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Hybrid Route to Produce Acrylic Acid from Sugarcane Molasses

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This work presents the synthesis of acrylic acid by hybrid route from sugarcane molasses fermentation and later acid lactic dehydration. Lactic acid was produced by sugarcane molasses fermentation using the *Lactobacillus plantarum* CCT 5731 bacteria in bioreactor BioFlo 415 at 37 °C. After of 46.4 h of fermentation 50.6 g/L of lactic acid was obtained with productivity of 1.1 g/L.h which was subsequently concentred to 152 g/L and stored to dehydration stage. Both commercial lactic acid and lactic acid obtained through fermentation stage were dehydrated by catalysts supported on basic zeolite (NaY) in a tubular reactor at 300 °C and continuous flow of CO_2 (30 mL/min). The largest selectivity (25.7 %) for acrylic acid was obtained when the commercial lactic acid and KBr/NaY were used. When lactic acid obtained by fermentation a maximum acrylic acid selectivity of 16.7 % was achieved using KI/NaY. All chemicals species were characterized by high performance liquid chromatography (HPLC).

1. Introduction

In recent decades, biomass has played an important role in the industry especially for its abundance and relative low cost (Lee et al. 2010). In Brazil, the sugarcane is used to sugar and ethanol production (Dias et al. 2013). In the purification of sugar is obtaining a sub-product know as sugarcane molasses (Chauhan et al. 2011), which is a brownish viscous that is generally used in the production of ethanol (Ghorbani et al. 2011). However, the sugarcane molasses is a carbon source ideal for the production of small molecules such as lactic acid by fermentation route. Lactic acid has shown great importance in the food industry, textile, leather, pharmaceutical (Rojan et al. 2009). This is a highly reactive molecule that may be reactant in reactions of dehydration, decarboxylation, condensation, reduction, dehydrogenation, esterification and polymerization that means a potential feedstock for renewable chemicals (Zhang et al. 2008). From dehydration of lactic acid may be produced the acrylic acid (Yan et al. 2011), which is nowadays mainly produced by oxidation of propylene in the petrochemical industry and used as raw material in the production of polymeric products (Lee et al. 2010). These polymers are characterized by their transparency, easy adhesion, elasticity, and stability to heat and to light. They are applied to the coating of surfaces, textiles, adhesives, paper treatment, fibers, detergents, superabsorbent materials, etc (Xu et al. 2011). On the other hand, acrylic acid production by fermentative process present an innovative process of great importance, because the possibility of low cost for its production and because of a renewable raw material (Lunelli et al. 2007). However, this last route is under study and some improvements are needed to become economically competitive.

In this context, the present work aims to develop the synthesis of acrylic acid by hybrid route (fermentation-catalytic dehydration) from of sugarcane molasses fermentation and subsequently catalytic dehydration of lactic acid to obtain as final product acrylic acid, highlighting the use of sugarcane molasses as a promising raw material to the chemical production with high added value.

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2. Experimental

2.1 Materials

Sugarcane molasses was donated by Usina Iracema, a large scale industrial plant and L*actobacillus plantarum* bacteria was purchased from André Tosello Foundation. Catalysts were prepared through a confidential procedure and the commercial DL-lactic acid (~ 90 %) was acquired of Sigma-Aldrich.

2.2 Sugarcane molasses fermentation to obtain lactic acid

Sugarcane molasses fermentation was divided in two steps: studies in Shaker and fermentation in laboratory scale. Previous studies in shaker were performed to determine the working conditions (sucrose concentration, yeast extract concentration and temperature) to be implemented in a bioreactor BioFlo 415. *Lactobacillus plantarum* bacterium was reactivated in Man–Rogosa–Sharpe (MRS) agar for 48 h at 28 °C. After this time, an aliquot was transferred to a test tube containing 10 mL of MRS liquid medium and maintained for 48 h growth temperature. Thereafter, 5 mL tube were removed and added to 125 mL Erlenmeyer flask with 45 mL of MRS liquid medium and again held under the same conditions for 48 h. In the final step, 300 mL of sugarcane molasses were prepared in Erlenmeyer with 14 % v/v inoculum and known concentrations of sucrose (14 g/L, 23 g/L and 33 g/L) and extract yeast (2 g/L, 4 g/L and 6 g/L). Hence, fermentations at 31 °C, 34 °C and 37 °C were carried out for 24 h and 200 rpm. Then, 4 mL samples were collected at 6 h, 10 h and 24 h to monitor the process and the lactic acid and sugars (fructose, glucose and sucrose) were characterized using a high performance liquid chromatography, Agilent 1260, equipped with a refractive index detector and a Bio-Rad Aminex HPX-87H column (300×7.8 mm) at 25 °C, and 4mM H_2SO_4 was used as mobile phase at a flow rate of 0.6 mL/min and sample injection volume of 15 µL. Identified the best conditions of sucrose and yeast extract concentration and temperature, the fermentation was conducted in a bioreactor BioFlo 415 of 7 L. This step began with the preparation of the cultivation in the conditions used in the first three step of culture growth studies carried out in shaker level. Then, the contents of the Erlenmeyer flask (50 mL) was added to another 1000 mL Erlenmeyer flask containing 450 mL of MRS liquid medium and kept on shaker for 30 h, at optimal temperature. Finally, 2,580 mL of sugarcane molasses composed of the best conditions of sucrose and yeast extract were added to the bioreactor and 150 mL of water ware also added. Then, the above mixture was sterilized at 121 °C for 30 min. After cooling, 420 mL of inoculum was added to the bioreactor and the fermentation was carried out to 200 rpm and temperature determined in previous studies. During the fermentation the pH was kept to 5 by addition of 4N NaOH solution and a pulse of sugarcane molasses solution was given in time where the pump power of the base (4N NaOH) stopped working (24.2 h) and the fermentation was maintained for 46.4 h. Subsequently, the biomass was characterized by gravimetric method and the lactic acid and sugars were characterized by HPLC using a methodology described above.

2.3 Catalytic dehydration of lactic acid to acrylic acid

The dehydration of both commercial and lactic acid obtained from fermentation of sugarcane molasses (Figure 1) to produce acrylic acid over the catalysts supported on basic zeolite (KBr/NaY, KI/NaY and $Ca_3(PO_4)_2$/NaY) and the support (modified NaY) were carried out in a fixed-bed reactor of 0.1075 m inner diameter and 0.130 m of length. The catalyst (2.24 g) was placed in the middle of the reactor and quartz wool was placed in both ends (bottom 1.16 g, top 2.24 g) and pre-treated at 573 K for 0.5 h under Ar (0.0018 m^3/h). The feedstock (lactic acid solution, 152 g/L) was pumped into the preheating zone (LHSV = 3 h^{-1}) and driven through the catalyst bed by CO_2. The liquid products were condensed and collected every 0.33 h. Then, the concentration of lactic, acetic, propionic and acrylic acids were measured by HPLC at 30 °C and using the methodology described to sugar analysis.

Figure 1. Lactic acid. a) Commercial, b) obtaining by fermentation of sugarcane molasses

The selectivity and conversion were calculated according to the equations 1 and 2.

$$\text{Conversion of lactic acid} = \frac{\text{molar quantity of lactic acid that reacted}}{\text{molar quantity of lactic acid feed to reactor}} \text{x}100 \quad (1)$$

$$\text{Selectivity} = \frac{\text{carbon molar quantity of the final product}}{\text{molar quantity of lactic acid that reacted}} \text{x}100 \quad (2)$$

3. Results and discussion

3.1 Sugarcane molasses fermentation

From studies in shaker was determined that, in the considered conditions, the highest concentration of lactic acid (11.5 g/L), after 24 h of fermentation, was obtained with 37 °C, 33 g/L of sucrose and 4 g/L of yeast extract. Therefore, in the fermentation of sugarcane molasses in bioreactor BioFlo 415 these conditions were maintained and its results are show in the Figures 2 and 3. A priori of fermentation, the sugarcane molasses was autoclaved in the bioreactor BioFlo 415. This bioreactor model presented fluid loss during autoclaving for which reason 150 mL of water ware increased to correct this loss. However, the increased volume of water was greater than the volume of fluid lost, whereby the sugarcane molasses solution presented dilution at the start of fermentation. Next to 22 h of fermentation, it was observed that NaOH feeding pump was not working for which was decided to give a pulse of sugarcane molasses solution (223.6 g/L of sucrose) at 24 h. The measure of sugars in HPLC showed that just before of pulse the fructose, glucose and sucrose had been almost completely degraded obtaining a concentration of lactic acid of 40.9 g/L. After the pulse was possible to increase the concentration of lactic acid, obtaining a maximum concentration of lactic acid of 50.6 g/L at 46.4 h of fermentation and low concentration of sugars (1.1 g/L of fructose, 0.1 g/L of glucose and 0.1 g/L of sucrose) (Figure 2). Moreover, the higher productivity was of 2.9 g/L.h at 9.8 h of fermentation and decrease to 1.1 g/L.h at 46.4 h. Biomass concentration suffered rapid increase during the first 9.8 hours of fermentation and then fluctuated around 3 g/L.

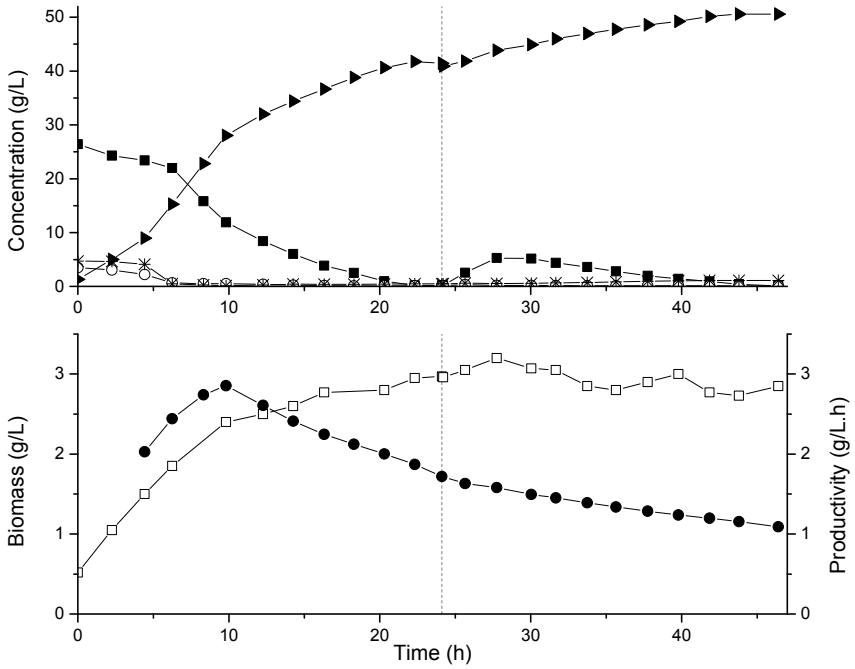

Figure 2. Sugarcane molasses fermentation by Lactobacillus plantarum. ● Biomass, ◊ Fructose, ○ glucose, ►lactic acid, □ productivity, ■ sucrose

3.2 Catalytic dehydration of lactic acid

The results of catalytic dehydration of both commercial lactic acid and lactic acid obtaining by sugarcane molasses fermentation are showed in the Figure 3.

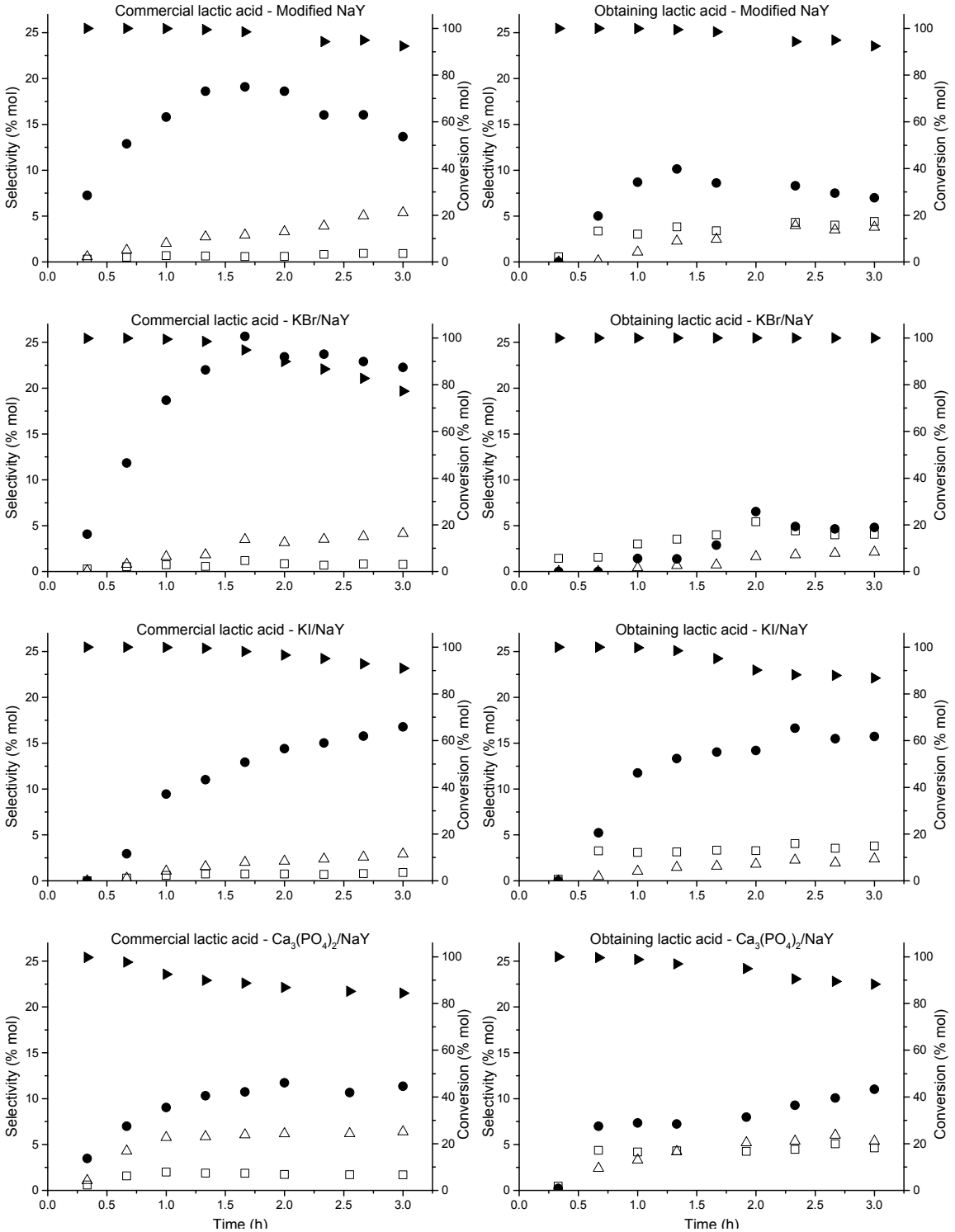

Figure 3. Results of the catalytic dehydration of commercial acid lactic and lactic acid obtaining by sugarcane molasses fermentation. acetic acid, ● acrylic acid, ► lactic acid, Δ propionic acid

These tests were conducted primarily in commercial lactic acid to evaluate the catalysts catalytic activity in the dehydration of lactic acid because the lactic acid obtained by fermentation of sugarcane molasses has residual compounds, such as sugars and salts, which can contribute to the catalytic deactivation and obscure its physical appearance. After each reaction, the condensate was a colorless liquid with a small immiscible phase in the surface which was identified as 2,3-pentadione by gas chromatography; also acetaldehyde was identified. Figure 3 depicts the results of selectivity and conversion of the commercial acid lactic catalytic dehydration (results expressed in molar percentage). Generally, for all reactions, it was observed a conversion near to 100% with substantial decrease in the selectivity to acrylic acid. The catalysts support showed selectivity for acrylic acid around 19 % at 16.7 h of reaction and subsequently deactivation. The KBr/NaY presented higher selectivity to acrylic acid (25.7 %) than the support, but it was also deactivated. The KI/NaY was not deactivated and presented a selectivity of 16.8 % at 3 h of reaction and the $Ca_3(PO_4)_2$/NaY showed a selectivity of 11.3 % to acrylic acid and 6.4 to propionic acid as principal products. When lactic acid obtained from sugarcane molasses fermentation was used, a considerable decrease in selectivity for all catalysts was obtained, as expected (Figure 3). Of all used catalyst, the KI/NaY showed the best results with selectivity for acrylic acid of 15.7 % and it was not deactivated during the 3 h of reaction. The KBr/NaY catalyst that presented the best results for dehydration of commercial lactic acid was the most affected by the impurities of lactic acid obtaining from fermentation of sugarcane molasses. This catalyst presented a similar selectivity (less that 6.5 %) to both acrylic acid and propionic acid. Moreover, the $Ca_3(PO_4)_2$/NaY presented a slight decrease (0.3 %) in selectivity to acrylic acid (11.0 %), but it was not deactivated during of time of reaction.

4. Conclusions

This work explored the importance of sugarcane molasses as raw material to production of molecules with high added value that are commonly obtained from fossil fuels sources, as the acrylic acid. Besides possible improvements in the end product characteristic, the use of renewable feedstock contributes to many issues regarding environmental concerns.

Lactobacillus plantarum CCT 5731 showed great capacity to metabolize the sugars present in larger amounts in the sugarcane molasses such as fructose, glucose and sucrose with production of biomass around 3 g/L.

According to results of dehydration, the KI/NaY catalyst presented good potential for future studies due to its acceptable selectivity and high resistance to deactivating agents. However, when lactic acid from fermentation is used is recommended to remove the impurities that may lead to catalyst deactivation.

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References

Chauhan M.K., Chaudhary S., Kumar S., 2011, Life cycle assessment of sugar industry: A review, Renewable and Sustainable Energy Reviews, 15, 3445–3453.

Dias M.O.S., Junqueira T., Rossell C., Maciel Filho R., Bonomi A., 2013, Evaluation of process configurations for second generation integrated with first generation bioethanol production from sugarcane, Fuel Processing Technology, 109, 84-89.

Ghorbani F., Younesi H., Sari A., Najafpour G., 2011, Cane molasses fermentation for continuous ethanol production in an immobilized cells reactor by Saccharomyces cerevisiae, Renewable Energy, 36, 503-509.

Lee J.M., Hwang D.W., Hwang Y.K., Halligudi S.B., Chang J.S., Han Y.H., 2010, Efficient dehydration of methyl lactate to acrylic acid using $Ca_3(PO_4)_2$–SiO_2 catalyst, Catalysis Communications, 11, 1176-1180.

Lunelli B.H., Duarte E.R., Vasco de Toledo E.C., Wolf Maciel M.R., Maciel Filho R., 2007, A new process for acrylic acid synthesis by fermentative process, Appl. Biochem. Biotechnol., 137-140, 487-499.

Rojan J., Anisha G.S., Nampoothiri K.M., Pandey Ashok, Direct lactic acid fermentation: Focus on simultaneous saccharification and lactic acid production, Biotechnology Advances, 27, 145-152.

Xu Z., Zhu L., Chen, H., 2011, Comprehensive Biotechnology, vol 3: Industrial Biotechnology and Commodity Products, Acrylic Acid, 2nd Ed., Moo-Young M., Ed., Burlington: Academic Press, 201-206.

Yan J., Yu D., Sun P.,Huang H., 2011, Alkaline earth metal modified NaY for lactic acid dehydration to acrylic acid: Effect of basic sites on the catalytic performance, Chinese Journal of Catalysis, 32, 405-411.

Zhang J., Lin, J., Cen, P., 2008, Catalytic dehydration of lactic acid to acrylic acid over sulfate catalysts, The Canadian Journal of Chemical Engineering, 86, 1047–1053.