



Intensification of epoxidation of soybean oil using sonochemical reactors

Vivek P. Chavan, Anand V. Patwardhan, Parag R. Gogate*

Department of Chemical Engineering, Institute of Chemical Technology, Matunga, Mumbai 400019, India

ARTICLE INFO

Article history:

Received 9 August 2011

Received in revised form 14 January 2012

Accepted 29 January 2012

Available online 6 February 2012

Keywords:

Epoxidation

Soybean oil

Hydrogen peroxide

Phase transfer catalyst

Sonochemical reactors

ABSTRACT

The epoxidation reaction of vegetable oils has been looked upon as an alternative option for synthesis of epoxides with an objective of replacing the petroleum-based epoxides. The present work illustrates epoxidation of soybean oil using tetra-n-butyl ammonium bromide as a phase transfer catalyst (PTC) in the presence of sonochemical devices such as ultrasonic horn and ultrasonic bath. Effect of various parameters such as pulse of ultrasound, power of ultrasound, effect of external temperature, amount of phase transfer catalyst, type of reactor configuration on the extent of conversion, etc. have been investigated. Under optimised conditions, the iodine value of oil was reduced from 132 to almost 19 at temperature of 80 °C using the ultrasonic horn. The intensification of epoxidation of soybean oil using ultrasound was observed in terms of substantial reduction in the reaction time for similar levels of conversion. It was found that the relative percentage conversion to oxirane using the conventional method was about 87% in 10 h while using ultrasound horn, almost 83% conversion was obtained in 4 h. The present work has clearly illustrated the utility of sonochemical reactors for intensification of epoxidation reaction opening a new opportunity for commercial exploitation.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

As most of the vegetable oils contain substantial unsaturation, they are useful for epoxide formation. Now-a-days, the environmental norms are getting more and more stringent to reduce the global warming. Vegetable oil based products are known to be sustainable and biodegradable, hence can be useful in reducing the global warming. The markets for vegetable-oil-based products are making an impact globally due to advantages like abundant availability, and environmentally friendly, economical processes. Fats and oils are the renewable resources that can be treated chemically or enzymatically to produce materials that can often act as a replacement of petroleum derivatives [1]. The approach based on the use of different oils (waste/off specification, non-edible or edible oils) for synthesis of value added chemicals such as epoxides has been considered as sustainable approach lowering the dependency on the petroleum based routes of synthesis, just similar to the synthesis of biodiesel from edible and non-edible oils using the transesterification route. There are also considerable and often underestimated challenges associated with the economics, management and public acceptability of all raw materials based on the crops, even for non-food use. In most cases the projections of petroleum reserves over the next few decades make it unlikely that

crop-derived commodity products that substitute for petroleum will be competitive [2,3]. Such sustainable routes of synthesis may not be cost effective at this stage but can be recommended for commercial exploitation considering the requirements of the future generation.

The unsaturation of the vegetable oils rich in oleic, linoleic and linolenic acyl groups may be used to introduce functional groups like epoxides. Fatty epoxides are used directly as plasticisers that are compatible with polyvinyl chloride (PVC) and as stabilisers for PVC resins to improve flexibility, elasticity, and toughness and to impart stability of polymer towards heat and UV radiation [4,5]. Epoxidation is the addition of oxygen bridge across an unsaturation, i.e. double/triple bonds to give epoxide. Epoxides, also known as oxiranes, are cyclic ethers with a three-member ring. The highly strained ring in the molecule makes them more reactive than other ethers. Epoxidation of vegetables oils is a commercially important reaction because the epoxides obtained from these renewable raw materials have wide applications such as plasticisers and polymer stabilisers, formation of polyurethane foam, synthetic detergents, coatings, lubricants and polyols [6–8]. Owing to the high reactivity of epoxides, epoxides also act as raw material for a variety of chemicals such as glycols, alcohols, carbonyl compounds, olefin compounds, alkanamines, and polymers like polyesters, polyurethanes, and epoxy resins [9].

Epoxidation of long chain olefins and unsaturated fatty acid derivatives such as soyabean oil have been carried out on an industrial scale [10]. Other epoxidised oils used as plasticisers are prepared from oils derived from linseed, rapeseed, olive, corn,

* Corresponding author. Tel.: +91 22 33612024; fax: +91 22 33611020.
E-mail addresses: pr.gogate@ictmumbai.edu.in, paraggogate@yahoo.co.in (P.R. Gogate).

safflower, and cotton seed. Epoxidised oil with higher oxirane content and lower α -glycol is considered to be of better quality [11,12]. On industrial scale, the epoxidation of plant oils, referred to as vegetable oils is carried out from reaction of unsaturated oil with a peroxy-carboxylic acid such as peroxyacetic acid and performic acid, obtained through acid-catalysed oxidation of respective organic acid with aqueous hydrogen peroxide [8]. The different methods used to produce epoxides from olefinic type molecules are: (i) epoxidation with percarboxylic acids [13], which is most widely used in industry and can be catalysed by acids or by enzymes; (ii) epoxidation with organic and inorganic peroxides, which includes alkaline, and nitrile hydrogen peroxide epoxidation [14]; (iii) epoxidation with halohydrines, using hypohalous acids (HOX) and their salts [13]; (iv) epoxidation with molecular oxygen [13]. Epoxidation with molecular oxygen using silver as catalyst is the cheapest and simplest route but it gives very low yield in terms of oxirane content. Epoxidation of vegetable oil with molecular oxygen leads to the degradation of the oil to smaller volatile compounds like aldehydes, ketones, and short chain dicarboxylic acids [9]. Therefore, it is not an efficient route for epoxidation of vegetable oils. Hence, for clean and efficient epoxidation of vegetable oils, the available technologies are epoxidation with percarboxylic acids and epoxidation with organic and inorganic peroxides [1]. It has been generally observed that the reaction times for obtaining desirable levels of conversion (80–90%) are usually in the range of 6–10 h [1,4,6,8] depending on the operating conditions and hence there exists ample scope for applying the process intensification principles to the epoxidation reactions. Ultrasonic reactors can be effectively used for the intensification of chemical processing applications and many of the chemical reactions limited by intrinsic kinetics or by mass transfer can be effectively intensified using ultrasound [15,16]. Use of ultrasound results in the formation of hot spots with conditions of very high temperatures and pressures locally. This is expected to increase the intrinsic kinetic rates leading to decreased reaction times for similar levels of conversion. Also the local turbulence and acoustic streaming generated by the cavitation events aids in improving the micromixing in the reaction system which can improve the efficacy of the phase transfer catalysts [17,18]. With this background, the use of ultrasonic irradiations has been investigated in the present work for the intensification of epoxidation of soybean oil.

2. Materials and methods

2.1. Materials

Soybean oil (edible grade, Glycine Max) was obtained from Sahakari Bhandar (Mumbai, Maharashtra, India). Glacial acetic acid (AR grade), benzene (extra pure), aqueous hydrogen peroxide (30%, w/v), sulfuric acid (98%) and tetra-*n*-butyl ammonium bromide (LR), hydrobromic acid (33%), periodic acid dihydrate, Potassium iodide, sodium thiosulfate (AR), starch soluble (AR), crystal violet were procured from S.D. Fine-Chem. Ltd., Mumbai, India. Wij's reagent was procured from Merck India Ltd., Mumbai, India. Benzyl trimethyl ammonium hydroxide (methanolic solution 40%) was procured from SISCO Research Laboratories Pvt. Ltd., Mumbai, India. All the chemicals were used as received from the respective suppliers.

2.2. Experimental set-up for acoustic cavitation

The sonochemical reactors used in the present work were ultrasonic bath and ultrasonic horn, which were procured from Dakshin India Ltd., Mumbai. Ultrasonic bath operates at a frequency of 25 ± 2 kHz or 40 ± 2 kHz and rated power of

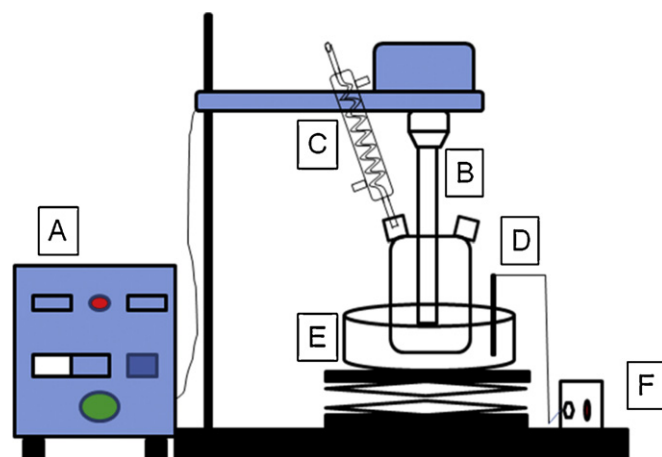


Fig. 1. Experimental set-up for acoustic cavitation (horn): A, generator; B, horn; C, condenser; D, reactor; E, oil bath; F, temperature controller.

200 W. The unit consists of 6.5 L stainless steel tank of size $300 \text{ mm} \times 1500 \text{ mm} \times 150 \text{ mm}$ ($L \times B \times H$) provided with piezoelectric transducers at the bottom. A 500 mL flat glass reactor equipped with six blade stirrer, condenser and thermocouple was suspended into the ultrasound cleaner. Liquid in the tank can be heated to a maximum temperature of 70°C using an electric heater and temperature controller. The other configuration of sonochemical reactor used in the work was ultrasonic horn reactor operating at a frequency of 20 kHz with rated power of 120 W. Ultrasonic horn was fitted with PZT transducer with tip diameter of 2 cm. The horn was immersed into a 300 mL capacity glass vessel, which was also provided with a condenser and thermocouple. The horn tip was immersed 5 mm below the liquid surface so that possibility of vortex formation is avoided and there are no decoupling losses in the energy transfer. Thermostatic oil bath was used to maintain the temperature of the reaction mixture. The experimental set-up of ultrasonic horn is shown in Fig. 1 and the glass reactor was immersed in the cleaning tank at the centre position in the case of ultrasound bath as shown in Fig. 2.

2.3. Experimental procedure

The experimental procedure described by Swern [19] was used in the present work. Initially soybean oil was taken in glass reactor and then acetic acid, sulfuric acid and tetra-*n*-butyl ammonium

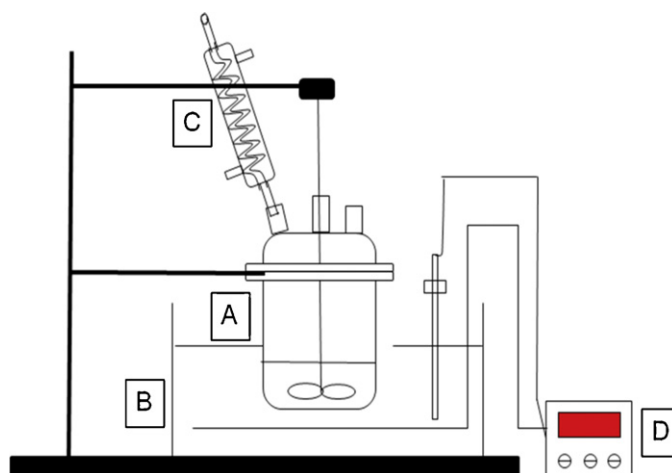


Fig. 2. Experimental set-up for ultrasound bath: A, reactor (500 mL); B, ultrasound cleaner; C, condenser; D, temperature controller.

Download English Version:

<https://daneshyari.com/en/article/687536>

Download Persian Version:

<https://daneshyari.com/article/687536>

[Daneshyari.com](https://daneshyari.com)