

Pilot Plant Study of Recovery of Lactic Acid from Ethyl Lactate

Prashant P. Barve, Imran Rahman,* and Bhaskar D. Kulkarni

Chemical Engineering and Process Development Division, National Chemical Laboratory (NCL), Pune - 411 008, India

Abstract:

Purified lactic acid is used for production of biodegradable polymer. Esterification with ethanol and subsequent hydrolysis in distillation columns to produce purified lactic acid without catalyst has obvious advantages. In this paper, we present a pilot-plant study of ethyl lactate hydrolysis to produce 3.86 kg/h lactic acid (99.85% purity) using three distillation columns. Simulation of distillation columns at steady state has been carried out, and the results obtained tally with the experimental results of the pilot plant.

1. Introduction

Poly(lactic acid), a biodegradable polymer, as a substitute for petrochemicals-based polymers is beneficial from the environmental viewpoint. Production of biodegradable polymers is becoming increasingly important as a result of diminishing resources of crude oil.¹ Therefore, alternative renewable biomass and its transformation through fermentation to L-lactic acid have created a lot of interest.

Purification of dilute lactic acid obtained from bacterial fermentation is difficult due to its low vapor pressure, tendency to undergo self-esterification, and the presence of troublesome impurities.¹ Esterification of crude lactic acid obtained from the fermented broth and subsequent distillation of its ester followed by hydrolysis yield alcohol and pure lactic acid.²

Purification of lactic acid through reactive batch distillation was investigated by several investigators.^{1,3,4} Earlier Schopmeyer et al.⁵ suggested esterification of lactic acid (40–60 wt %) in the presence of a homogeneous catalyst in a jacketed kettle. The homogeneous catalyst used was sulfuric acid which leads to corrosion problems. Li et al.⁶ and Kumar et al.⁷ investigated the esterification of lactic acid with methanol in a reactor, followed by hydrolysis of methyl lactate using a cation-exchange resin as catalyst in a continuous column.

In this paper, an experimental study on hydrolysis of ethyl lactate on a pilot-plant scale (3.8 kg/h) at steady state is reported and compared with simulation results. The hydrolysis section consists of three columns. The distillation simulation model is

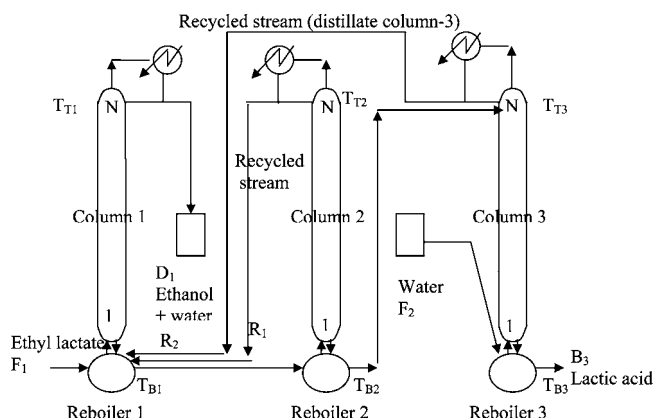


Figure 1. Schematic of reactive distillation column.

obtained by incorporating the reaction terms in the mass and heat balance equations of the conventional model for distillation. The kinetic data and vapor–liquid equilibrium for esterification of lactic acid described by Delgado et al.^{8,9} respectively, have been used.

2. Experimental Section

2.1. Materials. Ethyl lactate (>99% purity) was obtained from Godavari Sugar Mill, India.

2.2. Analysis. Analysis of ethanol and ethyl lactate was performed on a gas chromatograph (Shimadzu GC-14 B) equipped with a flame ionization detector. A DB-1, 30 m column (J&W Scientific, U.S.A.) was used with nitrogen as a carrier gas at a flow rate of 1.5 mL/min. The injector and detector temperatures were maintained at 220 and 300 °C, respectively. The oven temperature was varied over the range 120–240 °C with the ramp rate of 4 °C/min. The HPLC analysis for free lactic acid was performed on a C18 Hypersil BDS column using a Dionex HPLC system comprising Dionex Summit P 680A pump and Dionex ASI 100 autosampler. The mobile phase consisted of 0.01 M potassium dihydrogen phosphate (pH = 2.5) with 7% acetonitrile as an organic modifier. The chromatographic peaks were monitored using a UV detector at a detection wavelength of 205 nm.

2.3. Apparatus. Figure 1 shows a schematic representation of the distillation assembly. The distillation assembly consisted of a glass column (i.d. = 25 mm, height = 1000 mm) packed with glass packing (10 stages) attached to a jacketed mild steel glass-lined (MSGL) reboiler (6 L capacity). The distillation column was equipped with a distillate receiver and packed with Raschig rings supplied by M/s Silicaware Pvt. Ltd., Mumbai

* Author for correspondence. E-mail: r.imran@ncl.res.in.

- (1) Seo, Y.; Hong, W. H.; Hong, H. H. *Korean J. Chem. Eng.* **1999**, *16*, 556–561.
- (2) Vikroy, T. B. Lactic Acid. In *Comprehensive Biotechnology*; Moo-Young, M., Ed.; Pergamon Press: Oxford, 1985.
- (3) Kim, J. Y.; Kim, Y. J.; Hong, W. H.; Wozny, G. *Biotechnol. Bioprocess Eng.* **2000**, *5*, 196–201.
- (4) Kim, Y. J.; Hong, W. H.; Wozny, G. *Korean J. Chem. Eng.* **2002**, *19*, 808–814.
- (5) Schopmeyer, H. H.; Arnold, C. R. U.S. Patent 235,370, 1944.
- (6) Li, M. A.; Yang, Z.; Jichu, Y. *Chin. J. Chem. Eng.* **2005**, *13*, 24–31.
- (7) Kumar, R.; Nanavati, H.; Noronha, S. B.; Mahajani, S. M. *J. Chem. Technol. Biotechnol.* **2006**, *81*, 1767–1777.

(8) Delgado, P.; Sanz, M. T.; Beltran, S. *Fluid Phase Equilib.* **2007**, *255*, 17–23.

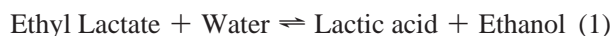
(9) Delgado, P.; Sanz, M. T.; Beltran, S. *Chem. Eng. J.* **2007**, *126*, 111–118.

Table 1. Experimental details for hydrolysis of ethyl lactate

run	F_1 (kg/h)	F_2 (kg/h)	D_1 (kg/h)	B_3 (kg/h)	R_1 (kg/h)	R_2 (kg/h)	T_{B1} (°C)	T_{T1} (°C)	T_{B2} (°C)	T_{T2} (°C)	T_{B3} (°C)	T_{T3} (°C)
RN1	3.284	2.520	1.896	3.864	1.253	4.770	95.00	85.50	98.30	92.00	106.50	96.30
RN2	3.528	2.696	1.760	4.164	1.272	4.889	95.00	84.70	98.60	92.70	108.00	96.60
RN3	3.432	2.572	1.848	4.044	1.276	4.807	95.00	85.50	98.30	92.10	106.50	96.30
RN4	3.209	2.560	1.828	3.964	1.267	4.81	95.60	85.90	98.50	92.10	108.40	96.10
RN5	3.240	2.588	1.827	3.976	1.293	4.85	95.20	86.70	98.40	91.90	106.80	97.10

(India). To avoid heat losses to the surroundings, the column was insulated with an asbestos sheet. Sensors (Pt-100) were provided at the top and bottom of the column to measure temperatures. Reflux was measured by means of a reflux-splitter with timer arrangement and attached to SCADA (Supervisory Control and Data Acquisition). Each column was provided with feed pumps for feed to the column at a controlled rate and a reboiler with an overflow outlet to maintain a constant level and allow product withdrawal. Recycle streams were measured by weighing on a balance and were fed to the column by a metering pump. Condensers were equipped with a chiller capable of achieving a condenser temperature of +6 °C.

2.4. Experiment in Three Hydrolysis Columns. Continuous reactive hydrolysis of ethyl lactate was performed in pilot-scale columns shown in Figure 1 to produce 3.86 kg/h of pure lactic acid (65% w/w) as per the following reaction scheme.



The feed to the first stage of the hydrolysis column was ethyl lactate and distillate from hydrolysis columns 2 and 3. The distillate of the first column consisted of ethanol and water. The overflow of reboiler 1 was fed to reboiler 2, and distillate was returned to reboiler 1. Again, the overflow of reboiler 2 was fed to reboiler 3, and distillate was recycled to reboiler 1.

At column temperature, 90% of the ethyl lactate undergoes hydrolysis. As the equilibrium was disturbed by fractionating the alcohol, the hydrolysis process progresses in an effort to restore the alcohol to the equilibrium concentration. Ethanol and water vapors rising in the column pass through the condenser and are collected as distillate. The overflow of reboiler 1 containing lactic acid, ethyl lactate, ethanol, and water moves to the reboiler 2. In the second column approximately another 10% of the ethyl lactate was hydrolysed, and the remaining ethyl lactate along with lactic acid, water, and ethanol was fed to column 3. The distillate of column 2 consisted of ethanol, water, and ethyl lactate and was removed by partial condenser. A water stream was also added in reboiler 3 to complete the hydrolysis of the remaining ethyl lactate. Pure lactic acid (65–70%) is drawn off from the reboiler and sent to an evaporator for concentration to the desired strength. The distillate which contains water, ethanol, and ethyl lactate was recycled to reboiler 1.

Initially, ethyl lactate and distilled mixture were fed to column. Data collection started once all the column attained steady state. Samples from the top and bottom streams were collected at regular intervals and analyzed for the product composition. Both bottom and distillate flow rates were measured, and the overall material balance was verified.

The objective to obtain the pure lactic acid at the bottom with 100% conversion of ethyl lactate to lactic acid is achieved in this three-column configuration.

3. Results and Discussion

Simulation of reactive distillation processes involves the simultaneous solution of material and energy balances and stoichiometric relationships.¹⁰ This corresponds to the solution of a considerably large set of nonlinear equations combined with the thermodynamic model for predicting the vapor–liquid equilibrium (VLE). It is recognized that the chemical reaction may be distributed over several stages. VLE data were correlated using the UNIQUAC model to describe the chemical and phase equilibria simultaneously.^{8,9} Material balance equations were solved simultaneously using the Newton–Raphson method for obtaining component mole fraction on each stage.¹⁰ The energy balance equation was solved to obtain the vapor flow rate. The temperature on each stage was computed by the Newton–Raphson method.

The lactic acid esterification with ethanol without addition of a catalyst is assumed to follow the Arrhenius rate law with $k_1^\circ = 5.298 \times 10^8 \text{ mol g}^{-1} \text{ min}^{-1}$, $E_{A,1} = 64.44 \text{ kJ/mol}$.⁸ The expression for the reaction equilibrium constant was obtained by Delgado et al.⁹

The assumptions made for modeling the reactive distillation column are the following: the vapor and liquid phases are in equilibrium on each tray; no reaction occurs in the vapor phase; the liquid phase is always homogeneous; the heat of reaction is considered negligible.

Convergence of the column model depends on starting guesses for the composition profile and flow rates in the column. The use of the Newton–Raphson method requires a proper starting guess for the composition profile.

The algorithm ends up when global material balance to the column is verified. A nonplausible column is obtained when the Newton–Raphson method exceeds a prespecified maximum number of iterations failing to satisfy the global material balance.

3.1. Comparison of Experimental and Simulation Results. The experimental data obtained during the pilot plant trials at steady state for five different runs are given in Table 1. Typically it takes about 5–6 h to attain the steady state. The operating parameters in Table 1 were obtained after conducting a number of pilot-plant trials. The parameters which gave the best performance are considered optimal and reported in Table 1. F_1 is the flow rate of ethyl lactate into reboiler 1 while F_2 is the D.M. water flow rate into reboiler 3. D_1 is distillate from column 1 consisting of ethanol and water. The product consisting of lactic acid and water is withdrawn from reboiler, B_3 . The bottom and top temperatures of columns 1, 2, and 3 are denoted by $T_{T1}T_{T2}T_{T3}$ and $T_{B1}T_{B2}T_{B3}$, respectively. Distillate from columns 2 and 3 are recycled stream (R_1 and R_2) to reboiler 1. Columns 1 and 2 are operated under conditions of reflux

(10) Suzuki, I.; Yagi, H.; Komatsu, H.; Hirata, M. *J. Chem. Eng. Jpn.* **1971**, *4*, 26.

Table 2. Experimental and simulation details for hydrolysis of ethyl lactate

column		feed		distillate composition				bottom composition				temperature (°C)		bottom flow rate (kg/h)	distillate flow rate (kg/h)
		F_1	F_2	LA	EtOH	EL	water	LA	EtOH	EL	water	bottom	top		
1	sim.	3.284	–	0.2216	0.0477	0.2040	0.5260	0	0.6460	0	0.3533	95.00	80.00	–	1.896
	expt.	–	–	0.2790	0.1070	0.1290	0.4840	0	0.6870	0	0.3420	93.50	80.00	–	1.955
2	sim.	–	–	0.4400	0.0273	0.0418	0.5170	–	–	–	–	98.70	80.00	–	–
	expt.	–	–	0.4100	0.0410	0.0610	0.4900	–	–	–	–	100.00	80.00	–	–
3	sim.	–	2.520	0.6530	0.0000	0.0000	0.3470	–	–	–	–	106.10	92.72	3.864	–
	expt.	–	–	0.6530	0.0000	0.0000	0.3470	–	–	–	–	104.70	96.76	3.787	–

Table 3. Column performance for variation in flow rate of RN1 by simulation

column	distillate composition				bottom composition				temperature (°C)		bottom flow rate (kg/h)	distillate flow rate (kg/h)
	LA	EtOH	EL	water	LA	EtOH	EL	water	bottom	top		
column 1	0.3070	0.0790	0.1050	0.5090	0	0.6950	0.0050	0.3050	95.00	80.00	–	2.029

equal to 1, while column 3 is a stripper. The lactic acid purity found by HPLC was 99.85%.

Three hydrolysis columns were individually simulated for a specified feed, bottom and distillate. Distillate from column 2 and 3 is returned to reboiler of columns 1. These two recycled streams were determined by material balance calculations. The experimental conditions and the results of a typical run to produce 3.86 kg/h of lactic acid (65% w/w) are given in Table 2. The simulation results matches with experimental results.

As the reflux ratio increased from 1 to 1.5 in column 1, a decrease in ethyl lactate hydrolysis from 90% to 86% was observed. A sensitivity study was also carried out by changing the flow rate of feed (about $\pm 3\%$) through simulation for RN1. It was observed that a -3.0% change in flow rate does not affect the conversion of ethyl lactate. When there is a $+3.0\%$ change in ethyl lactate feed, the expected column configuration shown for RN1 in Table 1 is simulated. In the distillate the presence of ethyl lactate is noticed as shown in Table 3, which can be reduced to zero by increasing the number of stages to 15.

4. Conclusions

This paper demonstrates a process for obtaining lactic acid from ethyl lactate. The feasibility of the process is evaluated

by experiments and simulation. The advantage of this process is that the complete hydrolysis of ethyl lactate is achieved without using catalyst and thus avoids corrosion problems. The optimal operating parameters for the process are fixed, and the process is verified by simulation.

NOMENCLATURE

$E_{A,1}$	apparent activation energy, kJ/mol
EL	ethyl lactate
EtOH	ethanol
F_1	feed to reboiler 1
F_2	feed to reboiler 3
k_1^0	pre-exponential factor for the esterification reaction, mol/g min
LA	lactic acid
N	number of stages

Received for review December 16, 2008.

OP800312K