditions [7] and structured products are obtained.

The immiscibility of the reactants, glycerol and oil leads to mass transfer limitation in the glycerolysis of oils. Different approaches have been used in the literature to improve the contact between the reactants and hence reduce mass transfer limitation. Lipase-catalyzed glycerolysis has been carried out in different reaction media such as organic solvents [8], compressed fluids [9], and ionic liquids [10] in order to improve the mass transfer. Recently, the uses of different surfactants to increase the interfacial area [11] and ultrasound irradiation [12] have also been proposed to reduce mass transfer limitation.

This paper is part of a wider project for the optimization of MAG production by enzymatic glycerolysis of sardine oil. First, different tert-alcohols were evaluated as the solvent used to

* Corresponding author. Tel: +34-947 258810. Fax: +34-947-258831; E-mail: tersanz@ubu.es

create a homogeneous phase [13]. Tertiary alcohols enhance the enzyme activity and accelerate the reaction rate as compared to the solvent-free system [14]. In a previous work, tert-pentanol was selected as the solvent and the effect of the glycerol:oil molar ratio was evaluated for its effect on kinetic behavior and MAG yield. The glycerolysis product was subsequently fractionated by a two-step molecular distillation to obtain a concentrated product of MAG and DAG rich in PUFA [15]. In this work, a different tertiary alcohol, tert-butanol (TB) was used as the solvent. TB has been used in different glycerolysis systems of vegetable oils such as olive oil [16,17], palm oil [18], camellia oil [19] and sunflower oil [8,20].

The main objective of this work is to present a detailed kinetic study of enzymatic glycerolysis of refined sardine oil in TB as the solvent catalyzed by a commercial lipase Lipozyme® 435. The amount of TB added to create a monophasic system has been optimized based on liquid-liquid equilibrium (LLE) data previously determined [13]. This value was compared with the amount of TB added to other glycerolysis systems. The results in terms of MAG and DAG yields were compared with literature data reported for different type of oils and related to the high activity of the lipase for short and medium chain length fatty acids.

First, the external and internal mass transfer resistances were analyzed in the heterogeneous system of the immobilized lipase. Mass transfer limitation can play an important role in the reaction rate. However, in most glycerolysis studies reported in the literature, no mass transfer studies were performed.

Mathematical models are needed to predict and optimize the industrial process. However, not many works in the literatures deal with the kinetic modeling of glycerolysis. One of the first works was carried out by Moquin et al. [9]. In that work, the kinetics of the non-catalyzed glycerolysis of soybean oil in supercritical CO₂ medium were correlated by a sequence of reversible reactions to take into account the parallel hydrolysis reaction. The same model was used by Valerio et al. [11] in the kinetic study of solvent-free lipase-catalyzed glycerolysis of olive oil by Novozym 435 with Triton X-100 as surfactant. Although glycerolysis and hydrolysis reactions were proposed, no information on the experimental FFA (free fatty acid) production and rate of change of glycerol were provided and only the TAG (triacylglycerols), MAG and DAG concentrations were used in the fitting procedure to obtain the kinetic parameters. The mechanism of glycerolysis and hydrolysis of pure POP (1,3-palmitin-2-olein) by *Rhizopus arrhizus* lipase was studied by Tan et al. [21] by including hydrolysis, esterification and isomerization of MAG and DAG. Cheirsilp et al. [22] proposed a Ping-Pong Bi Bi model that focused on the kinetics of the hydrolysis and esterification steps involved in the glycerolysis of palm oil in an acetone/isooctane mixture (3:1 v/v). Water was dissolved in glycerol (10% w/v of water added to glycerol) and therefore a large amount of water was present in the reaction medium. Recently, Voll et al. [17] proposed a kinetic model based on the ordered-sequential Bi Bi mechanism for a lipase-catalyzed glycerolysis system of olive oil in TB as the solvent. In that work, the reaction products were expressed as

total amount of MAG, DAG, TAG and FFA by weight percentage on a solvent-free basis composition. No experimental information on the glycerol concentration rate of change was provided. Fiametti et al. [12] used a similar model to the one proposed by Voll et al. [17] in the glycerolysis of olive oil by ultrasound irradiation. However, the parameters were not provided in the open literature although they could be available upon request to the authors.

In this work, a similar approach to that previously proposed by Moquin et al. [9] was used. The kinetic parameters were compared when possible with previous values reported in the literature. This model was able to consider the concentration of all the compounds involved in the glycerolysis system: TAG, DAG, MAG, FFA, glycerol and water.

2. Experimental

2.1. Materials

Refined sardine oil was kindly provided by Industrias Afines S.L. (Spain) with a water content of $0.19 \pm 0.03\%$. Glycerol was purchased from Sigma Aldrich with a purity of $\geq 99.5\%$ and a water content of $0.18 \pm 0.04\%$. TB was purchased from Merck with a purity of $\geq 99\%$ and a water content of $0.20 \pm 0.03\%$. The products were stored over activated 3 Å molecular sieve to keep them dry. The food grade lipase Lipozyme® 435 from *Candida antarctica* (immobilized on a macroporous hydrophobic acrylic resin) was donated by Novozymes A/S (Bagsvaerd, Denmark). The water content of this lipase was $3.5 \pm 0.3\%$ as determined in triplicate by Karl-Fisher titration with a Mitsubishi CA-20 moisture meter. According to Novozymes A/S, the specific activity of the lipase is ≥ 8000 propyl laurate units/g. No additional water was added to the system. Therefore, water present in the reaction medium came only from the reactants.

2.2. Enzymatic glycerolysis of sardine oil

Different vials containing a mixture of sardine oil, glycerol and TB were incubated at different temperatures from 303 to 333 K in a water bath with stirring. Different molar ratios of substrate and enzyme dosage were also studied. The amount of TB added was fixed at a mass ratio of 1.5:1 (TB:substrates) on the basis of previous studies on LLE [13]. At selected time intervals (from 5 min up to 8 h), a sample of the reaction mixture was withdrawn and filtered through a microfilter (0.45 µm, Sartorius RC) to stop the reaction by removing the lipase. All samples were stored at 255 K prior to analysis.

The reusability of Lipozyme® 435 in this process was tested by recycling the immobilized enzyme in six batches. After each run, the lipase was washed once with TB, and then twice with hexane in order to eliminate the remaining compounds. Afterwards, the lipase was dried at 303 K and stored in a desiccator under vacuum. No significant reduction in enzyme activity was found. Anyway, a fresh biocatalyst was used in each run.

TB was evaporated under vacuum using a rotary evaporator (Heibolph VV2000) at 333 K. This way, TB can be reused by

دانلود مقاله



<http://daneshyari.com/article/59157>



- ✓ امکان دانلود نسخه تمام متن مقالات انگلیسی
- ✓ امکان دانلود نسخه ترجمه شده مقالات
- ✓ پذیرش سفارش ترجمه تخصصی
- ✓ امکان جستجو در آرشیو جامعی از صدها موضوع و هزاران مقاله
- ✓ امکان پرداخت اینترنتی با کلیه کارت های عضو شتاب
- ✓ دانلود فوری مقاله پس از پرداخت آنلاین
- ✓ پشتیبانی کامل خرید با بهره مندی از سیستم هوشمند رهگیری سفارشات