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Process Intensification for Ethyl Lactate Production Using Reactive Distillation

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Ethyl lactate is an important organic ester, which is biodegradable and can be used as food additive, perfumery, flavor chemicals and can effectively replace toxic and halogenated solvents for a wide range of industrial applications. In this work the simulation of the intensified process for ethyl lactate production by esterification of lactic acid with ethanol using a reactive distillation system was investigated. The intensified process includes the fermentation for the lactic acid production from sucrose and, reactive distillation process for ethyl lactate production by lactic acid esterification. A NRTL model parameter set has been established to predict the composition and temperatures for the system components. The simulation was carried out with the aid of the Aspen Plus™ process simulator. The results showed that the process intensification proposed in this work, based on fully renewable raw material, provides great opportunities to achieve higher conversion and improve the operational performance.

1. Introduction

The current dependence on oil for energy and production of numerous chemicals and products together with the climate change caused by fossil fuels has drawn significant attention on finding alternative renewable resources for the production of biofuels and chemicals. The synthesis of products through biotechnological processes makes it possible to discover and explore innumerable routes to obtain products with high aggregate value and very low environmental impact. Ethyl lactate is an important organic ester, which is biodegradable and can be used as food additive, perfumery, flavor chemicals and can effectively replace toxic and halogenated solvents for a wide range of industrial applications (Tanaka et al., 2002). Bearing this in mind, in this work the simulation and investigation of the intensified process for ethyl lactate production by esterification of lactic acid with ethanol using a reactive distillation system were carried out. Reactive distillation combines chemical reaction and separation in a compact device that can lead to significant economic advantage in term of investment and operation costs.

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2. Lactic Acid

Lactic acid is the acid with higher occurrence in nature. Traditionally, it has been used in food, pharmaceuticals and chemistry industries, but its market is continuously expanding as a result of the development and commercialization of new applications (Datta, 2004), for example, the synthesis of bioabsorbable and biodegradable polymers (poly-lactic acid) and green solvents (ethyl lactate) (Lunelli et al., 2010).
Lactic acid can be produced by chemical synthesis or fermentation. The biotechnological production of lactic acid has several advantages such as low cost of raw materials, mild operating conditions (temperature and pressure), low energy consumption, use of renewable raw materials, low toxicity of the catalysts, besides the specificity of the product because the fermentative process produces optically pure stereoisomers (L (+) or D (-) lactic acid) (Pondey et al., 2001). Lactic acid can be biosynthesized by some bacteria and filamentous fungi.
The lactic acid production by fermentation process can be represented by the following reactions:

$$\text{Sucrose (S)} + \text{Biomass (X)} \leftrightarrow \text{SX} \tag{1}$$

$$\text{SX} \leftrightarrow \text{Lactic Acid (LA)} + \text{X} \tag{2}$$

The stoichiometric reaction of the process can be written according to:

$$\mathrm{C}_{12}H_{22}O_{11} + H_2O \rightarrow 4CH_3CH(OH)COOH \tag{3}$$

To simulate the lactic acid production by sucrose fermentation the following model was considered:

$$\frac{dX}{dt} = \mu_{\max}\frac{S}{K_S+S}\frac{K_i}{K_i+S}\left(1-\frac{P}{P_{\max}}\right)X + D(X_0 - X) \tag{4}$$

$$\frac{dP}{dt} = \left[\alpha\mu_{\max}\frac{S}{K_S+S}\frac{K_i}{K_i+S}\left(1-\frac{P}{P_{\max}}\right)+\beta\right]X + D(P_0 - P) \tag{5}$$

$$\frac{dS}{dt} = -\frac{1}{Y_{X/S}}\mu_{\max}\frac{S}{K_S+S}\frac{K_i}{K_i+S}\left(1-\frac{P}{P_{\max}}\right)X + D(S_0 - S) \tag{6}$$

The specific growth rate is given by

$$\mu_X = \mu_{\max}\frac{S}{K_S+S}\frac{K_i}{K_i+S}\left(1-\frac{P}{P_{\max}}\right) \tag{7}$$

where, S, X and P are the concentrations of substrate, cells, and lactic acid, respectively; S_0 is the feed substrate concentration; X_0 is the feed biomass concentration; D is the dilution rate; μ_X is the specific growth rate; $Y_{X/S}$ is biomass yield in function of substrate; α is growth-associated constant for the Luedeking-Piret; β is non growth-associated constant for the Luedeking-Piret; K_S is the Monod constant; K_i is the inhibition constant by substrate.

3. Ethyl Lactate

Interest in lactate esters is increasing due to the emphasis on environmentally friendly solvents derived from renewable resources. Ethyl lactate is an important organic ester, biodegradable solvent with excellent properties and low toxicity being produced by lactic acid aqueous solution and ethanol, via an esterification process, according to the following equation.

$$CH_3CH(OH)CO_2H + C_2H_5OH \longleftrightarrow CH_3CH(OH)CO_2C_2H_5 + H_2O \tag{8}$$

According to Asthana et al. (2005) ethyl lactate can be produced and efficiently separated with high yields by esterification of lactic acid with excess of ethanol, using a single operational step, through the reactive distillation process.
The concept of reactive distillation is based on a combination of reaction and distillation processes in order to improve the performance of both processes (Figure 1). Although it is an old concept and has been used successfully in some traditional processes, its application has broadened significantly in recent years, also being used in modeling, simulation and control strategies and can thus become an important tool for intensification and integration processes (Sharma and Mahajan, 2003).

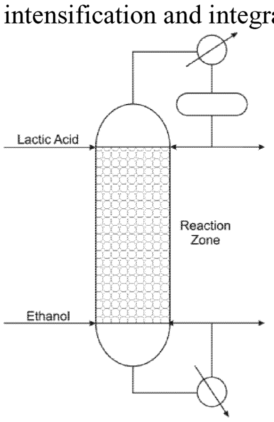

Figure 1: Reactive distillation column

4. Results and Discussion

Initially, a mathematical model (Eq. 4–6) to simulate the continuous fermentative process for lactic acid production was developed. The concentration profiles of substrate, biomass and lactic acid are shown in Figure 2.

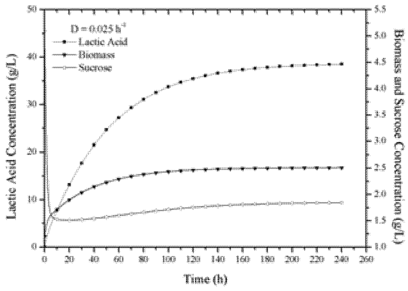

Figure 2: Concentration profile in continuous fermentation process

As an extension to the current work, an intensified ethyl lactate process via lactic acid fermentation was proposed. The simulation was carried out with the aid of the Aspen Plus^{TM} process simulator. This process includes the lactic acid production from sucrose fermentation and, the reactive distillation process for ethyl lactate production by lactic acid esterification. The broth withdrawn from fermenter was centrifuged for cell separation; the cells were recycled to the fermenter and, the liquid broth (lactic acid solution) was fed with ethanol in a reactive distillation column for ethyl lactate production (Figure 3).

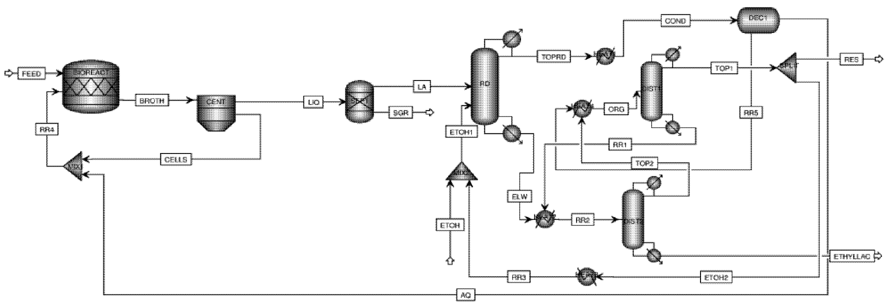

Figure 3: Intensified ethyl lactate process flowsheet

The reactive distillation system is composed by four components: lactic acid, ethanol, ethyl lactate and water. A Non-Random-Two-Liquid (NRTL) model parameter set was used to predict the composition and temperatures for the components of the systems. When Vapor-Liquid Equilibrium (VLE) data were not available for a given binary mixture, the parameters were estimated via UNIFAC (Universal Functional Activity Coefficients) and then used in the NRTL model.

The VLE compositions were analyzed for the four components in the reactive distillation process. It was observed the presence of two homogeneous azeotropes formed by the binary interaction of ethanol/water and water/ethyl lactate, as shown in Figures 4 and 5. The composition of the azeotropes are presented in Table 1.

Table 1: Azeotrope boiling temperature and composition

System	Type	Temperature (ºC)	Composition
Ethanol/Water	homogeneous	78.15	0.956/0.044
Water/Ethyl Lactate	homogeneous	99.76	0.793/0.207

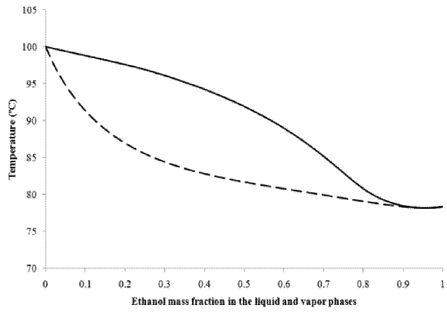

Figure 4a:T-xy diagram for ethanol/water binary mixture (P=1atm)

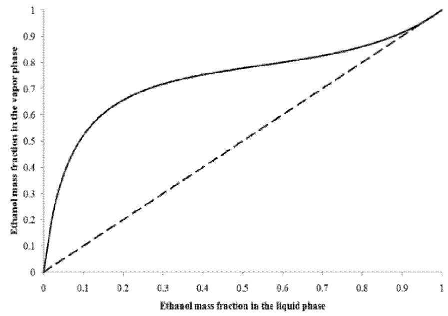

Figure 4b:X-y diagram for ethanol/water binary mixture (P=1atm)

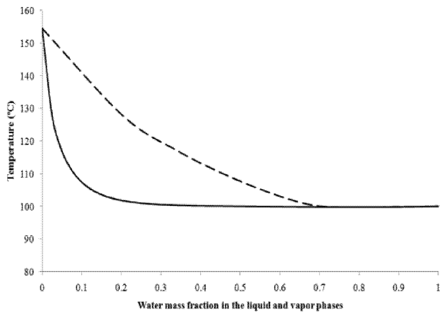

Figure 5a: T-xy diagram for water/ethyl lactate binary mixture (P=1atm)

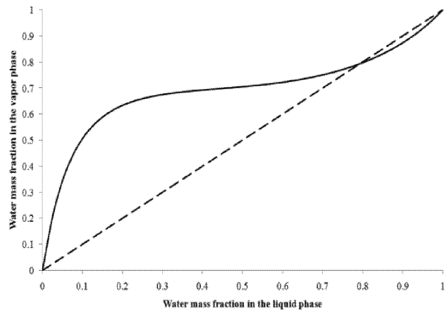

Figure 5b: X-y diagram for water/ethyl lactate binary mixture (P=1atm)

The top and bottom products of the reactive distillation column were separated by conventional distillation processes carried out below the azeotropic point of the binary mixtures (ethanol/water and water/ethyl lactate). The concentration profiles in the liquid and vapor phases obtained in reactive distillation column are shown in Figures 6a and 6b, respectively. The operating conditions of the reactive distillation column (RD) are presented in Table 2.

Table 2: Reactive distillation column operating conditions

Condenser/Top Stage		Reboiler/Bottom Stage	
Temperature (ºC)	79.16	Temperature (ºC)	139.95
Distillation rate (kmol/h)	9.30	Bottoms rate (kmol/h)	6.45
Reflux rate (kmol/h)	10.23	Boilup rate (kmol/h)	17.16
Reflux ratio	1.1	Boilup ratio	38.14
Column stage number			29
Column reactive stages			24

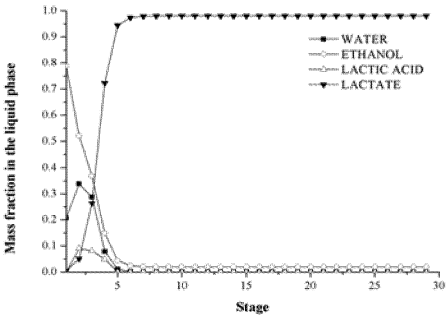

Figure 6a:Mass fraction profiles in the liquid phase along the stages of the reactive distillation column (RD) (P = 1 atm)

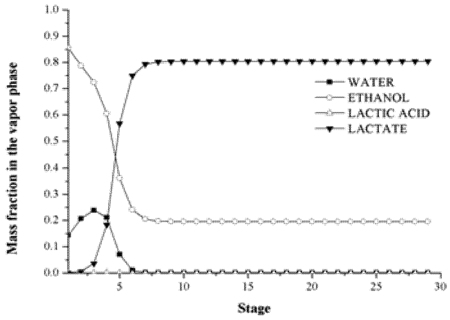

Figure 6b: Mass fraction profiles in the vapor phase along the stages of the reactive distillation column (RD) (P = 1 atm)

5. Conclusions

With the development of an intensified process based on the reactive distillation, it is shown by simulation, that it is possible to improve the operating performance of the process for ethyl lactate production, allowing achieving high conversions. It is renewable sources based process, and it is possible to reach ethyl lactate stream with molar composition of 99% as a bottom product from the lactic acid esterification reaction (RD column) and separation process (DIST2 column), which shows the process efficiency. The recovered ethanol (98.6% molar) was recycled to the reactive distillation column and the residual water (50% molar) to the fermenter.

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