Chemical Engineering and Processing 102 (2016) 70–87

Contents lists available at ScienceDirect

Chemical Engineering and Processing: Process Intensification

journal homepage: www.elsevier.com/locate/cep

Epoxidation of oleic acid under conventional heating and microwave radiation

Adriana Freites Aguilera[a], Pasi Tolvanen[a], Kari Eränen[a], Sébastien Leveneur[a,b], Tapio Salmi[a,*]

[a] Laboratory of Industrial Chemistry and Reaction Engineering, Johan Gadolin Process Chemistry Centre, Åbo Akademi University, Biskopsgatan 8, FI-20500 Åbo/Turku, Finland

[b] LSPC-Laboratoire de Sécurité des Procédés Chimiques, INSA Rouen, 685 Avenue de l'Université, FR-76801 Saint-Etienne-du-Rouvray, France

ARTICLE INFO

Article history:
Received 24 July 2015
Received in revised form 30 December 2015
Accepted 20 January 2016
Available online 22 January 2016

Keywords:
Epoxidation
Vegetable oil
Oleic acid
Chemical intermediates
Biolubricants
Microwaves
Process intensification

ABSTRACT

Epoxidized vegetable oils are used as chemical intermediates and biolubricants. Epoxidation of oleic acid as model compound for vegetable oils was performed in a batch-loop reactor. The system comprised a loop where the mixture was pumped through a cavity in which microwaves were irradiated. The reaction was executed by peroxyacetic acid formed in situ from acetic acid and hydrogen peroxide.

An extensive kinetic study of oleic acid epoxidation in the batch-loop reactor was conducted by varying the reaction temperature (40–60 °C), the stirring and pumping speeds as well as the molar ratios of the components. Both conventional heating and microwave irradiation were used in the experiments. Epoxidation of the double bonds in oleic acid proceeded as the main reaction, while acid-catalyzed ring opening of the epoxide appeared as the side reaction.

The results obtained showed that temperature, acetic acid amount and hydrogen peroxide amount accelerated both rate of epoxidation and ring opening processes. A clear enhancement of the epoxidation kinetics was accomplished with microwave heating in comparison to conventional heating, which was attributed to selective heating by the microwaves that enabled a higher interfacial mass transfer. Microwave application to epoxidation of vegetable oils is a promising process that successfully meets all the green chemistry requirements: energy saving and eco-friendly process and products.

1. Introduction

Biomass is the biological material extracted from living organisms, especially plants that originate from forests, fields, animals and oceans. During the past decade, the importance given to the use of biomass for chemical processes has escalated very quickly. The concept of green/environmentally friendly processes has caught a lot of scientific interest and has become one of the priorities of the efforts in science and technology. This development is mostly attributed to the fact that biomass is a renewable and vast resource with high potential for energy production; besides, biomass comprises a chemical richness that enables the development of a variety of products that can further replace fossil oil products [1–18].

Oils extracted from plants, seeds and wood are one of many biomass resources and it can be used to elaborate a wide range of products, from food, soaps and domestic products, to lubricants and biodiesel. According to the *Statista*© portal [3], the global production of vegetable oil has been constantly increasing for the past decade and for 2013–2014, 168.4 million metric tons were produced.

Approximately 80% of the total production of oils is directed to food industry, while the rest goes for other purposes such as chemical industry and production of biofuels. The type of vegetable oil that is consumed world-widely the most is palm oil, followed by soybean, canola and sunflower oils. The increment of vegetable oil production is related to the fact that new green technologies have been developed in the past years.

Epoxidized fatty acids from vegetable oils have been employed for the synthesis of polyols, glycols, olefinic compounds and stabilizers for polymers as well as plasticizers for developing PVC-derived plastic ware. They are also very good biodegradable lubricants. In 2013 the world consumption of lubricants consisted in 41.35 million metric tons, of which the majority is petroleum derivatives. The development of biolubricants from vegetable oils offers an eco-friendly and sustainable alternative that can

* Corresponding author. Fax: +358 2 2154479.
E-mail address: Tapio.Salmi@abo.fi (T. Salmi).

http://dx.doi.org/10.1016/j.cep.2016.01.011
0255-2701/

substitute regular mineral oil-based lubricants and its contaminating wastes.

For an efficient production of epoxidized vegetable oils, a clean and efficient process is needed. Process intensification is a tool to develop cleaner, safer, smaller and less expensive processes with products of higher quality. Microwave irradiation in chemistry is considered one of the best process intensification methods [19–29]. The first publication on the use of microwave irradiation in chemical processes appeared in 1975 and since then, a wide range of publications have appeared. Microwave irradiation in chemistry is considered one of the best process intensification methods.

The reaction system is displayed in Fig. 1. The characteristic feature is the in situ generation of peracetic acid from acetic acid and hydrogen peroxide. Acetic acid reacts with hydrogen peroxide in the aqueous phase forming peracetic acid, which dissolves in the oil phase, where it epoxidizes the double bonds of the oil. Acetic acid is recovered and returns back to the aqueous phase, and the reaction cycle is completed. Thus acetic acid acts as a catalyst in the process. Besides this main process, ring opening of the epoxide can take place, and it is catalyzed by dissolved acids, in the present case mainly by acetic acid. Both water and acids can act as reactants in the ring-opening process.

The current work focuses on the epoxidation of a model compound for fatty acids, i.e., oleic acid under conventional heating and microwave irradiation. The aim of the work is to compare conventional and microwave heating and to find optimal conditions for reaching high oleic acid conversion and high epoxide selectivity. A new batch-loop reactor system was constructed to get an objective comparison of microwave and conventional heating and to reveal a possible non-thermal effect of the microwaves.

2. Experimental

2.1. Equipment

Two experimental configurations were used. They are described below.

In configuration 1, the reactor setup was constructed to work as a recycled batch-loop system (Fig. 2). Besides the un-baffled reactor vessel [1], the system comprised a loop where the mixture was pumped through a cavity [5] in which microwaves (MW) were irradiated. A heat exchanger [7] was incorporated as the energy source in experiments with conventional heating; both equipment (MW cavity and heat exchanger) remained fixed to the system even when they were not used to maintain the reaction setup unchanged. The vessel was surrounded by a jacket filled with a mixture of ethylene glycol for cooling or heating to control and maintain a constant reactor temperature. A six-blade radial stirrer connected to a turbine engine was implemented in the reactor to generate high turbulence. The diameter of the stirrer was 5 cm. A peristaltic pump [3] was incorporated in the system instead of a regular pump to avoid a contact with metal materials that can trigger catalytic decomposition of hydrogen peroxide and peroxyacetic acid. A reflux condenser [8] was incorporated in the system to prevent evaporation. Two thermocouples were located inside the reactor (T2) and in the middle of the MW cavity (T1). The registered temperatures were saved in a computer. Both probes were protected with Teflon. The software to handle the reactor and MW cavity temperatures were Picolog® and Fisiocomander® respectively. The microwave frequency was 2450 MHz. A glass tube was was used in the MW cavity.

For some experiments it was necessary to change configuration 1 to configuration 2 by placing a heat exchanger in front of the microwave cavity to increase the temperature in the cavity and generate a higher difference between the reactor and cavity temperatures.

Details of the experimental equipment are reported in Supporting material.

2.2. Experimental procedure

Oleic acid (OA), hydrogen peroxide (HP) and acetic acid (AA) were carefully weighted separately and the first two were added to the reactor vessel and heated until the desired temperature was reached. Stirring and pumping were switched on as soon as the chemicals were added to the reactor. At the same time, acetic acid was heated separately in a round-bottom flask with a refrigerating column to avoid evaporation. When both the reactor and the acetic acid solution had reached the desired temperature, stirring and pumping were stopped and acetic acid was added to the mixture. After adding acetic acid, stirring and pumping were switched on again and, after 4–7 min, the first sample was withdrawn.

Up to 8 mL samples were withdrawn with a syringe during each experiment and deposited in flasks. The samples were cooled down under cold tap water and some minutes were waited until

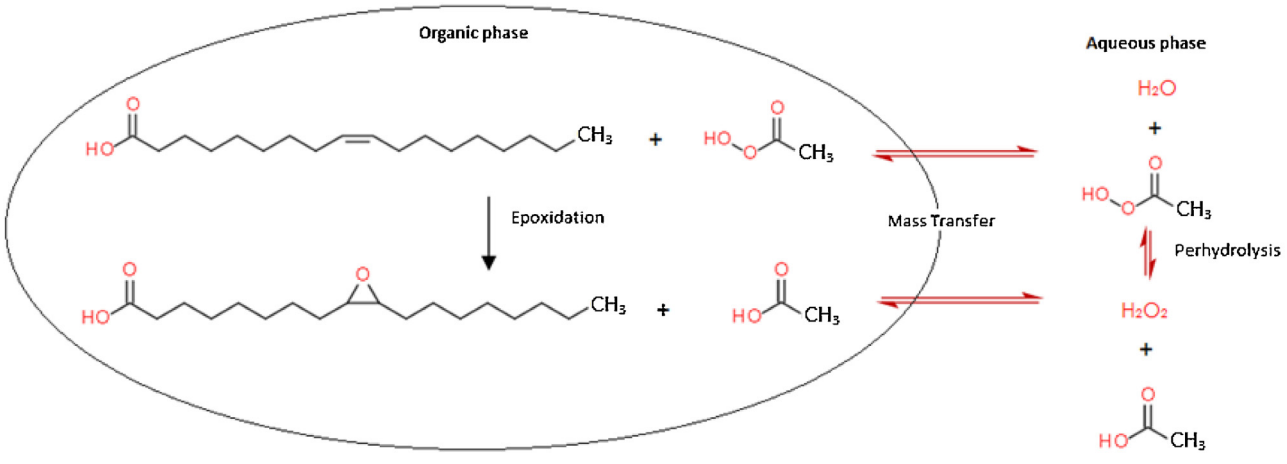

Fig. 1. Reaction scheme for vegetable oil epoxidation and ring opening.