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Lactic acid purification by reactive distillation system using design of experiments

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ABSTRACT

In this study, lactic acid purification using reactive distillation system was evaluated. Factorial experimental design is used to evaluate the influence of parameters and their interactions, such as ethanol/lactic acid molar ratio, reboiler temperature and catalyst concentration on yield of lactate. The results showed that the process for lactic acid purification proposed in this work, provides large potential to achieve high yield of ethyl lactate (~100%) and lactic acid with 3 times higher concentration than the raw material.

1. Introduction

The presence of hydroxyl and carboxylic acid groups in lactic acid molecule allows a wide variety of chemical reactions producing a host of high value and large volume products ranging from food preservatives, green solvent and oxygenated chemicals to biodegradable polylactic acid thermoplastics [1]. The demand for lactic acid has been estimated to grow yearly at 5–8%. The annual world market for lactic acid production was expected to reach 259,000 metric tons by the year 2012 and is forecasted to reach 367,300 metric tons by the year 2017 [2].

Lactic acid purification is one of the most costly steps of the production process [3–5]. Therefore, the development of an efficient method for the recovery of lactic acid from fermentation broth is very important.

Reactive distillation (RD) has been proposed as a promising technique for the recovery of lactic acid with high purity and high yield from the fermentation broth [6]. In RD process, chemical reaction and distillation separation are performed simultaneously within a fractional distillation apparatus. This process has become an attractive alternative to conventional processes because of the following reasons: simplification or elimination of the separation system leading to capital savings, improved conversion of reactants, reduced recycling costs, improved selectivity of desired products, reduced catalyst requirement, reduced by-product formation, and heat integration [6].

The lactic acid recovery involves two reversible reactions, esterification and hydrolysis, catalyzed by an acid catalyst, according to the following equations (Eqs. (1) and (2)).

Esterification: $C_3H_6O_3 + C_2H_5OH \leftrightarrow C_5H_{10}O_3 + H_2O$ (1)

Lactic acid + ethanol → ethyl lactate + water

Hydrolysis: $C_5H_{10}O_3 + H_2O \leftrightarrow C_3H_6O_3 + C_2H_5OH$ (2)

Ethyl lactate + water → lactic acid + ethanol

Many studies using reactive distillation for lactic acid recovery have been reported [6–15]. Mo et al. [10], Edreder et al. [11], and Mujtaba et al. [12] studied simulation approach using commercial simulators, such as Aspen Plus® and gPROMS. Kumar et al. [6] and Seo et al. [7] investigated the recovery of lactic acid in a batch reactive column using a heterogeneous catalyst and feed concentration of 20 wt.%.

Although previous works to produce ethyl lactate achieved high yields, they require multiple unit operations [13–15] and lactic acid feed solution is usually 20 wt.% concentrated [7,8,13–15]. Each additional unit operation in the downstream process represents an increase in the total capital and operating costs. Furthermore, fermentation broth containing a dilute solution of lactic acid (1.6–16 wt.%) was used, which requires a prior concentration to achieve 20 wt.% or more as used in the literature.

In this work, lactate ester production was conducted mainly with dilute lactic acid solutions and excess of ethanol, in order to purify fermentation-derived lactic acid without prior purification.

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In addition, lactic acid in aqueous solutions above ~30 wt.% produce linear dimer and higher oligomer acids which can reduce the yield of lactate [16]. Thus, the objective of this work was to evaluate the lactic acid purification by RD using a diluted lactic acid solution (when compared with literature). Design of experiments was used to evaluate the influence of operating parameters and their interactions on the lactate yield. This technique is a useful tool to evaluate the effect of each variable and their interactions in the process response.

2. Experimental

2.1. Materials

Lactic acid 85% supplied by Ecibra (São Paulo, Brazil) was diluted with distilled water to ~120 g/L. Ethanol 99.5% was supplied by Dinâmica (São Paulo, Brazil) and sulfuric acid 95–97% used as catalyst was supplied by Ecibra (São Paulo, Brazil). Ethyl lactate 98% supplied by Sigma–Aldrich (St. Louis, Missouri, EUA) was used to build the calibration curve for ethyl lactate quantification (regression coefficient of 0.9984). The lactic acid concentrations were determined using the calibration curve (regression coefficient of 0.9998) obtained with standard solutions of DL-lactic acid 90% supplied by Sigma–Aldrich (St. Louis, Missouri, EUA).

2.2. Method of analysis

Analyses of lactic acid were performed in an equipment of high performance liquid chromatography (HPLC), Agilent model 1260, equipped with UV detector (UV–vis) connected in series with the chromatography column Bio-Rad Aminex, model HPX-87H (300 × 7.8 mm). The equipment was controlled through OpenLab software. Sulfuric acid solution with 5 mM was used as mobile phase at flow rate of 0.6 mL/min. The column temperature was kept constant at 37 °C. An injection volume of 25 μL was used in each run. For lactic acid detection and quantification, the wavelength of 215 nm was used in the UV detection system [17].

Analyses of ethyl lactate were performed in an equipment of gas chromatography (CG), Agilent Technologies model 7890A, equipped with FID (flame ionization detector) and a DB-FFAP column (30 m × 250 μm × 0.25 μm). The column program heating was 100–125 °C at 2.5 °C/min and held temperature constant at 125 °C for 4 min. Helium (99.9% purity) was used as carrier gas at a flow rate of 3 mL/min. The injector and the detector temperatures were maintained at 240 °C and 250 °C, respectively. In each run, an injection volume of 1 μL was used.

2.3. Reactive distillation system

The experiments were performed in a tray column of Fischer® Labodest® (Waldbuttelbrunn, Germany) as shown in Fig. 1. The reactive distillation column consists of 10 Oldershaw type plates, made in borosilicate glass. The plate distance is 30 mm with dynamic hold-up per plate of 2 mL and static hold up of 0.2 mL. The column had a silvered vacuum jacket for thermal isolation [18]. Lactic acid and ethanol with sulfuric acid were fed in the middle of the column (7th tray from the bottom to the top) by using a peristaltic metering pump. The reactions were performed in a semi-batch reactive distillation column during 2 h at a total reflux ratio. After this time, reflux ratio was set to zero. Ethanol and water were collected predominantly in the distillate stream, while lactic acid, ethyl lactate and sulfuric acid in the residue stream.

The residue stream of the esterification process was fed again in the same apparatus for the hydrolysis step. The diluted lactic acid solution was fed at the middle of the column. Hydrolysis was performed in a semi-batch mode at a partial reflux ratio. The hydrolysis occurred at 90 °C during 4 h. The residue stream was further analyzed as described before.

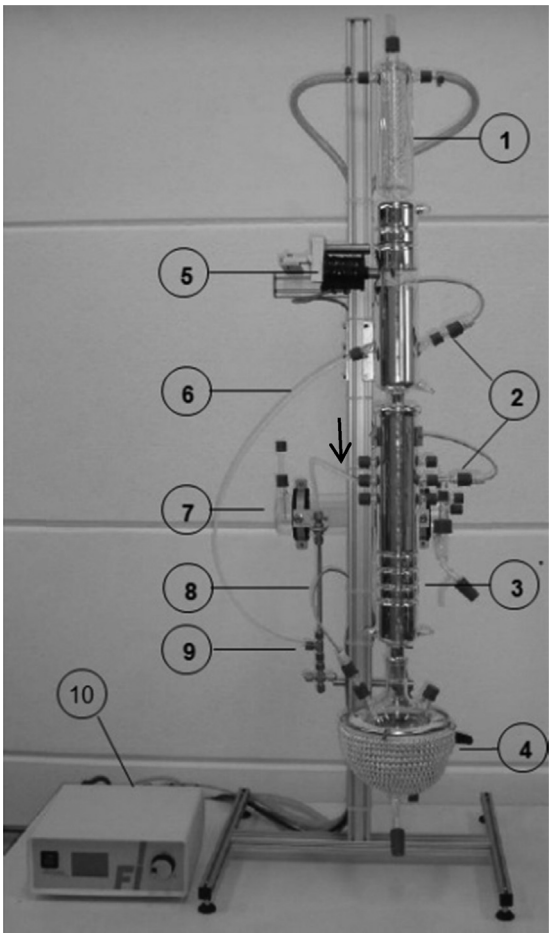

Fig. 1. Reactive distillation system. (1) Condenser, (2) thermocouples, (3) RD column, (4) reboiler, (5) solenoid valve, (6) recycle, (7) decanter, (8) pre-reactor, (9) T-mixer, (10) controller, (↓) feed line.

2.4. Design of experiments for esterification

The design of experiments is an efficient procedure for planning experiments so that the data obtained can be analyzed to yield valid and objective conclusions. There are many possible factors, some of which may be critical and others that may have little or no effect on the process response. So, screening experiments are an efficient way, with a minimal number of runs, of determining the important factors [19].

Experiments were performed varying the ethanol/lactic acid molar ratio (MR), reboiler temperature (T_{reb}) and catalyst concentration (Cat wt.%) which were represented by dimensionless coded variables X_1,X_2 and X_3, respectively. The response variable was yield of ethyl lactate (Y_{EL}). A 2^3 full-factorial central composite design with 6 axial (star configuration) and 3 central points was used, resulting in 17 experiments. The experimental ranges are shown in Table 1. Coded and real variable values are related by the general Eq. (3):

$$X_i = \frac{\xi_i - \xi_0}{\Delta\xi_i} \quad (3)$$

where X_i is the dimensionless coded value of the ith factor, ξ_i is the real value of the ith factor, ξ_0 is the real value of the ith factor at the central point, and $\Delta\xi_i$ is the step change value of the real variable i [20].