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Evaluation of Operational Parameters for Ethyl Lactate Production Using Reactive Distillation Process

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Ethyl lactate is an environmentally bio-based solvent with a wide range of industrial applications. In this work, ethyl lactate was produced by synthesis using reactive distillation process. Through factorial experimental design, the influence of operating conditions as molar ratio ethanol: lactic acid, reboiler temperature and catalyst concentration on ethyl lactate were evaluated. A mathematical model was developed in order to describe the response of interest as function of operating conditions. The experimental results showed that the reactive distillation seems to be an alternative and simple energy-saving process with lower investment and operation costs to obtain ethyl lactate which normally requires a stage to the reaction and a stage to the reaction products separation. Each additional step in the downstream represents an increase in the operating and equipment investment costs.

1. Introduction

The production of chemical building blocks and polymer precursors from renewable and sustainable resources is an attractive method for bypassing traditional fossil-fuel-derived materials (Bykowski et al., 2014), with impact on environment and in the product characteristic. Consequently, replacing conventional solvents with more environmentally benign media is one of the basic principles of the Green Chemistry and a subject of significant of both academic and commercial interest. From this perspective, ethyl lactate is currently being advertised as an environmentally benign bio-based solvent for chemical transformations (Dandia et al., 2013). Ethyl lactate or ethyl (S)-2-hydroxypropanoate (CAS 97-64-3) 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 (Lunelli et al., 2011). It can be found naturally in small quantities in a variety of foods, as chicken, wine and some fruits (Pereira et al., 2014) or it can be produced by synthesis using common biorefinery products as ethanol and lactic acid. Ethanol is an important raw material for the chemical industry, being the most widely used biofuel for transportation. It can be produced from several biomass crops, as sugar crops, starch crops or cellulosic feedstocks (Pereira et al., 2014). Lactic acid has a wide variety of applications such as cosmetics, pharmaceutical products, chemistry, food and more recently in the medical area (Komesu et al., 2014). The biotechnological process for lactic acid production offers several advantages: low substrate costs, production temperature and energy consumption (Komesu et al., 2013). The synthesis involves a liquid phase reversible esterification reaction catalysed by an acid, according to the following reaction.

$$CH_3CH(OH)CO_2H + C_2H_5OH \leftrightarrow CH_3CH(OH)CO_2C_2H_5 + H_2O \quad \text{(R.1)}$$

Lactic acid + ethanol $\leftrightarrow$ Ethyl lactate + water

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The conventional way to produce ethyl lactate is in a batch reactor, where the esterification reaction between ethanol and lactic acid is carried out until equilibrium is reached, and then the equilibrium mixture is fed to a set of separation units in order to recover ethyl lactate with the desired purity (Pereira et al., 2014). It is a relatively inefficient approach because it requires a large reactor volume (Wasewar et al., 2009), high energy costs and investment in several reaction and separation units. On the other hand, the reactive distillation is an alternative process that potentially brings significant advantages, when compared with conventional process, such as reduction of capital and operating costs, high selectivity and reduced energy consumption (Mo et al., 2011).

Reactive distillation is a unit operation in which chemical reaction and distillation separation are carried out simultaneously within a fractional distillation apparatus (Perry and Chilton, 1999). The term 'catalytic distillation' is also used for systems where a catalyst (homogeneous or heterogeneous) is used to accelerate the reaction (Taylor and Krishna, 2000). It is applied specifically to reversible chemical reactions in the liquid phase, where the conversion of the reactants is limited by equilibrium reactions (Seo et al., 1999). Thus, reactive distillation is a promising technology for efficient production of ethyl lactate.

In this work, lactate ester formation was conducted mainly with dilute lactic acid solutions (~50 g/L) and a large excess of ethanol, in order to purify fermentation-derived lactic acid with no previous process for removing water. In addition, because of its bifunctional nature, lactic acid undergoes intermolecular esterification in aqueous solutions above ~30 wt% to form linear dimer and higher oligomer acids which can reduce the yield of lactate (Asthana et al., 2006). In this fashion, the objective of this work was the development of preliminary experiments in the bench-scale reactive distillation column in order to verify the feasibility of the ethyl lactate formation as well as to identify operating conditions and, consequently, achieving high lactic acid conversion.

2. Materials and Methods

2.1 Materials

Lactic acid 85 % supplied by Ecibra (São Paulo, Brazil) was diluted with distilled water to ~50 g/L, which is the usual concentration of fermentation-derived lactic acid. Ethanol 99.5 % was supplied by Dinâmica (São Paulo, Brazil) and sulphuric acid 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 (from 10 to 80 g/L) for ethyl lactate quantification.

2.2 Reactive distillation system

The experiments were made in a tray column of FISCHER® LABODEST® (Waldbuttelbrunn, Germany) as depicted in Figure 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 (Rios et al., 2012). Lactic acid and ethanol with sulphuric acid were fed in the middle of the column (7^{th} tray from the bottom to the top) by using a peristaltic metering pump. Ethanol and water were collected predominantly in the distillate stream, while lactic acid, ethyl lactate and sulphuric acid in the residue.

2.3 Experimental design

Experiments were performed varying the molar ratio ethanol: lactic acid (MR), reboiler temperature (T_{reb}) and catalyst concentration (Cat w%), which were represented by dimensionless coded variables X1, X2 and X3, respectively. The response variable was yield of lactate.

A 2^3 factorial experimental design with three central points was used, resulting in eleven experiments. The experimental ranges and the yields of lactate are shown in Table 1.

The experiments were carried out in a randomized order and three replicates at central point (C) of the design were performed to allow the estimation of the pure error (runs 9, 10 and 11). The effect of each process variable and their interactions in the response variables were calculated using the software STATISTICA 7.0 from Statsoft Inc. (2004) using 95 % of confidence level.

2.4 Chromatographic analysis

The ethyl lactate samples were analyzed in an equipment of gas chromatography (CG), Agilent Technologies model 7890A, equipped with FID (Flame Ionization Detector) and a DB-FFAP column (30 m x 250 μm x 0.25 μm). The column program heating was 100 °C to 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.

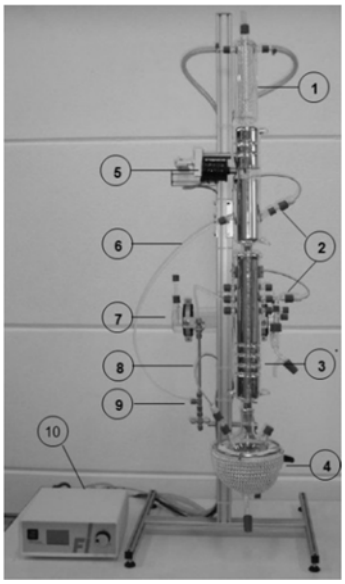

Figure 1: Reactive distillation system. Legend: (1) condenser, (2) thermocouples, (3) RD column, (4) reboiler, (5) solenoid valve, (6) recycle, (7) decanter, (8) pré-reactor, (9) T-mixer, (10) controller

Table 1: Design matrix and yields of lactate

	Coded variables			Real variables			Yields
Runs	X1	X2	X3	MR	T_{reb} (°C)	Cat (wt %)	
1	-1	-1	-1	10	100	2	14.17
2	+1	-1	-1	50	100	2	83.26
3	-1	+1	-1	10	150	2	16.00
4	+1	+1	-1	50	150	2	54.20
5	-1	-1	+1	10	100	10	13.54
6	+1	-1	+1	50	100	10	87.61
7	-1	+1	+1	10	150	10	7.35
8	+1	+1	+1	50	150	10	81.86
9 (C)	0	0	0	30	125	6	38.39
10 (C)	0	0	0	30	125	6	26.44
11 (C)	0	0	0	30	125	6	35.37

X1= MR= molar ratio; X2= T_{reb}= reboiler temperature; X3= Cat= catalyst concentration

3. Results and discussions

Table 1 shows the ethyl lactate yields obtained in the experimental runs. Ethyl lactate yield (Y_{EL}) was calculated by Eq(1).

$$Y_{EL} = \frac{moles\ of\ ethy\ lactate\ produced}{moles\ of\ lactic\ acid\ initial} \quad (1)$$

Table 2 depicts the effects of the MR, T_{reb} and Cat w% on ethyl lactate yield, with a confidence level of 95 %. According to Table 2, only the molar ratio ethanol: lactic acid was statistically significant for ethyl lactate yield. The most important effects and their interactions are shown in Pareto chart (Figure 2).
The regression model for ethyl lactate yield (Y_{EL}), considering only the statistically significant variables, is given by Eq(2). The factor X1 represent coded value of molar ratio ethanol: lactic acid (MR).

$$Y_{EL} = 41.65 + 31.98 \times X_1 \quad (2)$$

Table 2: Estimated effects on ethyl lactate yield with a confidence level of 95 %.

Factor	Regression coefficient	Standard error	t(2)	p
Mean	41.65364	1.873531	22.23269	0.002017
(1)MR	31.98375	4.393820	14.55852	0.004685
(2)Treb	-4.89625	4.393820	-2.22870	0.155644
(3)Cat	2.84125	4.393820	1.29329	0.325146
1 by 2	-3.80625	4.393820	-1.73255	0.225315
1 by 3	5.16125	4.393820	2.34932	0.143251
2 by 3	1.91125	4.393820	0.86997	0.476039

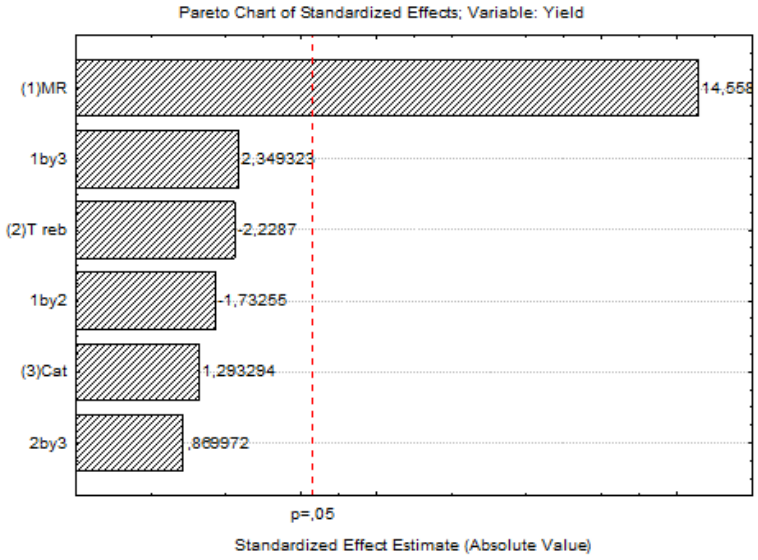

Figure 2: Pareto chart of effects for ethyl lactate yield.

The model was evaluated through the ANOVA (Table 3). In order to evaluate if the models are statistically significant with a confidence level of 95 %, one criterion is to attend the F-test. F values are calculated by the ratio between the mean square of regression and the mean square residual ($F_{1,9}$ calculated) and by the ratio between the mean square of lack of fit and the mean square of pure error ($F_{7,2}$ calculated). Then, these values are compared with tabulated F values considering the same confidence level.

According to Table 3, the $F_{1,9}$ calculated (67.23) was higher than $F_{1,9}$ tabulated (5.12) and 88.19 % of the variation is explained by the model, showing thus, that the linear model to the ethyl lactate yield is statistically significant to a confidence level of 95 %. In addition, the $F_{7,2}$ calculated (3.77) was lower than $F_{7,2}$ tabulated (19.35); this means that the model given by equation 3 can be used to make predictions in the range studied.

Observing equation 3, the ethyl lactate yield increase with the molar ratio ethanol: lactic acid because the excess of ethanol shifts the equation to the right, towards the desired product. Asthana (2006) has reported that water in dilute lactic acid solutions limits the extent of esterification and thus large alcohol excess and high energy costs are required. In this work, a dilute lactic acid solution was used in order to purify fermentation-derived lactic acid with no previous process for removing water.

Table 3: ANOVA of ethyl lactate yield model (confidence level of 95 %)

Source of variation	Sum of squares	Degrees of freedom	Mean square	$F_{calculated}$	$F_{tabulated}$
Regression	8183.68	1	8183.68	67.23	5.12
Residues	1095.52	9	121.72		
Lack of fit	1018.30	7	145.47	3.77	19.35
Pure error	77.22	2	38.61		
Total	9279.21	10			

The response surface of ethyl lactate yield in function of Cat and MR, and in function of T_{reb} and MR, considering only statistically significant variables, are given in Figures 3 and 4, respectively. Considering good column performance in order to obtain high ethyl lactate yield, it is favourable to work with MR= 50. Higher values of MR than studied in this work were not investigated because excess of ethanol is eliminated by increasing reboiler duty, which represents an increase in the total operating costs.
The factorial experimental design allowed the determination and evaluation of the relative significance of parameters: MR, T_{reb} and Cat w%.

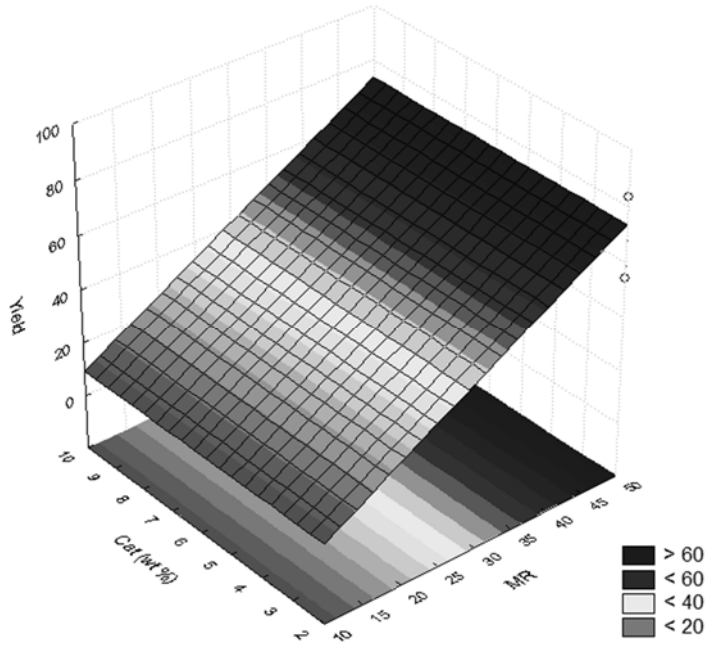

Figure 3: Response surface of ethyl lactate yield in function of catalyst concentration and molar ratio

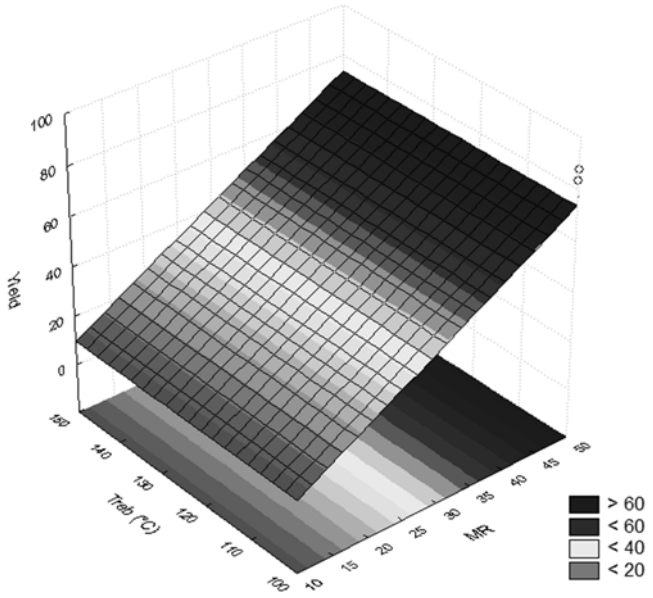

Figure 4: Response surface of ethyl lactate yield in function of reboiler temperature and molar ratio

4. Conclusions

The influence of molar ratio ethanol: lactic acid, reboiler temperature and catalyst concentration on the ethyl lactate production using reactive distillation process was investigated in this work. Among the investigated

operation conditions, only molar ratio ethanol: lactic acid was statistically significant on ethyl lactate yield to a confidence level of 95 %. An ethyl lactate yield of around 87.61 % was obtained. It can be concluded that the ethyl lactate production using a bench-scale reactive distillation column may be a feasible alternative to achieve high lactic acid conversion.

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References

Asthana N. S., Kolah A. K., Vu D., Lira C. T., Miller D. J., 2006, Reactive separations for producing bio-based organic acid esters. DOE PROJECT No. DE-FG36-04GO14249. <http://www.osti.gov/scitech/servlets/purl/937553/> accessed 19.02.2015

Bykowski D., Grala A., Sobota P., 2014, Conversion of lactides into ethyl lactates and value-added products, Tetrahedron Letters, 55, 5286-5289.

Dandia A., Jain A. K., Laxkar A. K., 2013, Ethyl lactate as a promising bio based green solvent for the synthesis of spiro-oxindole derivatives via 1,3-dipolar cycloaddition reaction, Tetrahedron Letters, 54, 3929-3932.

Komesu A., Martins P. F., Lunelli B. H., Morita A. T., Coutinho P. L. A., Maciel Filho R., Wolf Maciel M. R., 2013, Lactic acid purification by hybrid short path evaporation, Chemical Engineering Transactions, 32, 2017-2022.

Komesu A., Martins P. F., Lunelli B. H., Oliveira J., Filho R. M., Maciel M. R. W., 2014, Evaluation of lactic acid purification from fermentation broth by hybrid short path evaporation using factorial experimental design, Separation and Purification Technology, 136, 233-240.

Lunelli B. H., Morais E. R., Wolf Maciel M. R., Maciel Filho R., 2011, Process intensification for ethyl lactate production using reactive distillation, Chemical Engineering Transactions, 24, 823-828.

Mo L., Shao-Tong J., Li-Jun P., Zhi Z., Shui-Zhong L., 2011, Design and control of reactive distillation for hydrolysis of methyl lactate, Chemical Engineering Research and Design, 89, 2199-2206.

Pereira C. S. M., Rodrigues A. E., 2014, Ethyl lactate main properties, production processes, and applications, Alternative solvents for natural products extraction green chemistry and sustainable technology, Eds. Chemat F. and Abert Vian M., Springer-Verlag Berlin Heidelberg.

Perry R. H., Chilton C. H., 1999, Chemical Engineers' Handbook. 7th ed. Mc-Graw-Hill, New York, USA.

Rios L. F., Martínez E. L., da Silva N. de L., Dantas T. S. S., Maciel Filho R., Wolf Maciel M.R., 2012, Biodiesel production by an integrated reactive separation system: a comparative study. Chemical Engineering Transactions, 26, 255-260.

Seo Y., Hong W. H., Hong T. H., 1999, Effects of operation variables on the recovery of lactic acid in a batch distillation process with chemical reactions, Korean J. Chem. Eng, 16, 556-561.

Taylor R., Krishna R., 2000, Modelling reactive distillation, Chemical Engineering Science, 55, 5183-5229.

Wasewar K., Patidar S., Agarwal V. K, 2009, Esterification of lactic acid with ethanol in a pervaporation reactor: modeling and performance study, Dasalination, 243, 305-313.