Chemical Engineering Journal 181–182 (2012) 655–660

Contents lists available at SciVerse ScienceDirect

Chemical Engineering Journal

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

Lactic acid production by alkaline hydrothermal treatment of corn cobs

Cristina Sánchez, Itziar Egüés, Araceli García, Rodrigo Llano-Ponte, Jalel Labidi *

Chemical and Environmental Engineering Department, University of the Basque Country, Pza Europa, 1, 20018, Donostia-San Sebastián, Spain

ARTICLE INFO

Article history:
Received 18 October 2011
Received in revised form 6 December 2011
Accepted 9 December 2011

Keywords:
Corn cobs
Thermal conversion
Catalyst
Lactic acid

ABSTRACT

An experimental study was carried out for the corn cobs thermal conversion to obtain the maximum content in lactic acid. For this purpose, under the same conditions (275 °C and 30 min) different concentrations of $Ca(OH)_2$ as alkaline catalyst were used (from 0.32 M to 1 M). The maximum content of lactic acid (6.72 ± 0.31 g/L) was obtained with 0.7 M of $Ca(OH)_2$. With this catalyst concentration, different reaction conditions were used (250, 275 and 300 °C and 15, 30 and 45 min). The optimal conditions to produce the highest yield of lactic acid from corn cobs in alkaline conditions were determined at 300 °C and 30 min, achieving 44.76 ± 2.59% respect to the total cellulose and hemicellulose contained in the initial corn cobs (7.38 ± 0.43 g/L of lactic acid).

1. Introduction

Lignocellulosic materials are characterized to be abundant and inexhaustible, renewable, with low pollution character and with low price. Due to these properties, lignocellulosic materials represent an important source to obtain polymeric materials, energy and a wide variety of chemical compounds with high added value [1–3]. Among lignocellulosic materials, corn cobs are classified as abundant agricultural wastes with high content in hemicelluloses and cellulose (about 30–40 wt.% hemicelluloses and 33–41 wt.% cellulose of the dry material). Owing to their composition, corn cobs present a great potential for producing a lot of added-value chemicals [4].

The hemicellulosic fraction is made up of amorphous heteropolysaccharides containing different structural units (xylose, glucose, arabinose, mannose, galactose or rhamnose), which can be substituted with phenolic, uronic or acetyl groups [5]. For hemicelluloses recovery, xylooligosaccharides can be produced from xylan-rich lignocellulosic biomass by different hydrothermal processes. These obtained xylooligosaccharides can be used for synthesis of biopolymers such as lactic acid [6]. Cellulose, the main component of biomass, has become an attractive substrate because of its conversion to useful chemical products, as well as for it potential for the production of bioethanol. The cellulose molecules are a linear homopolymers composed of a repeating unit of glucose linked by $(1 \rightarrow 4)$-β-glycosidic bonds. The associated cellulose molecules form subunits called microfibrils, which are grouped forming fibrils with crystalline and amorphous structures parts [7–9].

Lactic acid (2-hydroxypropionic acid) is an organic acid bearing a hydroxyl group an acid function, and has particularly gained interest for use in producing biodegradable lactic acid polymers, solvents, metal pickling and food additives [10,11]. Due to the recent increase in environmental concerns, the technical applications of lactic acid include use as a preservative in food, pharmaceuticals and cosmetics, and in the production of polylactic acid (PLA). PLA is a biodegradable polyester used in health-demanded new materials such as medical sutures and clips for wound closure, controlled drug or in artificial prostheses that may be an environment friendly alternative to plastics derived from petrochemical materials [12–15]. Lactic acid also has potential applications as controlled release systems for pesticides and drugs [16].

Lactic acid can be manufacture by chemical synthesis or by fermentation of different carbohydrates such as starch, glucose or xylose. Presently, most lactic acid is produced by fermentation of glucose, but a minor quantity is produced by chemical synthesis employing highly toxic and expensive feedstock [17,18]. The fermentation is a complex and sensitive process, especially the recovery steps, because it has a limited production capacity and it takes 2–8 days to complete the reaction. The pH and temperature also must be carefully monitored, and the yields to lactic acid are 85–95% based on fermentable sugars [19].

The hydrothermal processing of lignocelullosic wastes is one of the most prominent methods for converting biomass in lactic acid, because under a high temperature and high pressure, water behaves as a reaction medium having unusual properties, and acts as an effective alkaline catalyst [20,21]. Some studies showed that lactic acid may be formed by this process without the addition of

* Corresponding author. Tel.: +34 943017178; fax: +34 943017140.
E-mail address: jalel.labidi@ehu.es (J. Labidi).

1385-8947/$ – see front matter
doi:10.1016/j.cej.2011.12.033

any catalyst through a base catalytic effect of high-temperature water [22], but the addition of an alkali under hydrothermal conditions can facilitate the lactic acid formation and increase the reaction yield [23].

The main purpose of this study was to determine the best reaction conditions to produce lactic acid by thermal conversion of corn cobs. Different reaction conditions have been proposed varying the alkaline catalyst content, the temperature and reaction time. To promote the lactic acid formation, most of reported studies used as alkaline catalyst NaOH or $Ca(OH)_2$ with a concentration ranging from 0.32 M to 2.5 M [22–24]. In this work both catalysts have been used under the same conditions (0.32 M, 275 °C and 30 min) to determine the most suitable. $Ca(OH)_2$ was chosen as the best.

The catalyst concentration has been varied to determine the optimal concentration to be used in the experimental study. Using the optimum catalyst concentration determined previously, different alkaline thermal treatments have been carried out. In the experimental study, the temperature (250, 275 and 300 °C) and the time of reaction (15, 30 and 45 min) have been varied to determine their effects on the reaction yield.

2. Materials and methods

2.1. Raw material characterization

The corn cobs used as raw material in this investigation were kindly supplied by an independent farmer from Pontevedra (Spain). The raw material with constant moisture, were grounded in a mill and then sieved, to obtain 0.4 mm as the size fraction according with the standards that will be used. Milled corn cobs were chemically characterized using TAPPI standards in terms of moisture (TAPPI T264 cm-97), ash (TAPPI T211 om-93), extracts (TAPPI T204 cm-97), Klason lignin (TAPPI T222 om-98), α-hollocellulose [25], cellulose [26], hemicellulose and others.

2.2. Alkaline hydrothermal process

By using the alkaline hydrothermal treatments, cellulose and hemicellulose are mainly converted into glucose, which discomposed to other products including aldehydes or ketones, from which lactic acid or other organic acids are produced (such as formic, acetic or acrylic acid) [27].

The reaction was carried out in a Mini Compact Reactor of 100 mL (Parr 5500) equipped with a Reactor Controller 4848 that supports a maximum pressure of 200 bar and a temperature range of −10/350° C. In each experiment 1.23 g of finely milled corn cobs with 50 mL of dissolution were used. To carry out the treatments, different reaction conditions were used; firstly, the selected catalyst $Ca(OH)_2$ concentration was varied (0.32, 0.5, 0.6, 0.7, 0.8 and 1 M) under the same conditions of temperature and reaction time (275 °C and 30 min). After obtaining the optimal catalyst concentration to produce the higher concentration in lactic acid, different experiments were carried out varying the temperature and reaction time to improve the lactic acid yield. In total, as it can be seen in Table 1, 9 experiments were performed using different conditions: at temperature of 250, 275 and 300 °C and reaction time of 15, 30 and 45 min.

2.3. Quantification of lactic acid and other organic acids

To determine the lactic acid content, the hydrolysated sugars and the rest of formed compounds in liquors after alkaline hydrolysis processes, a High Performance Liquid Chromatography (HPLC) Jasco LC-Net II/ADC was used, equipped with a refractive index detector, photodiode array detector and Rezex ROA-Organic Acid H+ (8%) column. As mobile phase, 0.005 N H_2SO_4 dissolution were prepared with 100% deionised and degassed HPLC water. As injection conditions 40 °C, 0.35 mL/min flow and 40 μL as injection volume were used. For the calibration curve, a standardized solution of lactic acid was used. To determine the rest of liquors compounds, high purity glucose, xylose, arabinose, xylitol, formic acid, acetic acid, ethanol, and acrylic acid were used.

Table 1
Experiments conditions for $Ca(OH)_2$ as catalyst.

Experiment	T (°C)	t (min)
1	250	15
2	250	30
3	250	45
4	275	15
5	275	30
6	275	45
7	300	15
8	300	30
9	300	45

2.4. Characterization of precipitated solid fraction

2.4.1. Fourier transform infrared spectroscopy (FTIR)

The remaining solid fraction was filtered and washed, and then characterized by FTIR. For this purpose, a PerkinElmer 16PC instrument by direct transmittance with an MKII Golden Gate SPEACAC accessory was used. Spectra were recorded over 20 scans with a 4 cm^{-1} as resolution in the range between 4000 cm^{-1} and 600 cm^{-1}. By the FTIR spectroscopy, the most characteristic bands of initial raw material were compared with the obtained solid residues after hydrothermal conversion.

3. Results and discussion

3.1. Composition of corn cobs

The main components compositions (% on an oven-dry weight basis) resulted after corn cobs characterization, were 0.95 ± 0.03 ash, 2.43 ± 0.03 extracts, 23.13 ± 3.40 lignin, 36.75 ± 0.54 cellulose, 29.98 ± 3.6 hemicelluloses and others 6.76 ± 1.52.

Table 2 presents obtained corn cobs compositions reported results by other authors.

From these results, it can be concluded that corn cobs are a suitable feedstock for lactic acid production due to their high content in cellulose and hemicellulose.

3.2. Election of catalyst concentration

In order to determine the optimal catalyst concentration preliminary experiments were carried out. According to Fig. 1, the maximum content in lactic acid (6.73 ± 0.31 g/L) at 275 °C and 30 min was obtained using $Ca(OH)_2$ 0.7 M as catalyst. The achieved yield at these conditions was 40.82 ± 1.88% of lactic acid, respect to the total content in cellulose and hemicelluloses in the initial raw material. Using $Ca(OH)_2$ 0.32 M with the same conditions (275 °C and 30 min), the minimum content in lactic acid (4.09 ± 0.12 g/L) was obtained, corresponding to yield of 24.82 ± 0.75%.

Table 2
Composition (%) of corn cobs according to other authors.

Component	Reference		
	[4]	[5]	[28]
% Hemicellulose	39.0	31.1	33.7–41.2
% Cellulose	34.3	34.3	30.0–41.7
% Lignin	14.4	18.8	4.5–15.9