Epoxidation of soybean oil at maximum heat removal and single addition of all reactants

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ABSTRACT

The epoxidized soybean oil is obtained through the reaction of a lower peracid with the unsaturations of the vegetable oil molecules. The reaction is highly exothermic and temperature control is fundamental to avoid runaway. In industrial practice, a semibatch process is employed, in which performic acid is generated *in situ* by the addition of hydrogen peroxide to oil and formic acid vigorously mixed. Hydrogen peroxide is added gradually as the key procedure to maintain proper temperature control; as a result, the process time is usually long. In the present work the intensification of this process is investigated under conditions of a highly effective heat removal system and all reactants are added at once, thus making the process simpler and faster but still safe. A simple mathematical model was tested to represent the experimental data.

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1. Introduction

Epoxidized soybean oil is largely used especially as a co-stabilizer and a secondary plasticizer of PVC (polyvinyl chloride), with a worldwide production of more than 2000 kton/yr [1]. The application of this material as a primary plasticizer of PVC and building block for other bio-based chemicals has been growing significantly in the past years, mainly due to better quality of the epoxidized products and improved competitiveness (cost) over petroleum based traditional materials.

The epoxidation of vegetable oils is a well-know reaction, with patent applications as early as of 1946 [2], but current industrial processes rely on technologies that are limited primarily by the heat removal capacity of the equipment, since the reaction is highly exothermic. The most commonly used industrial process employs lengthy batch reactions (more than 8 h total time), with temperature controlled by the gradual addition of hydrogen peroxide, resulting in significantly high investments to obtain products with specified quality, in addition to several safety concerns.

The reaction occurs in a two liquid phase system, with mass transfer between the phases, as presented schematically in Fig. 1. In the aqueous phase, formic acid reacts with hydrogen peroxide to produce performic acid:

(1)
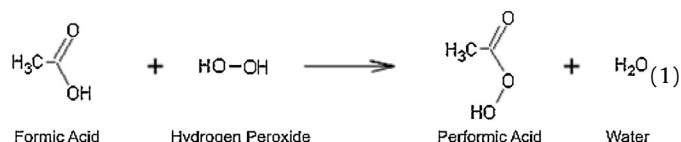
Performic acid is then transferred to the organic (oily) phase to react with the double bonds of the soybean oil triglyceride molecules, as represented by:

(2)
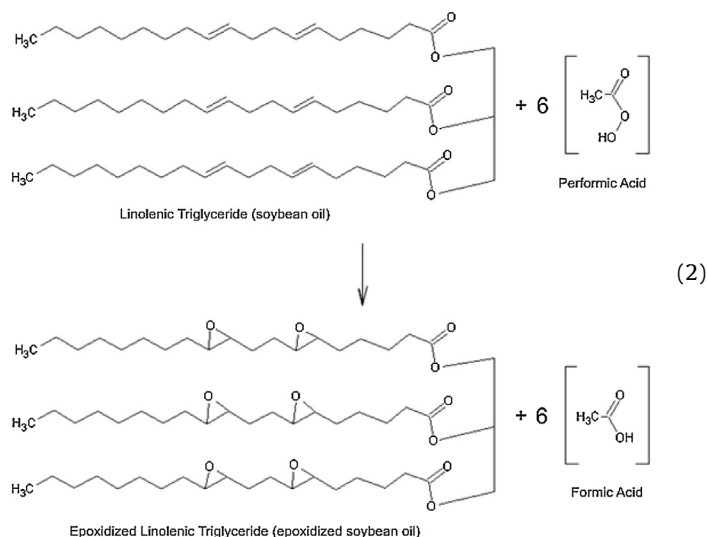
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organic phase — Formic Acid + Epoxidized Soybean Oil ← Performic Acid + Soybean oil

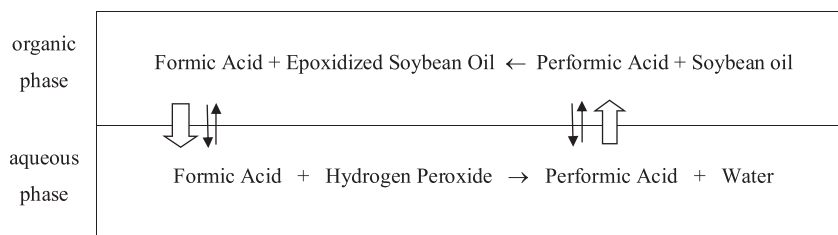aqueous phase — Formic Acid + Hydrogen Peroxide → Performic Acid + Water

Fig. 1. Scheme of the two-phase model and mass transfer between phases.

The resulting formic acid then transfers back to the aqueous phase to be again oxidized by the hydrogen peroxide. The reaction cycles between these four steps (two steps of mass transfer between the aqueous and the oily phase, and two main reactions, one in each phase), gradually consuming hydrogen peroxide in the aqueous phase and the double bonds of the triglyceride in the oily phase.

As expected, mixing plays an important role in the effective kinetics, as the droplet size depends on the shear, thus on the stirring speed, determining the magnitude of the contact area between the two phases and diffusion length inside the droplets. Mass transfer is directly affected by surface area. Mixing also plays an important role in the heat transfer between the reaction medium and the cooling system of the reactor. The apparent viscosity of the reaction mixture is determined by droplet size, temperature, stirring velocity.

Most of the literature studies of this reaction adopted a simplified approach by considering the two-phase system as a pseudohomogeneous system, thus simplifying the description of the effective reaction kinetics by overlooking the complex mass transfer phenomena involved [3]. The literature presented very little data to clarify potential optimizations and debottlenecking of the processes, in order to maximize conversion, reduce reaction times, and improve safety [4].

Literature has also covered the use of different catalysts [5] and complexing agents [6], seeking for better conversion. The industry, however, has adopted the simplified process that employs no catalysts, with formic acid as the preferred choice, due to its reactivity and cost effectiveness, considering optimized quantities and separations processes. The process with formic acid has been described in patent applications as early as 1949 [7]. The use of the most common catalysts and solvents also results in undesired oxirane ring-opening [8]. The use of other acids [9,10] and vegetable oils [11,12] has also been studied in the literature. The use of inorganic acid as catalyst is possible, but can contribute to undesired side reactions of oxirane ring cleavage [13], thus reducing overall oxirane index of the final product. Hydrogen peroxide may also contributes to the undesired oxirane ring-opening [14]. Previous studies of the process [15] employed gradual feeding of peroxide to mimic the industrial practice and to control the temperature rise due to the exothermic reaction.

There are also papers describing potential process intensification, focusing mainly on reaction improvement such as ultrasound [16], agitation and formation of a microemulsion [17]. Some studies have also been conducted to evaluate the feasibility of continuous processes [5,18,19], but relied mostly on theoretical models, and focused on cascade of continuous stirred tank reactors, packed bed tubular reactor, and continuous-flow micro-reactors. Fed-batch and pulse-fed-batch process were studied both experimentally and using a mathematical model [15].

In the present work, soybean oil was employed due to its commercial relevance—consequence of its fairly high iodine index and low cost. Formic acid (and hydrogen peroxide) was chosen due to the current use in industrial processes. No additional (inorganic) acid was employed as catalyst, and the addition of peroxide was studied with pulse-wise addition changing the number of pulses. The present work reports and discusses experimental runs that provide better understanding of the epoxidation process under maximum heat removal conditions. The effect of splitting the peroxide charge in different number of pulse additions was investigated to show the feasibility of using only one shot of peroxide at once as an efficient and safe process. Also, a preliminary, simplified mathematical model of the process was tested with the experimental data to interpret the results.

2. Experimental methodology

The experiments were carried out in a 500 mL glass reactor, with controlled stirring, immersed in a 20 L, highly agitated, thermostatic bath with water temperature controlled within $\pm 1\,°C$. The temperatures of the reaction mixture and of the cooling bath were measured by two thermocouples and registered in a computer through a data acquisition system. A stirrer with accurate speed control (Ika Labortechnik, RW20DZM) was employed with a stainless steel mixing paddle of 45 mm diameter.

The reagents, soybean oil (batch LO613A7:40, produced by Bunge, Brazil), hydrogen peroxide 60 wt% (Peróxidos do Brasil) and formic acid 85 wt% (reagent grade, Calgon) were used as received without further purification.

First, the amounts of soybean oil (250 g) and formic acid (15 g) were weighed and transferred to the reactor, stirred and left to heat up to the equilibrium with the thermostatic bath. The hydrogen peroxide solution was weighed (100 g) and then transferred to the reactor, and the data acquisition systems turned on; this instant is considered to zero time of the reaction. In runs with several (N) pulse-like feedings of peroxide solution, the same total amount of peroxide solution (100 g) was split in equal amounts (100/N g), weighed and added to the reactor at different times (every new pulse addition was made only after the temperature had dropped to at least to 25% of the maximum temperature rise of the previous pulse). Unless otherwise stated, the runs were carried out using a stirring speed of 400 rpm.

At the end of the process, the final conversion was determined by measuring the oxirane oxygen index (a measurement of the percent of oxygen atoms that are present in the form of an oxirane ring) and iodine index (a measurement of the concentration of double bonds), by standardized titration methods ASTM D 1652/AOCS Cd 9-57 and AOCS Cd 1-25, respectively. As an indication, the maximum theoretical oxirane oxygen index for the soybean oil used in the experiments would be 7.36%. The Iodine Index of the neat soybean oil, prior to reaction, is 126, while the specification for epoxidized soybean oil indicates an Iodine Index of less than 3.

As the reaction progresses, the color of the reaction mixture changes from light yellow (mixture of soybean oil and formic acid) to a bright orange (partially epoxidized triglycerides) and then to a light almost white cream (reaction complete, low concentration of unsaturations). Further studies may consider to correlating the