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Bread residues conversion into lactic acid by alkaline hydrothermal treatments

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HIGHLIGHTS

- Bread residues were converted hydrothermally into lactic acid.
- Effect of different catalyst, temperature and time of reaction were studied.
- Optimum conditions to obtain a high production of lactic acid were determined.
- Other products as formic acid, acetic acid, xylitol or acrylic acid were produced.

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ABSTRACT

Bread residues can be converted into a suitable feedstock for chemicals production due to their high starch content. The present study was focused on the production of lactic acid from bread residues using alkaline catalysts. NaOH, KOH, $Ca(OH)_2$, LiOH and K_2CO_3 were used at 300 °C, 30 min and 0.5 M catalyst concentration. The preliminary experiment showed that KOH, NaOH and $Ca(OH)_2$ are the best catalyst. Using these catalysts further experiments were carried out varying the catalyst concentration at the same operation conditions. The maximum yields of lactic acid from bread residues (% respect to the total initial raw material) were obtained at 300 °C, 30 min by using 0.4 M of KOH (38.11 ± 0.2%), 0.6 M of NaOH (34.46 ± 0.21%) and 3.5 M $Ca(OH)_2$ (72.90 ± 4.45%).

1. Introduction

Bread is considered as a basic component of the human diet in many countries. In Spain, it is estimated that one person consumes around 46–58 kg of bread per year. Bread residues are generated in industrial factories and removed due to the poor quality of wheat, deficiencies in baking technology, storage, distribution systems or by new market demands (commercial bread without crust). According to statistical data in Spain 30% of all produced bread (660 million of kg from 2200 million of kg produced) end up as leftovers. Bread residues can be used like feed for animals or bread-crumbs production.

Bread is a leavened product obtained from fermentation of wheat flour sugars liberated from starch by the action of natural flour enzymes. Bread contains from 50% to 75% of water, and the remaining part is flour (14.5% moisture, 13% proteins and 0.5% ashes) [1]. According to 100% flour, rest of the ingredients will be in following measurements like leavening agent yeast 2%, sugar 4%, salt 2% and shortening agent (ghee or margarine) 3% [2]. The starch is an key component in bread dry weight so bread residues can be considered a suitable alternative to chemicals production [3].

Starch is one of the main homopolysaccharides used for energy storage, and it can be found in seeds, roots, tubers, stems, leaves, fruits or pollen. The starch has remarkable physical and chemical characteristics and great nutritional quality. This polysaccharide is commonly used in thickening, stabilizing, texturizing, gelling, fat replacement, film forming, encapsulation, moisture retention and shelf life extension [4] or can be converted into ethanol, lactic acid or another chemicals [5,6]. In concrete, the aim of this work focuses in the chemical conversion of bread residues into lactic acid.

Lactic acid has especially gained interest for using in biodegradable lactic acid polymers production (polylactic acid, PLA), solvents, metal pickling and additives in food, pharmaceuticals and cosmetics [7,8]. PLA is a biodegradable polyester derived from renewable sources (mainly starch and sugars) [9]. It is used in health-demanded new materials such as clips and medical sutures for wound closure, controlled drugs or in artificial prostheses being

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an environment friendly alternative to plastics derived from petrochemical materials [10–13]. In addition, PLA is a promising material for food packaging due to its low toxicity and its environmental advantages [14].

The production of lactic acid can be carried out by chemical synthesis or by fermentation from sugars or starch. Fermentation processes are the most common methods to produce lactic acid, but it is necessary between 2 and 8 days of production and this process has a limited production capacity. In addition, it is a complex and sensitive process in which pH and temperature must be carefully controlled obtaining 85–95% lactic acid yield from fermentable sugars [15–17].

Lactic acid by hydrothermal process is an important method because under high temperatures and pressures water becomes an effective catalyst and good reaction media with unusual properties [18,19]. Lactic acid may be produced by hydrothermal processes through a base catalytic effect of water combine with high temperatures, but this process may be improved with the addition of alkali [20–22].

The present work was focused in the valorization of bread residues into lactic acid by using different alkaline catalysts (NaOH, KOH, $Ca(OH)_2$, LiOH and K_2CO_3). By this way, the effects of different catalysts, concentrations and reaction conditions on lactic acid production from starch of bread residues were determined.

2. Materials and methods

2.1. Raw material conditioning and characterization

Mixture of white and whole bread residues were kindly supplied by independent Spanish producers. Bread was dried up to constant moisture and finely milled until obtaining homogeneous powder (less than 0.5 mm).

Bread residues were characterized to determine their chemical composition. The moisture was measured by overnight drying in an oven at 80 °C. Ash content was determinate by ignition in a muffle furnace at 800 °C. Elemental analysis was carried out in a Euro EA 3000 series elemental analyzer from EuroVector SpA, Milano, Italy; total oxidation of the sample (10 mg) was conducted at 1020 °C; combustion products were separated in a chromatographic column (PTFA column for CHNS, 2 m; carrier gas, He, 70 kPa; purge flow, 80 ml/min; oxygen pressure, 35 kPa). Starch content was determined by spectrophotometry using a calibration curve of D-glucose. All determinations were performed in triplicate.

2.2. Alkaline hydrothermal processing

Milled bread residues were subjected to alkaline hydrothermal processes using a 100 mL Mini Compact Reactor (Parr 5500) equipped with a Reactor Controller 4848 that supports a maximum pressure of 200 bar and temperature range of −10/350 °C. The established operation conditions were temperature 300 °C with continuous stirring (500 rpm by 4 bladed propeller stirrer), 30 min as reaction time and 1:25 as solid/liquid ratio. NaOH (98%), KOH (85%), Ca $(OH)_2$ (95–100%), LiOH (98–100%) and K_2CO_3 (99%) solutions (0.5 M) were used as alkaline catalysts. 2 g of finely milled bread residues with 50 mL of alkaline solution was used in each experiment. These reaction conditions were fixed on a basis of previous experiments [22] and potato starch was used for comparison.

After that, the best catalysts were studied to improve the lactic acid yield, maintaining temperature and agitation time (300 °C and 30 min) but varying the catalyst concentration.

2.3. Instrumental methods

Lactic acid, hydrolysated sugars and other compounds concentration were quantitatively determined after alkaline hydrolysis in a High Performance Liquid Chromatography (HPLC) Jasco LC Net II/ADC with column oven (CO-2065Plus) and quaternary gradient pump (PU-2089Plus) equipped with a refractive index detector (RI-2031Plus), photodiode array detector (MD-2018Plus) and Rezex ROA Organic Acid H+(8%) column. Filtered (Phenex Filter Membranes 0.45 mm, 47 mm, nylon) 0.005 N H_2SO_4 prepared with 100% deionised and degassed water (Water, gradient HPLC grade, Scharlab) was used as mobile phase. As injection conditions 40 °C, 0.35 mL/min flow and 40 μL as injection volume were used. For the calibration curves, standardized solutions of commercial L(+)-lactic acid (85%), xylose (⩾99%), glucose (⩾99%), arabinose (⩾99%), acetic acid (⩾99.5%), formic acid (⩾85%), xylitol (⩾99%) and ethanol (⩾96%) were used.

3. Results and discussion

3.1. Raw material characterization

Bread residues presented 5.6% moisture and 2.6% ash content. According to the elemental analysis, the following results were obtained: C: 43.14%, H: 7.24%, N: 2.36%, O: 47.26%. Finally, 75% starch content was determined in the raw materials for its conversion to lactic acid. The obtained starch content was suitable for converting bread residues into lactic acid.

3.2. Effect of alkaline catalyst on lactic acid yield

The obtained results with the selected operational conditions and their comparison with potato starch are presented in Fig. 1.

NaOH, KOH and $Ca(OH)_2$ presented the highest lactic acid yields (14.41 ± 0.31, 14.79 ± 0.45 and 14.15 ± 0.69 g/L of lactic acid respectively from bread residues and 14.44 ± 0.04, 14.30 ± 0.04 and 15.86 ± 0.04 g/L of lactic acid respectively from potato starch). The similar lactic acid yields achieved using bread residues and potato starch could be justified by the presence of other components in the bread (sugars and other compounds) which could be converted to lactic acid at high temperatures.

In contrast, the lowest lactic acid yield was obtained without any catalyst confirming that the use of catalyst improved significantly the lactic acid production.

For better comprehension of obtained yields, lactic acid yields recalculated with respect to the total weight of initial raw materials were presented in Table 1. The results were showed in percentage of lactic acid respect to the initial total weight of bread residues. Again, the best results were obtained with KOH, NaOH

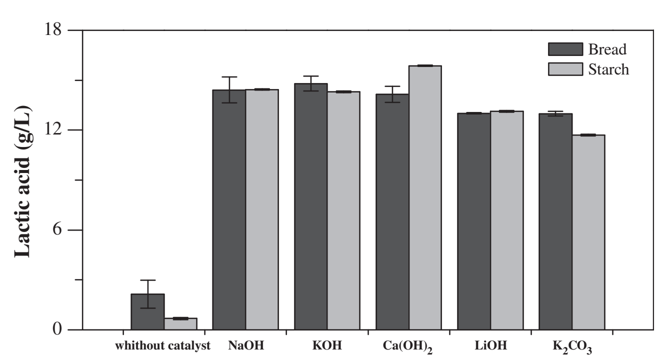

Fig. 1. Lactic acid concentrations resulted after bread residues and starch hydrolysis at 300 °C, 30 min and 0.5 M catalyst concentration.