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Enzymatic hydrolysis of canola oil with hydrodynamic cavitation

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ABSTRACT

A hydrodynamic cavitation system based on a venturi was used to test the effectiveness of cavitation for enhancing the enzymatic hydrolysis of canola oil using lipase from *Candida rugosa*. Cavitation led to the production of fine oil-in-water and water-in-oil emulsions with the enzyme in the water phase. Using venturi inlet pressures of up to 8 bar, the yield of fatty acids was only about 60% of the maximum possible. In contrast, a simple stirred batch reactor produced over 90% of the maximum possible yield with reaction rates equal to, or better than, those obtained in a cavitating system. It was concluded that cavitation inhibited the reaction in some way and is not effective for intensification of hydrolysis.

1. Introduction

Edible oil hydrolysis (lipolysis) is a primary unit process which is used by industries such as dairy, detergent, cosmetic, oleochemical, petroleum, and waste processing. Sustainable ways of obtaining free fatty acids and glycerol from triglycerides have been investigated by many researchers [1–3]. Traditional processes require operating conditions with high pressures and temperatures, or alkaline/acid conditions, and have high energy consumption. However they have short reaction times and get yields close to 100%. The most common of methods has been the Colgate Emery process which needs operating temperatures of 250 °C and up to 60 bar of pressure [4,5].

Alternative systems using enzymes can eliminate some of the disadvantages of these methods. Use of an aqueous enzyme as a catalyst speeds the reaction up. This intensification allows it to be carried out at milder conditions and to get more specific products with an equivalent yield [6]. However, because of the immiscibility of the oil and aqueous enzyme phases, the reactions to produce free fatty acids, glycerol and others hydrolysis products occur at the interface of these two phases. Therefore, increases in the interfacial area between the phases can enhance the extent of reaction [4,7].

The kinetics of oil hydrolysis catalysed by enzymes has been widely studied for several years [3,4,7–10], and the main parameters affecting this reaction have been identified. Al-Zuhair et al. [7,9] showed that agitation, oil fraction, and temperature influenced the surface area between palm oil and water in a stirred reactor. They stated that, due to the adsorption–desorption dynamics of the enzyme at the interface, the rate of the reaction did not increase linearly with enzyme concentration and reaches a threshold at a critical enzyme concentration. Any further increase in enzyme concentration did not change the rate significantly.

Recently, numerous researchers have investigated process intensification of different applications, in particular with cavitation. Hydrodynamic cavitation has been proposed as a good way to intensify chemical processes, mass transfer and biological disruption [8,11]. Cavitation is defined as the generation, growth and the subsequent collapse of vapour bubbles in a liquid. The collapse of these bubbles creates high energy release, with high local temperatures and pressures, at a large number of reaction sites even though the overall reaction is carried out at ambient conditions [8]. In addition, the dissociation of water molecules within the bubbles can lead to the generation of free radicals. These substances have been shown to be very effective for intensification for some reactions such as the oxidation of potassium iodide [12].

Cavitation can occur when high liquid velocities cause the local pressure to drop below the vapour pressure of the liquid. The pressure, P, inside a device such as a venturi can be estimated from the relevant parts of Bernoulli's equation:

$$P = P_0 - \frac{1 - \left(A_0^2/A_v^2\right)\rho v_v^2}{2} \quad (1)$$

where P_0 is the upstream pressure, v_v is the fluid velocity in the venturi, ρ is the fluid density and A_0 and A_v are the cross-sectional areas of the upstream pipe and venturi respectively. If the value obtained is sufficiently lower than the vapour pressure of the liquid,

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bubble formation is likely within the region of high velocity. Once vapourisation occurs, predictions of P from Eq. (1) using the liquid density are no longer correct. Any downstream increase in pressure above the liquid vapour pressure leads to collapse of the bubbles.

For heterogeneous liquid/liquid reactions, the collapse of bubbles can take place near the interface between the two liquids. It results in mixing and disruption of the solution which scatters one phase inside the other. Thus an emulsion is generated raising the surface area between the phases, and causing faster mass transfer [4,7]. Recently, Patist and Bates [11] showed that ultrasonic processes can produce a very fine and stable emulsion with low energy input, increasing the surface area between two immiscible liquids.

Normally enhanced reaction rates in cavitation systems are associated with free radicals, locally high temperatures and pressures [13], enhanced mass transfer rates, or enhanced interfacial areas. Pandit and Joshi [1] compared acoustic and hydrodynamic cavitation systems for the enhancement of oil hydrolysis. For the hydrodynamic system, they used 200 L of oil–water mixture (with 1–10% oil) which was passed through a throttled cavitating valve without any enzyme, at 3–4 bar for about 40 h. They showed that hydrolysis can occur using hydrodynamic cavitation or ultrasonics (at 20 kHz for 10 h) at room temperature, and concluded that cavitation provided localised high temperatures and pressures that enabled the reaction to occur. This work has been cited in over 25 papers since but no other reports of hydrolysis with hydrodynamic cavitation have been found. However, ultrasonic cavitation has been used to enhance hydrolysis. Talukder et al. [14] found an optimal power for ultrasonic enhancement of hydrolysis of olive oil by *Chromobacterium viscosum* lipase in a two-phase water/isooctane system. They stated that this was associated with increased interfacial area, but they also noted a more rapid loss of lipase activity with sonication. Lee et al. [15] used ultrasound to enhance lipase activity in ionic liquids and concluded that it increased the mass transfer rates without causing loss of enzyme stability. Yachmenev et al. [16] concluded that it enhanced enzyme transport and opened up the surface of the solid substrate. No research was found that combined cavitation with enzyme hydrolysis.

In another enhanced hydrolysis process, Weatherley and Rooney [3] found that an electrostatic system used with enzymes could be as efficient as steam splitting performed at 240 °C and 33 bar. Giorno et al. [17] used microfiltration membranes to create emulsions for the study of the distribution of the *Candida rugosa* enzyme on the oil/water interface.

The aim of this study was to determine the effect of cavitation on the rate and yield of enzymatic hydrolysis of vegetable oil. The effect of pressure, enzyme concentration, emulsion type, and process operation were considered to enable a comparison with hydrolysis in a stirred reactor.

2. Materials and methods

Supermarket house brand canola oil (Pam's Products Ltd., New Zealand) was used for all experiments carried out in this study. All the oil used had the same manufacture identification and was assumed to be from the same batch. Typical canola oil contains triglycerides with a typical molecular mass of 882.1 g/mol (94.4–98.1%), phospholipids (up to 3.2%), free fatty acids (0.4–1.2%), an unsaponifiable oil part (0.5–1.2%) and other compounds (tocopherols, chlorophylls, sulphur, iron) [18]. The proportions of different types of lipid chains are: monounsaturated chains 67.6% (mostly oleic acid), polyunsaturated 27.2%, saturated chains 7.4%, others (trans saturated) less than 1%.

The lipase enzyme used was from *C. rugosa* (Sigma Chemical, Japan), with a specified concentration of 901 units per microgram of solid. It presents neither regioselectivity nor specificity for type

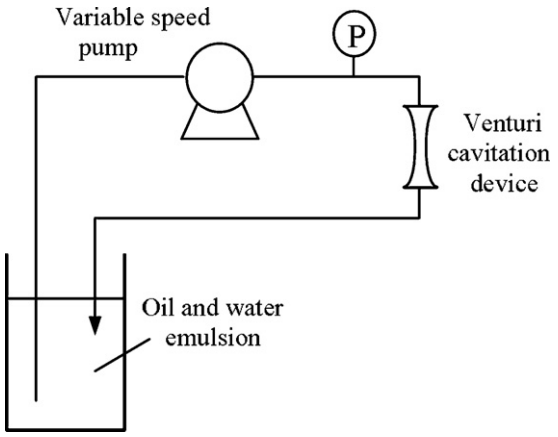

Fig. 1. Hydrodynamic cavitation apparatus.

of chain. However, it shows a level of discrimination against longer chains of fatty acids (C18–C22, mainly omega 3 fat) and a slow selectivity for unsaturated acids [6]. It was added to reverse osmosis water at a concentration of 1 g/L (unless otherwise stated) to form the aqueous phase. Optimal conditions of its activity are a temperature range of 33–39 °C, and pH of 7 but the enzyme is active in the pH range 5.5–9 [19]. All enzyme concentrations reported here are within the aqueous phase only.

A cavitation loop (Fig. 1) consisted of a 500 mL stainless steel beaker, a variable-speed magnetically coupled gear pump (GD-M35, Micropump Inc., WA, USA) and a venturi device (Fig. 2). The same device had been used previously to study the Weissler reaction [12]. For each run using the cavitation, 500 mL of the aqueous phase was added to the empty beaker and apparatus. Initially the aqueous phase was circulated at less than 1 bar gauge pressure (to prevent cavitation) while increasing the temperature to 36 °C. Indeed, it had previously been found [12] that cavitation of a dilute KI solution in the same system occurred from 1.8 bar gauge. Then 100 mL of the oil was added at about 1 mL/s to the loop immediately upstream of the gear pump by a variable-speed peristaltic pump (Masterflex Console Drive). Once the oil had been added, the gear pump speed was quickly increased to obtain the desired pressure (0.6–8 bar, upstream of the venturi) and the timer started. During the runs the solution temperature was controlled to within ±1 °C using a stainless steel cooling coil in the beaker through which water was circulated from controlled water bath with a temperature stability of ±0.1 °C. The water bath temperature set point was adjusted depending on the pressure, and hence power input, from the pump during a run. The pH of the solution in the beaker was measured continuously throughout all the runs but it was not controlled.

To compare the efficiency of the cavitation system, a 470 mL stirred batch reactor was set up using the same beaker and cooling coil, with a 36-mm axial impeller with 4 blades, and inserted at half the liquid depth. A volume of 392 mL of aqueous solution was poured into the beaker, the temperature was brought to the desired value, and 78 mL of oil was added directly to the beaker. At the start time the speed rate of impeller was quickly raised to 1850 rpm for

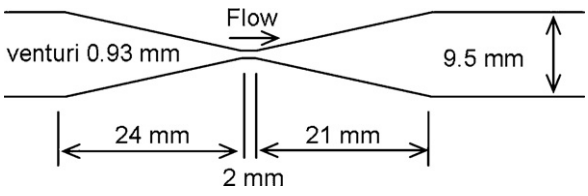

Fig. 2. Venturi device.