

A by-product oriented simulator with structured model: application for acrylic acid production from renewable sources

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Abstract

The synthesis of products through biotechnological process presents important advantages compared to chemical and petrochemical via. This is mainly because they make it possible to discover and explore innumerable routes of obtaining products with high aggregate value with very low environmental impact. The purpose of this work is the development of a deterministic model for biotechnological synthesis of acrylic acid in order to explore an alternative process. Together with the tubular reactor equations a kinetic model based on the structured model is presented. Several intermediates by-products are formed along the reaction pathway and it possible to drive the reactor either to produce acrylic acid and/or bioethanol. The proposed process makes possible to obtain acrylic acid continuously from sugar cane fermentation.

Keywords: Acrylic acid, sugar cane, structured model

1. Introduction

The sugar cane sector figures among the most traditional old extractives, manipulation and processing industrials of biomass in Brazil. In recent years, new economical potentials alternative products from sugar cane fermentation arise as consequence of new research and discoveries making it possible to explore biological routes to produce molecules with high economic value.

Biomass is an abundant natural and renewable domestic resource that has the potential to supplement fossil energy supply and help create a more secure energy future. The industry of the sugar cane in Brazil keeps the largest system of commercial production of energy from biomass of the world through ethanol and the almost total use of the bagasse as fuel.

The obtainment of other chemical products besides the ethanol, no longer using the alcohol as feedstock that is in the direct use of the glucose as substrate, through the fermentation is very attractive and demonstrates to have more and more potential with the advance of genetic engineering, fermentative process and downstream process. Among these products, acrylic acid is an interesting one. In fact, from the industrial point of view, the acrylic acid production by fermentative process is presented as an innovative process of great importance, due to the possibility of low cost for its production and due to be a renewable raw material.

This work presents an alternative dynamic structured model, with the objective to simulate the intrinsic reaction taking place in the fermentation process to obtain acrylic acid from biomass. With such a mathematical representation it is presented a by-product oriented simulator applied to acrylic acid production from renewable sources.

2. Structured model development

The kinetic model is based on the concepts of structured representation, and adapted from a structured growth model developed by Rotboll and Jorgensen [1] and a structured model for ethanol production developed by Stremel [2], so that the main phenomena taking place in the system is considered.

The simplified route for the acrylic acid production from fermentative process is represented in the Figure 1.

In glycolysis, a glucose molecule is degraded into a series of reactions catalyzed by enzymes to liberate two molecules of the pyruvate. Pyruvate is the end product of glycolysis; it can be further metabolized by the pyruvate dehydrogenase to acetyl-coenzyme-A and CO_2 or by pyruvate decarboxylase to acetaldehyde and this reduced to ethanol. Due to action of metabolization via the TCA (Tricarboxylic Acid) cycle pyruvate is converted to lactate by enzyme *lactate dehydrogenase*. The lactate undergoes dehydration, generating acrylic acid.

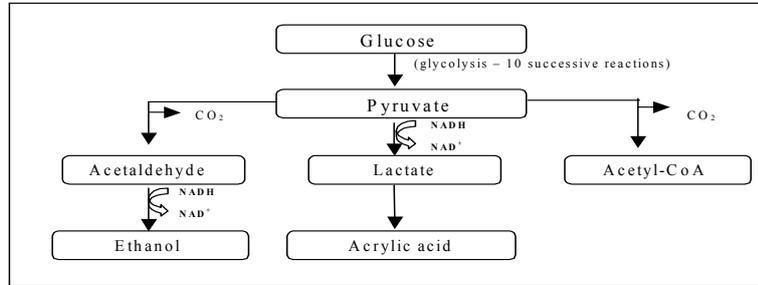


Figure 1- Representation of the process of acrylic acid and ethanol production from glucose degradation

The reactor is tubular continuously operated and the challenge is to define operating strategy and conditions to achieve the product with the desired specifications. A deterministic mathematical model built-up coupling the reactor and the kinetic equations is developed to represent the main phenomena taking place in the process. In the dynamic simulation of the tubular reactor was used *Saccharomyces cerevisiae* immobilized.

Saccharomyces cerevisiae is generally considered a robust, acid tolerant microorganism that is well accepted in an industrial process. In *S. cerevisiae*, the major flux of pyruvate metabolism is to ethanol, by way of pyruvate decarboxylase (PDC) and alcohol dehydrogenase (ADH). By providing an alternative route for regenerating NAD⁺ through lactate dehydrogenase (LDH), which catalyzes the reduction of pyruvate to lactate, is possible theoretically replace ethanolic fermentation [3]. The immobilized enzyme or cells technology may help in the future for integrating bioprocess with downstream processing with an effort to increase the productivity while minimizing product recovery cost [4]. The Figure 2 show the respiratory and fermentative metabolic route involved in the process of acrylic acid production. The ethanol production also is considered.

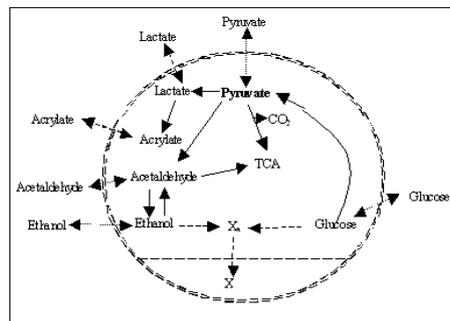


Figure 2- Representative respiratory and fermentative metabolic route

The reaction rates used in the structured model are given table 1.

Table 1- Reaction rates

$R_1 = k_1 \frac{S_{glucose}}{S_{glucose} + K_1} X_a + k_1 \frac{S_{glucose}}{S_{glucose} (K_{li} S_{acetaldehyde} + 1) + K_{1e}} S_{acetaldehyde} X_a$
$R_2 = k_2 \frac{S_{pyruvate}}{(S_{pyruvate} (1 + K_{2e} S_{acetaldehyde}) + K_2)} \frac{1}{(1 + K_{2i} S_{glucose})} X_a$
$R_3 = k_3 \frac{S_{pyruvate}}{S_{pyruvate} + K_3} X_a$
$R_4 = k_4 \frac{S_{pyruvate}}{S_{pyruvate} + K_4} X_a$
$R_5 = k_5 \frac{S_{acetaldehyde} \left(k_{5e} - \frac{1}{k_{5i} S_{glucose} + 1} \right)}{S_{acetaldehyde} + K_5} X_a$
$R_6 = k_6 \frac{S_{acetaldehyde} - k_{6r} S_{ethanol}}{S_{acetaldehyde} + K_6 + K_{6e} S_{ethanol}} X_a X_f$
$R_7 = k_7 \frac{S_{lactate}}{S_{lactate} + K_7} X_a$
$R_8 = k_8 \frac{S_{glucose}}{S_{glucose} + K_8} X_a$
$R_9 = k_5 \frac{S_{acetaldehyde}}{S_{acetaldehyde} + K_5} \frac{1}{(1 + K_{5i} S_{glucose})} \frac{1}{(1 + K_{5i} S_{ethanol})} X_a$
$R_{10} = k_{10} \frac{S_{glucose}}{S_{glucose} + K_{10}} X_a + k_{10e} \frac{S_{ethanol}}{S_{ethanol} + K_{10e}} X_a$
$R_{11} = \left(k_{11} \frac{S_{glucose}}{S_{glucose} + K_{11}} + \frac{S_{ethanol}}{S_{ethanol} + K_{11e}} \right) \frac{1}{K_{11i} S_{glucose}^2 + 1} X_a$
$R_{12} = k_{12} \frac{1}{K_{12i} S_{glucose}^2 + 1} X_a + k_{12e} \frac{S_{acetaldehyde}}{S_{acetaldehyde} + K_{12e}} X_a$

(k_i - constant reaction rate ($gg^{-1}h^{-1}$); K_i - affinity constant (gL^{-1}); K_{ji} - inhibition constant (Lg^{-1}); R_i - reaction rate (h^{-1}); S_i - extracellular concentration (gL^{-1}); X_i - intracellular concentration)

3. Results and discussion

The main intention this work was the development of a tool able to represent the main phenomena taking place in the cell mechanism so that several routes can be explored to achieve a desired product. To simulate the dynamic model was used the software FORTRAN. The set of differential partial equations was discretized using the Orthogonal Collocation Method with the Method of Lines and the resulting system of equations was integrated, in respect to the time, by LSODAR integrator. The parameters values used in the model can be changed by the users together with the operating as well as design conditions, so that the process can be extensively investigated. The mathematical model describing the dynamic behavior of the reactor leads to a non-linear distributed parameter problem requiring excessive computational time. In order to have a simplified bioreactor model even taking into account the cell internal structure it is possible to reduce the dimension of the system of partial differential equations. Bearing this in mind it was eliminated the dependent variables on radial position and formulated an approximation of the variables to take into account changes along that dimension. This dimensionality reduction was made by application of reduction techniques based on the Hermite Integrations Formulas. The profiles of the acrylic acid, lactate and substrate concentration in respect to time are shown in the Figure 4. In Figure 5 it is possible to visualize the acrylic acid and ethanol production, simultaneously from consumption of the glucose.

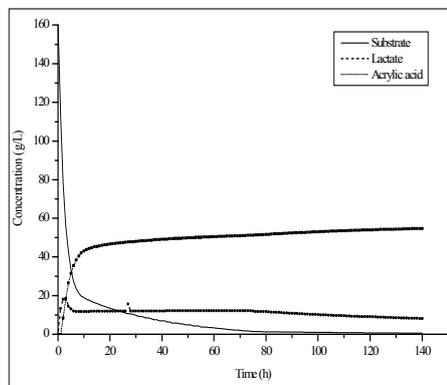


Figure 4 – Acrylic acid, lactate and substrate concentration

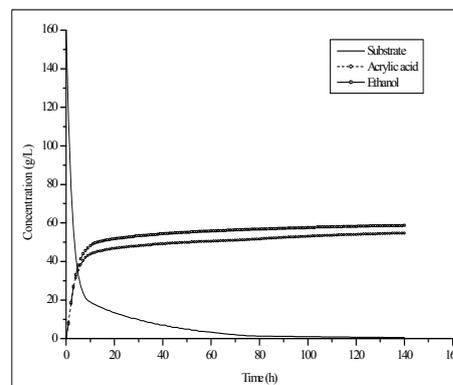


Figure 5 – Acrylic acid, ethanol and substrate concentration

The kinetic values for a given microorganism in this case, *Saccharomyces cerevisiae*, is dependent upon the system operating conditions including substrate composition. The acrylic acid production by fermentation occurs from glucose degradation and may be expressive depending upon the operational conditions, although smaller when compared with the usual production from petrochemical via. Through the model development was possible the

obtainment the acrylic acid and ethanol simultaneously from glucose fermentation. The majority of fermentation product was the ethanol. A possible way to overcome this, leading to higher acrylic acid production, is to minimize PDC activity using *PDC* mutants. This approach was successful used in reducing ethanol and increasing lactate, although the yields and productivities were still poor [5,6].

4. Conclusions

Structured models describing cultures kinetics are powerful tool in the control of bioreactors, as they are able to provide a mathematical description of the cellular fermentation mechanism of the process i.e. to predict the concentrations of intermediate products, desired product, substrate and cell concentrations. This is important also to help in the optimization and control decisions. The developed simulator is a very good tool to process design and to definition of operational strategies. The orthogonal collocation methods provides efficient and robust model of solution. Through the application of the reduction techniques it was possible to reduce significantly the number of differential equations to be solved reducing the complexity of the modeling as well as the computer time and burden.

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References

1. F. Lei, M. Rotboll and S. B. Jorgensen, A biochemically model for *Saccharomyces cerevisiae*. *J. of Biotechnol.*, 88 (2001) 205-211.
2. D. P. Stremel, Desenvolvimento de modelos estruturados alternativos para o processo de produção de etanol. UNICAMP, Campinas, SP, 2001.
3. C. D. Skory, Lactic acid production by *Saccharomyces cerevisiae* expressing a *Rhizopus oryzae* lactate dehydrogenase gene. *J. Ind. Microbiol. Biotechnol.*, 30 (2003) 22-27.
4. S.F. D'Souza, Immobilized enzymes in process. *Curr. Sci.*, 77 (1999) 69-79.
5. M.M. Bianchi, L. Brambilla, J. Lievense, C. L. Liu, D. Porro and F. Protani, Efficient homolactic fermentation by *Kluyveromyces Lactis* strains defective in pyruvate utilization and transformed with the heterologous Ldh genes. *Appl. Environ. Microbiol.*, 67(12) (2001) 5621-5625.
6. E. Adachi et al. (1988). In: Lactic acid production by *Saccharomyces cerevisiae* expressing a *Rhizopus oryzae* lactate dehydrogenase gene, C. D. Skory, *J. Ind. Microbiol. Biotechnol.*, 30 (2003) 22-27.