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Two-stage continuous flow synthesis of epoxidized fatty acid methyl esters in a micro-flow system

Wei He[a], Zheng Fang[b], Qitao Tian[a], Dong Ji[a], Kai Zhang[a], Kai Guo[a,c,*]

[a] College of Biotechnology and Pharmaceutical Engineering, Nanjing Technology University, Nanjing 210009, Jiangsu, PR China
[b] School of Pharmaceutical, Nanjing Technology University, Nanjing 210009, Jiangsu, PR China
[c] State Key Laboratory of Materials-Oriented Chemical Engineering, Nanjing Tech University, 30 Puzhu Rd S., Nanjing 211816, PR China

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ABSTRACT

A new protocol combining transesterification reaction with epoxidation process was reported. Besides, a novel continuous extraction device was employed in the integrated process to realize the automatic continuous flow synthesis of epoxidized fatty acid methyl esters (FAMEs). Furthermore, a capillary column containing desiccants was used in the post-processing, leading to dry product.

1. Introduction

Renewable energy has been developed rapidly recently due to the depletion of fossil fuel. As one of the main fossil fuel alternatives, biodiesel shows several unique advantages, such as biodegradable and non-toxic [1]. In the past several years, many new efficient and environmentally friendly synthetic methods have been applied in the preparation of biodiesel [2–4].

On the industrial level, one of the most extensively applied reactions on the unsaturation is epoxidation due to the high reactivity of oxirane ring [5,6]. Epoxidation of oleochemicals has been extensively investigated over the past several years since epoxidized products are good substitutes for phthalates which are banned by the EU and FDA [7]. Besides, epoxidized oleochemicals have been widely used as lubricants [8], plasticizers [9], stabilizers [10], cosmetics and biofuel additives [11,12]. Compared with epoxidized vegetable oil, epoxidized FAMEs show the unique plasticizing property in the synthesis of cellulosic resin and synthetic rubber. Furthermore, higher flexibility and longer ageing time were acquired by adding FAMEs into the products.

During the past decade, studies of epoxidized FAMEs have been reported by several groups. A novel catalyst, Ti/SiO_2, had been employed as a solid catalyst for the epoxidation of FAMEs [13]. A high epoxide yield was obtained at room temperature. Meanwhile, epoxidation of FAMEs in the presence of SO_3H-functional Bronsted acidic ionic liquid was also reported [14]. The conversion reached a maximum in 60 min at 343.15 K. Typically, commercially available epoxidized FAMEs are synthesized through the epoxidation reaction between FAMEs and the peracids. However, adding rate and temperature must be strictly controlled in order to make the process safe. In addition, side reactions, especially ring-opening reaction, are always present in the process [15]. Most of all, high quality epoxidized FAMEs are obtained provided that purified FAMEs are supplied (Scheme 1). To date, there is no report of direct synthesis of epoxidized FAMEs in a micro-flow system with soybean oil as a raw material.

As a common problem for most cases of micro-flow system, separation of the biphasic mixture was still carried out on a rhythmic mode. Thus, investigations concerning integration of purification in micro-flow system have been widely reported [4]. *N*-arylpyrazoles were synthesized continuously in a micro-flow system which was composed of separation units based on gravity and microreactor [16].

In this study, we developed a new method for the direct continuous synthesis of epoxidized FAMEs with soybean oil as a raw material in a micro-flow system consisting of microstructed reactors and separation units.

2. Experimental

2.1. General methods

The quantitative analysis of FAMEs was performed on a gas chromatograph system (Agilent 7890A) employing a 30 m × 0.32

* Corresponding author at: College of Biotechnology and Pharmaceutical Engineering, Nanjing Technology University, Nanjing 210009, Jiangsu, PR China.
E-mail address: guok@njtech.edu.cn (K. Guo).

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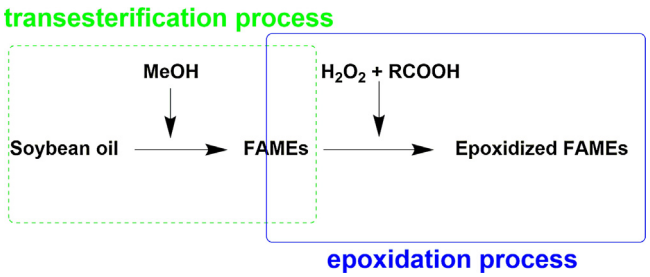

Scheme 1. Current synthetic route of epoxidized FAMEs.

mm, 0.25 μm film thickness DB-WAX capillary column. Epoxide number was analyzed by acetone-hydrochloride method [17]. All organic reagents were commercially available. Standard analytical reagents were obtained from Fluka. All micro-flow experiments were performed using commercially available Sandwich microreactor (Ehrfeld Mikrotechnik BTS GmbH).

As a fluid-temperature residence reactor, Sandwich microreactor (Fig. 1) is designed for several reactions under defined conditions in a continuous mode. Intensive cross-mixing of the process medium results in narrow residence time distribution. Besides, better heat exchange with the heat medium flowing through the process channel is obtained through the establishment of a heat exchange setup.

The slit-plate micromixer LH25 works (Fig. 2) according to the multilamination principle. When the fluids are fed into two concentric annular feed channels, streams of two different fluids are fanned out in a large number of small streams which are arranged alternately in an interdigital configuration.

The oil–water separator (Fig. 3) used in the study was made based on different adhesion forces towards equipment surfaces. The organic layer was obtained from the upper outlet, while, the aqueous solution was acquired from the bottom outlet.

2.2. General procedure for the continuous synthesis of epoxidized FAMEs

FAMEs were prepared by the transesterification of oil with methanol in the presence of basic catalysts. The mixture of methanol and sodium methoxide was merged with soybean oil using two medium pressure constant flow pumps (Shanghai Tauto Biotech Co., Ltd.). Then the reaction solution was introduced into the first microreactor. When the reaction was conducted for given time in a flow mode, the effluent went into a specific oil–water separator to separate the FAMEs from glycerol. A stream of acidic solution containing hydrogen peroxide (30 wt%), formic acid (98 wt%), catalyst and stabilizer was then mixed with the FAMEs and flowed into the second Sandwich microreactor (Fig. 4). Temperature inside the two Sandwich microreactors was adjusted by external heating cycle. The corresponding reaction mixture went into the same oil–water separator. Additionally, the process for obtaining neutral product was also realized in a continuous mode by using oil–water separators. Subsequently, drying process was conducted in a capillary column containing anhydrous sodium sulfate.

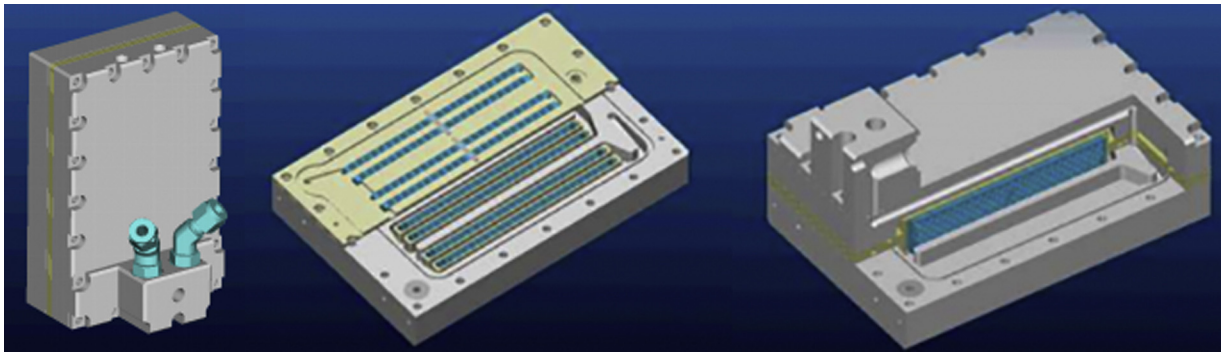

Fig. 1. The schematic diagram of Sandwich microreactor.

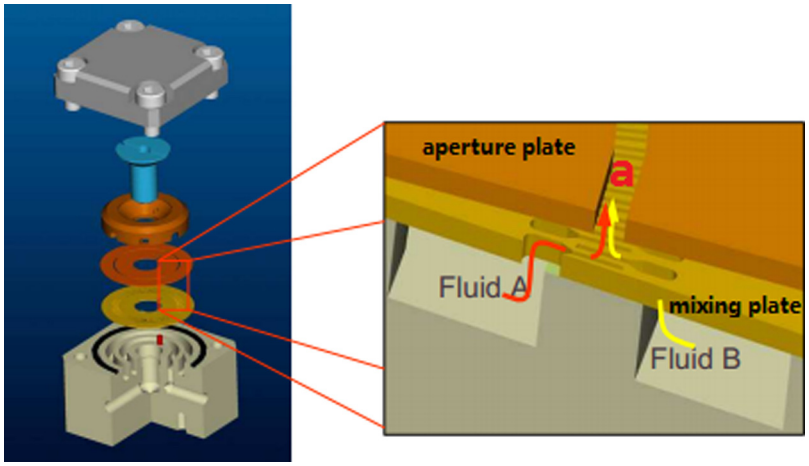

Fig. 2. The inside construction schematic diagram of LH 25.