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A Continuous Reactive Separation Process for Ethyl Lactate Formation

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Abstract:

The continuous formation of ethyl lactate (L_1E) from aqueous lactic acid solution and ethanol is carried out in a reactive separation column. Nearly complete conversion of lactic acid can be achieved with L_1E yield exceeding 85%; byproduct lactate oligomer esters and acids formed can be further converted to additional L_1E. Concentrated (88 wt % in water) lactic acid feedstock gives the best results, with as little as 40% excess ethanol required to achieve >95% conversion of lactic acid. Similar conversion can be obtained using 50 wt % lactic acid feed solution, but with much higher ethanol feed rates. Optimal column operation in both cases is observed with no reflux, so that operation is as a reactive stripping column. Limiting the quantity of ethanol added or vaporizing feed ethanol makes it possible to eliminate ethanol and water from the bottom stream of the column, thus simplifying recovery and purification of L_1E product and facilitating the recycle of byproduct oligomers. Reaction of oligomeric byproducts with excess ethanol over Amberlyst 15 cationic exchange resin in a batch reactor gives a high yield of L_1E, indicating that process yields of L_1E approaching 100% are feasible.

1. Introduction

Reactive distillation has found increasing application over the past several decades for conducting equilibrium-limited reactions. Prominent examples include production of methyl acetate by Tennessee Eastman[1] and production of methyl-*tert*-butyl ether as a gasoline additive. Excellent reviews detailing the growth of reactive distillation have been prepared by Mahajani et al.,[2] Sharma et al.,[3] and Hiwale et al.[4] In our laboratory, we have recently demonstrated the use of reactive distillation to recover propylene glycol and ethylene glycol from aqueous solution via formation of their acetals.[5] Here, we illustrate the use of reactive distillation for efficient production of biorenewable-based organic acid esters, specifically ethyl lactate.

Ethyl lactate holds promise as an effective, nontoxic replacement for petroleum-based solvents that have long dominated U.S. and world markets. But U.S. ethyl lactate production is low (10−15 million kg/yr), and the selling price of \$2.90−\$3.70 /kg reflects processing challenges and high feed costs. The recent advent of large-scale lactic acid production, primarily for production of polylactic acid polymers (PLA), ensures an ample, low-cost supply of the monomer lactic acid (L_1) and thus opens opportunities for expanded production, provided that low manufacturing costs can be achieved.

Prior work on lactate ester formation has been conducted primarily with dilute lactic acid solutions and a large excess of alcohol, mainly to purify fermentation-derived lactic acid for polylactic acid (PLA) formation.[6,7] Because lactic acid must be neutralized as it is formed, the raw fermentation product is typically sodium, calcium, or ammonium lactate. Direct ethyl lactate formation is possible from ammonium lactate via reaction with ethanol,[8,9] but ammonia inhibits lactic acid production and leads to undesired lactamide as a byproduct. Thus, addition of lime (CaO) during fermentation, direct acidulation with H_2SO_4 to precipitate $CaSO_4$, and esterification with excess ethanol is still a preferred route to pure L_1 monomer.[10]

Because of its bifunctional nature, lactic acid undergoes intermolecular esterification in aqueous solutions above ∼30 wt % to form linear dimer (L_2) and higher oligomer acids (L_3, L_4, etc.). The extent of homoesterification increases with increasing acid concentration, thus complicating the use of lactic acid as a reactive substrate. When mixed with an alcohol, lactic acid and its oligomers undergo esterification (Figure 1). The resultant esters simultaneously undergo hydrolysis and transesterification (alcoholysis), leading to a mixture of acid and ester monomer and oligomers whose distribution depends on water and ethanol content. Ethyl lactate (L_1E), typically the desired product, can be recovered from the mixture, but its yield is reduced from the theoretical maximum by the presence of the oligomeric compounds. The oligomer esters (L_2E, L_3E, etc. in Figure 1) have been reported to have use as plasticizers,[11−14] but no commercial market yet exists. Thus, the challenge in achieving high L_1E

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(1) Agreda, V. H.; Partin, L. R. U.S. Patent 4,435,595, 1984.

(2) Mahajani, S. M.; Chopade, S. P. In *Encyclopedia of Separation Science*; Wilson, I. D., Edlard, T. R., Poole, C. A., Cooke, M., Eds.; Academic Press: London, U.K., 2001; p 4075.

(3) Sharma, M. M.; Mahajani, S. M. Industrial Application of Reactive Distillation. In *Reactive Distillation*; Sundmacher, K., Kienle, A., Eds.; Wiley VCH: Germany, 2003; p 1.

(4) Hiwale, R. S.; Mahajan, Y. S.; Bhate, N. V.; Mahajani, S. M. *Int. J. Chem. React. Eng.* **2004**, *2*, Review R1.

(5) Dhale, A. D.; Myrant, L. K.; Chopade, S. P.; Jackson, J. E.; Miller, D. J. *Chem. Eng. Sci*. **2004**, *59* (14), 2881.

(6) Seo, Y.; Hong, W. H.; Hong, T. H. *Korean J. Chem. Eng.* **1999**, *16* (5), 556.

(7) Choi, J.; Hong, W. H. *J. Chem. Eng. Jpn*. **1999**, *32* (2), 184.

(8) Filachione, E. M.; Costello, E. J.; Fisher, C. H. *J. Am. Chem. Soc.* **1951**, *73* (11), 5265.

(9) Halpern, Y. U.S. Patent 6,583,310, 2003.

(10) Chahal, S. P. Lactic acid. In *Ullmann Encyclopedia of Industrial Chemistry*; Wiley-VCH, Verlag, GmbH & Co.: 2002.

(11) Rehberg, C. E.; Dixon, M. B. *J. Am. Chem. Soc.* **1950**, 5757.

(12) Olahorn, H. V. U.S. Patent 2,371,281, 1945.

(13) Fein, M. L. *J. Am. Chem. Soc.* **1951**, *73*, 5870.

(14) Rehberg, C. E.; Dixon, M. B. *J. Am. Chem. Soc.* **1952**, *74*, 1609.

10.1021/op0500640 CCC: \$30.25

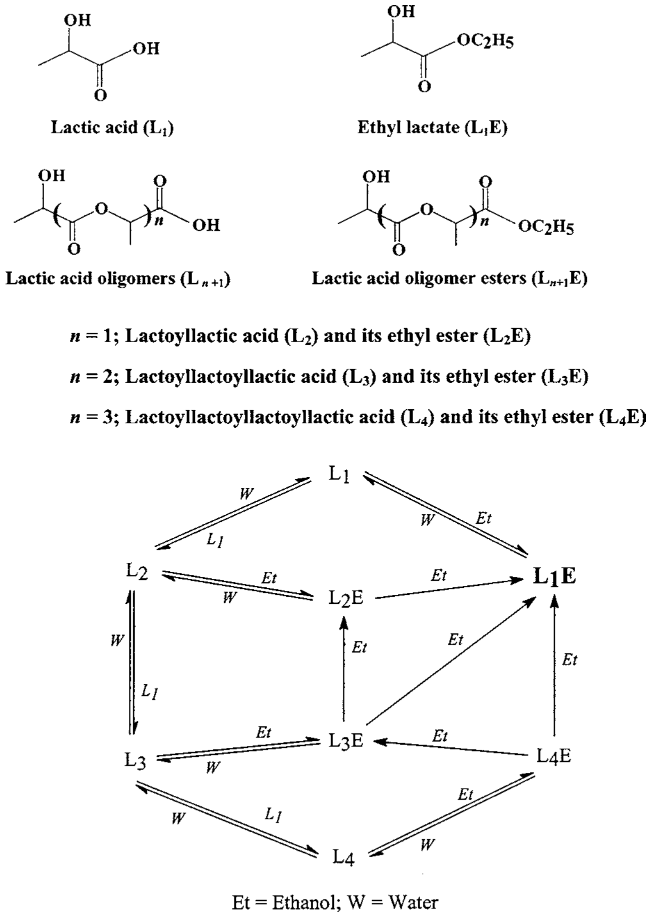

Figure 1. **Lactic acid oligomerization and esterification reactions.**

yields from lactic acid is to either (1) further convert the oligomeric byproducts to the monomer L_1E or (2) avoid the formation of oligomers altogether by working with dilute lactic acid solutions. The second option is less desirable, as water limits the extent of esterification, and thus large alcohol excess and high energy costs are required.

Concentrated or dehydrated lactic acid has been reacted with alcohol to achieve high L_1E yields and achieve complete esterification,[15,16] but these processes require multiple unit operations for separation and recovery of the lactate ester. Recently, Tretjak et al.[17] disclosed a continuous process wherein lactic acid and ethanol are partially converted in a stirred reactor. Reactor effluent is fed to a distillation column, where ethanol, ethyl lactate and water are removed as distillate and unreacted lactic acid and oligomers in the bottoms are recycled to the reactor. High purity ethyl lactate is recovered by distillation in a second column. A simpler, commercially practiced route to ethyl lactate is direct reaction of ethanol with dilactide, the cyclic dimer of lactic acid, and an intermediate in PLA formation. Unfortunately, the high cost of dilactide limits the potential for this pathway.

Application of inorganic membranes[18] to selectively remove water during lactic acid esterification has attracted significant attention. Datta et al.[19] reported the first membrane-based approach for L_1E production using electrodialysis to recover lactic acid from ammonium lactate salt. The acid was then reacted with alcohol, and water and ammonia produced were removed via pervaporation across a polyvinyl-based hydrophilic membrane. Jafar et al.[20] and Tanaka et al.[21] successfully extended the application of zeolite membranes for lactic acid esterification. Budd et al.[22] employed alternating layers of cationic and anionic polyelectrolytes on a Zeolite A membrane to prevent degradation and to achieve higher fluxes of water.

Although prior approaches to forming ethyl lactate can achieve high yields, they require multiple unit operations, use high-cost feedstocks, or are prone to process difficulties (e.g., membrane fouling). We present here a reactive separation method for producing ethyl lactate that includes secondary conversion of lactate oligomer esters to L_1E, thus giving near-theoretical yields in a simple, efficient process. We note one prior attempt to produce L_1E using reactive distillation was reported in the early 1920s, but that process involved the use of aromatics to break the ethanol−water azeotrope[23] and thus had a different goal than the present work.

The method presented departs from typical organic acid ester formation via reactive distillation, where the ester has either the highest volatility of the species present (e.g., methyl acetate)[1] or the lowest volatility (*n*-hexyl acetate),[24] in which case water is usually the most volatile component. In those cases, recovery of 100% pure ester is straightforward via optimization of column operating conditions. For ethyl lactate production, reactive distillation column operation does not fit into either of these categories, as products L_1E (bp 155 °C) and water have volatilities that are lower than ethanol (bp 78 °C) but higher than lactic acid (bp 122 °C at 15 mmHg) and its oligomers. A schematic of the proposed column is given in Figure 2; column operation is targeted at complete lactic acid conversion, removal of L_1E along with ester oligomers in a bottoms stream, and recovery of ethanol and water as distillate. We believe it is especially important to avoid the presence of water in the column bottom stream, as separating product ester from water by distillation leads to undesirable ester hydrolysis.[25,26] With L_1E and oligomer esters as the only bottom products, pure L_1E recovery is readily achievable by simple distillation. Oligomer esters can be refined for sale or further converted to give near-theoretical L_1E yield for the process.

2. Experimental Methods

2.1. Reagents. Three aqueous lactic acid solutions were used in experiments: 88 wt % (J. T. Baker, Inc.), 50 wt %

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(15) Cockrem, M. C. M. U.S. Patent 6,664,413, 1998.

(16) Kaimal, T. N. B.; Vijayalaxmi, P.; Ramalinga, B.; Laxmi, A. A. U.S. Patent 6,342,626, 2002.

(17) Tretjak, S.; Teissier, R., WO 2004/052825 A2, 2004.

(18) Benedict, D.; Parulekar, S.; Tsai, S. *Ind. Eng. Chem. Res.* **2003**, *42*, 2282.

(19) Datta, R.; Tsai, S. U.S. Patent 5,723,639, 1998.

(20) Jafar, J. J.; Budd, P. M.; Hughes, R. *J. Membr. Sci.* **2002**, *199*, 117.

(21) Tanaka, K.; Yoshikawa, R.; Ying, C.; Kita, H.; Okamoto, K. *Chem. Eng. Sci.* **2002**, *57*, 1577.

(22) Budd, P. M.; Ricardo, N. P. S.; Jafar, J. J.; Stephenson, B.; Houghes, R. *Ind. Eng. Chem. Res.* **2004**, *43*, 1863.

(23) Steffens J. A. U.S. Patent 1,421,604, 1922.

(24) Schmitt, M.; Hasse, H.; Althaus, K.; Schoenmakers, H.; Gotze, L.; Moritz, P. *Chem. Eng. Process.* **2004**, *43*, 397.

(25) Steinigeweg, S.; Gmehling, J. *Ind. Eng. Chem. Res.* **2003**, *42* (3), 3612.

(26) Smejkal, Q.; Hanika, J.; Kolena, J. *Chem. Eng. Sci.* **2001**, *56*, 365.

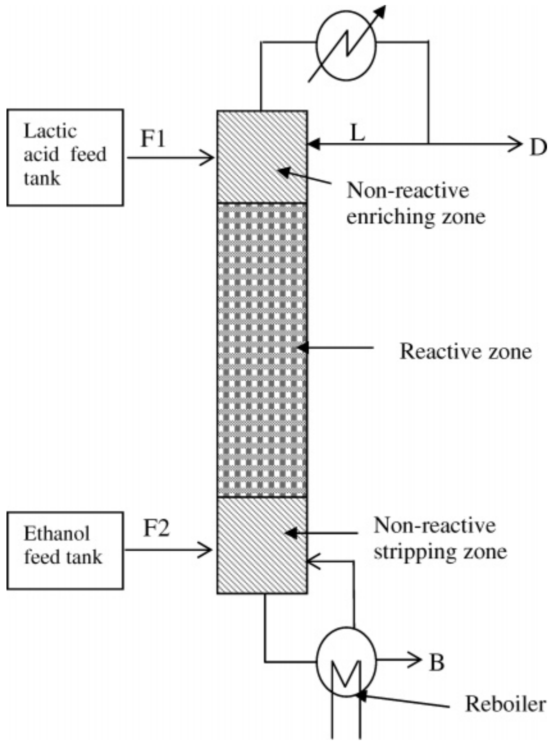

Figure 2. **Reactive separation column configuration.**

Table 1. **Composition of lactic acid feedstocks**

feed component	feed designation (nominal)		
	20 wt %	50 wt %	88 wt %
L_1 wt % (mol %)	23 (5.6)	46 (15.2)	58 (43.5)
L_2		3 (0.5)	22 (9.2)
L_3			6 (1.8)
L_4			2 (0.4)
H_2O	77 (94.4)	51 (84.3)	12 (45.1)
monomer equivalent concentration (M)	2.6	5.9	10.8

(Purac, Inc.), and 20 wt % (Aldrich). The compositions of these lactic acid feed solutions, including the distribution of acid oligomers as determined by the analytical methods outlined below, are given in Table 1. Absolute ethanol (99% purity) and HPLC grade water were procured from J.T. Baker. Ethyl lactate (98% purity) was purchased from Acros Organics. Purities of all chemicals were verified by gas or liquid chromatography. Water, L_1E, and ethanol used as calibration standards were purified by distillation before use; all other reagents were used as received. Dimer ethyl ester (L_2E) was produced in a reactive distillation experiment and was isolated by vacuum distillation.

2.2. Analysis. The presence of lactic acid (L_1) and oligomers (L_2, L_3, and L_4) and their esters (L_1E, L_2E, L_3E, and L_4E) was first confirmed by GC−MS analysis of their trimethylsilyl (TMS) derivatives. Concentrations of lactic acid, oligomers, and esters were determined by a combination of titration, GC analyses, and HPLC analyses. Total free acidity of reaction samples was measured by titration with 0.1 N aqueous NaOH. Total monomer lactic acid concentration was determined by dilution, addition of excess NaOH, and refluxing to hydrolyze all oligomers to monomer sodium lactate, and then back-titrating with 0.1 N H_2SO_4 to determine sodium uptake as monomer lactate salt.

Ethanol, water, and L_1E from reactive distillation experiments were analyzed by gas chromatography (Varian 3700 w/ TCD detection; 20 mL/min He as a carrier gas) using a packed stainless steel column (3.25 mm × 4 m) containing Porapak-Q as the stationary phase. The column temperature program involved initially holding at 140 °C for 2 min, heating to 220 °C at 20 °C/min, and holding at 220 °C for 6 min.

L_1 monomer and L_2−L_4 oligomers and their esters were quantitatively analyzed on a Hewlett-Packard 1090 HPLC using a reversed-phase C18 column (Novapak, 3.9 mm × 150 mm) held at 40 °C. Water/acetonitrile (ACN) mixtures, buffered at pH = 1.3, were used as mobile phase (1.0 mL/min) in a gradient mode (0% ACN ($t = 0$) to 60% ACN ($t = 20$ min) to 90% ACN ($t = 25$ min) to 0% ACN ($t = 28$ min)), and species were quantified by UV detection (Hitachi L400H) at a wavelength of 210 nm. Lactic acid (L_1) was identified and quantified by comparing HPLC retention time and peak area with a calibration standard prepared by diluting 20 wt % lactic acid feed to 7−8% and then titrating to determine exact monomer concentration. Standards for L_2−L_4 acid oligomers and their esters could not be obtained commercially; however, since 50 wt % lactic acid feed solution contains only L_1 and L_2, the response factor for L_2 was obtained from the combination of titration and HPLC of 50 wt % lactic acid solution. This L_2 response factor (area/g) was found to be 12% larger, on a mass basis, than the L_1 monomer response factor. Based on this result, the response factor (area/g) for L_3 was assigned a value 12% larger than that of L_2 and the response factor for L_4 was assigned a value 12% larger than that of L_3. These response factors were verified as suitable based on the combination of HPLC and titrations of the 88 wt % lactic acid feedstock: oligomer concentrations determined from the HPLC peaks using the calculated L_3 and L_4 response factors matched to within ±1% with those determined by titration and use of L_1 and L_2 response factors determined above.

The oligomer esters L_2E, L_3E, and L_4E, were quantified by HPLC. The response factor for L_2E was determined by injection of pure L_2E isolated from an experimental product stream by fractional vacuum distillation and found to be the same value as that for the L_2 acid. The L_3E and L_4E oligomer esters were thus assigned the same response factors on a mass basis as their corresponding acid oligomers; again this was verified to be a reasonable assumption based on comparison of oligomer concentrations of an esterified 88 wt % lactic acid mixture with corresponding results from titration, HPLC, and GC.

2.3. Continuous Reactive Separation Column. Continuous reactive separation experiments were performed in bench-scale and pilot-scale columns[5] according to the column setup shown in Figure 2. The columns consist of 50 mm ID Pyrex tubes of height 3.0 m for a bench-scale column and 5.5 m for a pilot-scale column. Each column is outfitted with an electronic reflux splitter to control the reflux ratio, a total condenser with a chiller capable of achieving a condenser temperature of −20 °C, and a reboiler with an overflow outlet to maintain a constant level and allow product withdrawal. The reboiler solution volume is ∼0.5 L for the bench-scale column and ∼1.0 L for the pilot-scale column. Each column has two feed pumps to dispense feed solutions to the column at a controlled rate. The columns have several ports along their length that allow internal temperature measurement, introduction of feed, and sample withdrawal. The columns are wrapped with electric heating tapes that are controlled by surface thermocouples and Omega controllers to a temperature just below the internal column temperature to minimize the heat loss. Heat loss is further minimized by insulating each column with bands of glass wool.

Each column is divided into three sections: a nonreactive stripping section (0.4 m in bench-scale, 1.0 m in pilot-scale), a reactive section, and a nonreactive enriching section (0.4 m in bench-scale, 0.8 m in pilot-scale). The reactive section, 1.7 m in height for the bench-scale column and 2.6 m in height for the pilot-scale column, is packed with Katapak-S structured packing[5] elements (Sulzer Chemtech Ltd.) filled with 0.25 mm Amberlyst-15 cationic exchange resin as the esterification catalyst. The Amberlyst 15, a robust, strongly acidic cationic exchange resin known to catalyze esterification reactions, has an acid site density of 4.6 meq/g dry resin. Structured packings such as the Katapak-S are widely used in industry because they facilitate high catalyst loadings (∼75 g resin per meter of column height in our 5 cm diameter column) and excellent interphase mass transfer. The packing has a height of an equivalent theoretical plate (HETP) of 0.6 m. Empty Katamax structured packing (Koch-Glitsch, Ltd.) is used to fill nonreactive column sections.

2.4. Procedures for Column Operation. Following a series of initial experiments, the columns were configured such that the aqueous lactic acid solution (F1 in Figure 2) was fed near the top of the rectification zone, while ethanol (F2 in Figure 2) was fed either 0.09 m above the reboiler or 1 m above the reboiler, exactly at the bottom of the reactive zone. The molar feed ratio of ethanol to lactic acid ranged from 1.4:1 to 10.3:1. In certain cases, both lactic acid and ethanol feeds were preheated, with ethanol fed either as a liquid near its bubble point or in partially vaporized form. The reflux ratio (L/D) ranged from 0.0 to 2.3. The reboiler duty was held constant for all experiments in both bench- and pilot-scale columns, so that comparisons in column performance could be made on a constant energy consumption basis.

The column was started by turning on the external heating tapes and reboiler heater, and setting the feed pumps to specified feed rates. Steady state was generally achieved after about 6 h of operation. Several samples were collected from distillate and bottom streams to ensure time invariant stream compositions, column temperatures were recorded, and steady-state feed, bottom, and distillate flow rates were measured by timed filling of graduated cylinders. The feed, bottom, and distillate compositions and flow rates were then entered into a spreadsheet to determine product yields and species and overall material balance closure for the experiment.

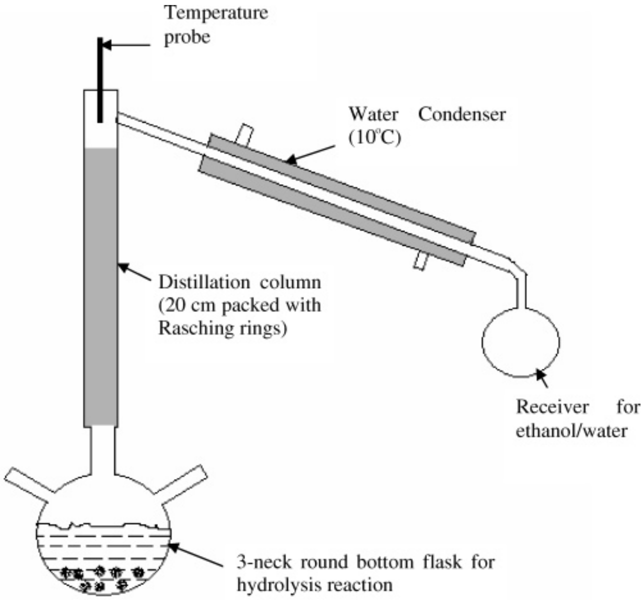

Figure 3. **Batch reactor for hydrolysis and transesterification.**

2.5. Hydrolysis and Transesterification of Oligomer Acids and Esters. To demonstrate the further conversion of unreacted L_1-L_4 acids and L_2E-L_4E esters formed in esterification to the desired L_1E product, bottom products from several pilot-scale reactive separation experiments were collected and vacuum distilled to remove water, ethanol, and most of the L_1E. The residue, containing L_1-L_4 acids and L_1E-L_4E esters, was then subjected to hydrolysis and transesterification to determine the extent to which additional L_1E could be formed.

Reactions were performed in either a closed batch mode with reflux or in a semibatch reactive distillation mode in which vapor produced during reaction was withdrawn from the reaction flask. A schematic of the reaction setup is provided in Figure 3. Amberlyst 15 cation-exchange resin was used as the catalyst in these batch reactions at a loading of 2.5−3 g of resin per 100 mL of solution. Typically, reactants were mixed and brought to the desired reaction temperature, and then catalyst was added. Samples were then collected periodically to follow the concentrations of reactive species over the course of reaction.

3. Results and Discussion

Lactic acid conversion is based on total L_1 equivalent fed. Yield of L_1E is defined as mol L_1E formed per mol of total L_1 equivalent fed; thus, 100% yield signifies that all L_1-L_4 acids are converted to L_1E.

3.1. Esterification in Bench-Scale Column. Preliminary experiments were performed in the bench-scale reactive distillation column to verify feasibility of the ethyl lactate formation and identify operating conditions for achieving high lactic acid conversion, eliminating water from the bottom stream, and obtaining high purity L_1E. No HPLC analyses were conducted for these experiments, only GC to determine ethyl lactate, water, and ethanol concentrations and titration to determine acid concentrations. Parameters varied in these initial experiments were the ethanol/lactic acid feed ratio, ethanol feed temperature, and reflux ratio.

Table 2. **Esterification of 88 wt % lactic acid in pilot-scale reactive distillation column**[a]

run	EtOH feed rate (mol/min)	molar feed ratio EtOH/LA	EtOH feed temp (°C)	reflux ratio (L/D)	lactic acid conversion (%)	L_1E yield (%)
E1	0.34	3.6:1	25	0	94	69
E2	0.24	2.5:1	25	0	93	70
E3	0.14	1.4:1	25	0	90	58
E4	0.34	3.6:1	78 (sat. liq)	0	95	65
E5	0.34	3.6:1	85 (vap)	0	95	59
E6	0.34	3.6:1	25	0.2	91	73
E7	0.34	3.6:1	25	0.5	85	69
E8	0.34	3.6:1	25	1	80	64
E9	0.34	3.6:1	25	0	94	68
E10[b]	0.34	3.6:1	25	0	83	66
E11[b]	0.34	3.6:1	85 (vap)	0	85	45
E12[c]	0.34	3.6:1	25	0	96	68

[a] Conditions: Lactic acid feed compostion = 88 wt % (aqueous); lactic acid monomer equivalent feed rate = 0.097 mol/min; water feed rate = 0.06 mol/min; lactic acid feed temp = 25 °C. Runs E1−E8, ethanol feed position = 0.09 m above reboiler; runs E9−E12, ethanol feed position 1 m above reboiler. [b] Runs E10, E11 carried out with azeotropic water/ethanol mixture (water feed rate = 0.108 mol/min). [c] Run E12, 3 wt % Amberlyst 15 cationic exchange resin catalyst added to reboiler.

The best results were obtained when vaporized ethanol (at 85 °C) and lactic acid solution (88 wt %) at 25 °C were fed in a 3:1 molar ratio to the column operating at a reflux ratio of zero (e.g., as a reactive stripping column). A lactic acid conversion of 85% with an L_1E yield of 66% was achieved, with water and ethanol concentrations in the bottom stream at 2 and 4 mol %, respectively (on an oligomer-free basis).

In addition to experiments directed at L_1E formation, we operated the bench-scale reactive distillation column at similar conditions to produce methyl lactate from methanol and 88 wt % lactic acid in a yield of 87%. We also demonstrated transesterification of methyl lactate to L_1E in a yield of 94% using a 3:1 ethanol/methyl lactate feed ratio.

3.2. Esterification in Pilot-Scale Column. 3.2.1. 88 wt % Lactic Acid Feed. The results of esterifying lactic acid as an 88 wt % solution in water in the pilot-scale column are described in Tables 2 and 3. For these experiments, lactic acid was fed ~0.14 m below the condenser and ethanol was fed either 0.09 or 1.0 m above the reboiler. In all runs in Table 2, the reboiler duty was held constant. In pilot-scale runs, species material balances closed to within ±7% in all cases, with many runs having smaller errors.

For many of the pilot-scale runs, the objective of eliminating water from the bottom stream of the distillation column was achieved. Removal of water from the reboiler was aided by its formation of a minimum-boiling azeotrope with ethanol, by the presence of excess ethanol, and by the high boiling point of L_1E which keeps reboiler temperature high. Further optimization via reduction of ethanol feed rate or preheating the ethanol feed stream (runs E3 and E5) led to elimination of both water and ethanol from the bottom stream. In both of these runs, L_1E was the predominant species in the bottom stream. Although other runs give higher conversion of lactic acid (95% in E4) and higher L_1E yield (73% in E6), conditions in E3 and E5 that eliminate water and ethanol from the bottom stream are the most attractive from a processing viewpoint (as discussed below).

Runs E1, E2, and E3 illustrate the effect of decreasing ethanol/lactic acid molar feed ratio from 3.56:1 to 1.4:1. Reducing ethanol feed rate lowered lactic acid conversion slightly but significantly decreased ethanol content in the bottom stream. The decline in ethanol concentration in the bottoms is a manifestation of maintaining a constant reboiler duty in operating the column (ethanol can be eliminated from the bottoms stream at any ethanol feed flow rate by increasing reboiler duty); nevertheless, any conditions that eliminate water and ethanol from the bottom stream are desirable because L_1E can easily be recovered from the bottoms stream in a single column, and the oligomer acids and esters can be further converted or recycled. Also, the oligomer ester (L_2E, L_3E, L_4E) yield increased about 10% as ethanol feed rate was lowered, as there was less alcohol present in the column for transesterification (alcoholysis) of the oligomer esters to L_1E.

Runs E1, E4, and E5 show the effect of preheating the ethanol feed stream on column performance with excess ethanol. Overall, the effect of preheating ethanol feed is similar to that of reducing the ethanol feed rate. Preheating ethanol to near its bubble point (E4) and then partially vaporizing it (E5) had surprisingly little effect on lactic acid conversion. The ethanol content of the column bottom stream

Table 3. **Product stream properties from esterification of 88 wt % lactic acid in pilot-scale reactive distillation column**

	bottom composition (mol %)										distillate composition (mol %)					
run	H_2O	EtOH	L_1	L_2	L_3	L_4	L_1E	L_2E	L_3E	L_4E	H_2O	EtOH	L_1E	reboiler temp (°C)	bottom flow rate mol/min	distillate flow rate mol/min
E1	0.0	46	1.4	1.2	0.4	0.1	45	4.6	0.6	0.2	45	54	0.8	99	0.15	0.34
E2	0.0	16	2.8	1.8	0.6	0.2	71	7.1	0.8	0.2	50	49	0.8	126	0.10	0.30
E3	0.0	1.4	6.5	2.4	0.9	0.2	77	9.5	1.6	0.4	65	34	0.9	159	0.070	0.21
E4	0.0	15	1.6	1.8	0.7	0.1	71	8.2	1.1	0.2	37	62	0.9	128	0.089	0.40
E5	0.0	1.9	2.4	2.1	0.9	0.2	79	11	1.6	0.4	34	65	1.2	159	0.072	0.45
E6	0.2	57	1.5	1.4	0.4	0.1	36	2.9	0.3	0.1	49	50	0.5	95	0.20	0.28
E7	0.8	64	3.2	1.3	0.3	0.1	28	1.8	0.2	0.0	53	47	0.4	91	0.24	0.21
E8	2.4	67	4.3	1.2	0.2	0.0	23	1.2	0.2	0.0	51	48	0.3	88	0.27	0.17
E9	0.1	49	1.2	1.2	0.4	0.1	43	4.3	0.5	0.1	41	58	0.8	98	0.15	0.32
E10	15.4	53	3.8	0.8	0.2	0.0	24	1.8	0.2	0.0	57	42	0.6	90	0.26	0.31
E11	1.6	1.2	12	2.9	1.2	0.4	65	12	2.2	0.5	45	54	0.8	162	0.068	0.53
E12	3.2	42	1.1	0.6	0.3	0.1	46	5.2	0.6	0.1	43	56	1.3	97	0.14	0.36

was strongly affected, with very little ethanol present with vaporized ethanol feed. This is because preheating feed ethanol is equivalent to providing additional reboiler duty. The L_2E−L_4E yield increased by about 20% when vaporized ethanol was fed, again a consequence of less ethanol in the column reboiler for transesterification of the oligomer esters to L_1E. The concentration of L_1E in the distillate was found to increase from 0.8 mol % to 1.1 mol % in distillate; the higher reboiler temperature was responsible for producing more L_1E vapor at the bottom of the column.

Experiments E1 to E4 were run with no reflux to the column, thus essentially making it a reactive stripping column. The presence of a small quantity of L_1E in the distillate stream of these runs, along with the bench-scale result that showed reduced L_1E in the distillate with reflux, prompted us to further explore column operation with modest reflux ratios in order to reduce L_1E in the distillate without adversely affecting acid conversion and L_1E yield. Runs E1 and E6−E8 delineate the effect of reflux ratio on overall column performance. As the reflux ratio increased, a decrease in overall lactic acid conversion from 94% to 79% was observed. In addition, substantial water and ethanol appeared in the bottom stream, with a corresponding decrease in reboiler temperature from 99 °C in E9 to 88 °C in E8. L_1E yield at first increased and then only dropped slightly as the reflux ratio was increased from 0 to 1. Unfortunately, increasing the reflux ratio did not eliminate L_1E from the distillate (it declined from 0.8 mol % in E1 to 0.3 mol % in E8). The L_1E in the distillate arises because of two prominent reasons: (1) the rectifying section in the pilot-scale column is too short to facilitate separation, and (2) L_1E forms a minimum-boiling azeotrope with water. (We have separately examined the vapor−liquid equilibria of the ethyl lactate−water−ethanol system and will report the results in a forthcoming paper.) Adding reflux therefore does not lead to any positive outcome for L_1E production, and we conclude that the continuous column is best operated without reflux as a reactive stripper.

Runs E1−E8 were run with ethanol fed 0.09 m above the bottom of the stripping section. In an effort to reduce ethanol content in the bottom stream, the ethanol feed location in run E9 was moved to 1.0 m above the reboiler. The results obtained are virtually identical to those of run E1, indicating that the ethanol feed location is unimportant at the conditions used. It is possible that further optimization involving a change in reboiler duty would lead to a dependence of column performance on ethanol feed location, but with the excess ethanol used, there is little fractionation taking place at the bottom of the column.

The use of an azeotropic ethanol−water mixture as the feed for L_1E formation was examined in runs E10 and E11. There would certainly be economic advantages of using such an azeotropic mixture in an ethyl lactate process, as the mixture could be isolated and directly recycled from the distillate stream. In E10, the ethanol−water mixture was fed at 25 °C, and in E11 the feed mixture was partially vaporized. The use of the azeotropic feed at room temperature resulted in a decrease in lactic acid conversion from 94% to 83% and an increase in water concentration in the reboiler from essentially 0 to 15 mol %. The concentrations of water and ethanol in the bottoms were both reduced substantially by vaporizing the azeotropic feed mixture, but lower acid conversion and lower L_1E yields were observed relative to the corresponding experiment with absolute ethanol (E5). Based on these results, a commercial-scale column for L_1E production using an azeotropic ethanol−water feed stream could be designed and operated that would avoid the presence of water and ethanol in the bottom stream. The ultimate decision regarding ethanol feed composition for L_1E production would thus depend on process economics.

In an effort to increase lactic acid conversion and L_1E yields, approximately 30 g of Amberlyst 15 cation-exchange resin were added to the reboiler flask in run E12. The net result of this addition was an increase in lactic acid conversion from 94 to 96%, but L_1E yield was not affected. The additional reaction taking place in the reboiler resulted in an increase in water content of the bottom stream. It is seen in comparing E9 with E12 that L_2−L_4 concentrations are lower upon addition of the resin, indicating that they were hydrolyzed to some extent. The concept of adding catalyst to the reboiler does not appear to have a positive effect on column performance.

3.2.2. 50 wt % Lactic Acid Feed. The low water content of 88 wt % lactic acid solution makes it relatively straightforward to achieve high acid conversion and L_1E yield without a large excess of ethanol. However, the presence of oligomeric species in the concentrated lactic acid feed reduces per-pass ethyl lactate yield and complicates column operation. We therefore explored the use of commercially available 50 wt % lactic acid feed, which contains only a small amount of L_2 (3 wt %) along with 46 wt % L_1, to increase overall yield of L_1E. For these runs, the total mass feed rates of lactic acid solution and ethanol were kept the same as those in E1−E12 with 88 wt % lactic acid, resulting in lower lactic acid throughput and higher ethanol/lactic acid feed ratios. Lactic acid was fed near the top of the rectification section (0.14 m below the condenser), and ethanol was fed 1 m above the reboiler. All runs were conducted without reflux to the column.

Results of esterification of 50 wt % lactic acid with ethanol under various operating conditions are tabulated in Tables 4 and 5. The effects of both ethanol/lactic acid feed ratio and feed temperatures on column performance have been examined. For both feeds at room temperature (E13), a lactic acid conversion of 79% was achieved with an L_1E yield of 78%. The bottom product contains very few ester oligomers; thus all the lactic acid converted goes to L_1E. Unfortunately, with room temperature feeds there are large quantities of water and ethanol in the bottom streams, an undesirable outcome. This is a direct result of the additional water content of the 50 wt % lactic acid feed.

The effect of raising lactic acid feed temperature to 100 °C was examined in run E14. A slight increase in lactic acid conversion and a corresponding increase in L_1E yield was observed, and water content in the bottom stream declined substantially. In E15, the ethanol molar feed ratio was

Table 4. Esterification of 50 wt % lactic acid in pilot-scale reactive distillation column[a]

run	EtOH feed rate (mol/min)	molar feed ratio EtOH/LA	lactic acid feed temp (°C)	EtOH feed temp (°C)	lactic acid conversion (%)	L_1E yield (%)
E13	0.35	7.1:1	25	25	79	79
E14	0.35	7.1:1	100	25	82	86
E15	0.5	10.3:1	100	25	83	86
E16	0.5	10.3:1	100	85 (vap)	94	80
E17	0.35	7.1:1	100	85 (vap)	91	66
E18	0.26	5.4:1	25	85 (vap)	87	72
E19	0.36	7.4:1	25	85 (vap)	88	70
E20	0.52	10.5:1	25	85 (vap)	93	82
E21	0.26	5.4:1	25	78 (sat. liq)	83	78

[a] Conditions: Lactic acid feed compostion = 50 wt % (aqueous); lactic acid monomer equivalent feed rate = 0.049 mol/min; water feed rate = 0.25 mol/min; ethanol feed position = 1 m above reboiler; reflux ratio = 0.

increased from 7.10 to 10.30; very little change was observed other than an increase in alcohol content in the bottom stream. Feeding ethanol as a vapor (E16, E17) led to a marked increase in lactic acid conversion with a corresponding elimination of water from the bottom stream and, for E17, elimination of ethanol from the bottom stream as well. A lower L_1E yield was observed with E17, but an increase in L_2E-L_4E was seen. This is expected, as removal of water from the liquid phase as it travels down the column will concentrate unreacted lactic acid and lead to oligomer formation. The results of E17 are important, as they illustrate the potential for more dilute lactic acid streams to be converted to L_1E while avoiding undesired water and ethanol in the bottoms stream. The results of E17 are similar to those in E3 and E5 with 88 wt % lactic acid feed.

The effect of the ethanol molar feed ratio on column performance was studied in experiments E18−E20, where lactic acid solution was fed at 25 °C and vapor ethanol was fed at 85 °C. Increasing ethanol feed rate increased lactic acid conversion and increased L_1E yield but unfortunately also forced ethanol into the bottom stream. Again, increasing reboiler duty may alleviate this problem, but varying reboiler duty was not a part of this study. Increasing ethanol rate also decreased the formation of L_2E-L_4E and L_2-L_4, the former via transesterification to form L_1E and the latter by enhanced conversion of lactic acid.

Finally, run E21 illustrates the outcome of feeding ethanol as a liquid near its bubble point. Lower lactic acid conversion and lower L_1E yield were obtained relative to E15 (vapor ethanol feed), and significantly higher ethanol content in the bottom stream was observed.

3.3. Discussion. Results of lactic acid esterification in the bench and pilot-scale columns show that L_1E can be produced in high yield in a single-pass operation. This is in contrast to prior methods such at Tretjak et al.,[17] where multiple operations are required. Given the equilibrium constant of ∼2.4 for monomer lactic acid esterification to L_1E,[21] the conversion of lactic acid and the ethyl lactate yield achieved significantly exceed the conversion that would be obtained by simple mixing of the feed streams. We did not expect to achieve complete conversion of lactic acid to L_1E in the relatively short column, but the conversions that were achieved, in the mid 90% range, are a promising sign that complete conversion can be achieved in a larger column with water and ethanol appearing only in the column distillate stream.

Column operation without reflux is possible in part because the vapor pressures of lactic acid and all oligomeric products in the range of ethanol and water boiling points are negligible. Thus, the rectifying section only functions to separate L_1E from ethanol and water; the incomplete separation achieved in this study indicates that either the pilot-scale rectifying section is too short to separate out L_1E or an azeotrope is formed that precludes L_1E separation.

The composition of the product streams, particularly the distribution of ethanol between distillate and bottoms streams, is heavily dependent on three factors: ethanol feed rate, ethanol feed temperature, and reboiler duty. In this study, the reboiler duty (energy/time) was kept constant by choice and because the reboiler heater has a limited capacity of about 750 W. Total energy input to the column was varied by preheating ethanol and lactic acid feed streams; in essence, this preheating is equivalent to adding reboiler duty as it provides more vapor flow in the column. The results show that the reboiler duty is sufficiently high to give excellent column performance for low ethanol/lactic acid feed ratios and for vaporized ethanol feed streams. Reaction conditions giving good column performance for feeds containing either 50 wt % lactic acid or 88 wt % lactic acid have been identified. The 88 wt % feed gives a greater throughput of

Table 5. Product stream properties from esterification of 50 wt % lactic acid in pilot-scale reactive distillation column

	bottom composition (mol %)										distillate composition (mol %)					
run	H_2O	EtOH	L_1	L_2	L_3	L_4	L_1E	L_2E	L_3E	L_4E	H_2O	EtOH	L_1E	reboiler temp (°C)	bottom flow rate (mol/min)	distillate flow rate (mol/min)
E13	9.5	73	3	0.4	0.0	0.0	14	0.2	0.0	0.0	68	32	0.3	83	0.28	0.36
E14	3.8	76	2.7	0.4	0.0	0.0	17	0.4	0.0	0.0	69	31	0.5	83	0.25	0.39
E15	3.3	81	2	0.3	0.0	0.0	13	0.2	0.0	0.0	68	32	0.5	82	0.33	0.37
E16	0.0	38	2.4	1.1	0.2	0.0	57	2	0.1	0.0	48	52	0.2	120	0.069	0.68
E17	0.0	0.0	8.4	2.1	0.3	0.0	84	5.1	0.4	0.0	50	50	0	159	0.038	0.56
E18	0.1	0.1	11	1.8	0.4	0.0	78	7.5	1.2	0.2	55	45	0.2	163	0.045	0.47
E19	0.1	7.9	9.8	1.6	0.2	0.0	75	4.7	0.4	0.0	49	51	0.2	139	0.046	0.57
E20	0.0	51	2.6	0.7	0.0	0.0	45	1.1	0.0	0.0	44	56	0.2	95	0.089	0.63
E21	0.2	35	9.2	1.1	0.1	0.0	52	2.2	0.2	0.0	61	39	0.2	105	0.073	0.44

lactic acid and requires as little as 40% excess ethanol to achieve high conversion. The drawback of the concentrated feed is the existence of oligomer acids and esters; these will require additional unit operations for conversion or separation from L_1E. High conversions are achievable with the 50 wt % lactic acid feed, but higher ethanol/lactic acid feed ratios are required. Unfortunately, under operating conditions where ethanol and water are excluded from the bottom stream, oligomer acids and esters form with 50 wt % acid in quantities similar to those for the 88 wt % acid. Thus, the advantage of using 50 wt % acid as a feed is lost, and 88 wt % acid is preferred because it has a lower alcohol requirement and contains less water to be evaporated in the column.

Formation of L_1E in a reactive separation column is thus both feasible and straightforward, complicated only by the presence of the lactate oligomers and their esters. To further increase the yield of L_1E, these oligomeric compounds can be either hydrolyzed to L_1 and recycled or further transesterified with ethanol to form additional L_1E. In the following section, we describe experiments that demonstrate the viability of these two routes for ultimately converting the oligomeric compounds to additional L_1E.

3.4. Conversion of Lactate Oligomer Acids and Esters to Ethyl Lactate. The column bottom stream from run E9 was vacuum distilled to remove water, ethanol, and most of the ethyl lactate, leaving an oligomeric residue consisting of L_1−L_4 acids and L_1E−L_4E esters. The composition of this residue is L_1 (10.0 wt %), L_2 (6.2 wt %), $L_3 + L_4$ (0.7 wt %), L_1E (8.7 wt %), L_2E (67.0 wt %), L_3E (6.5 wt %), and L_4E (1.6 wt %). This oligomeric residue was used as the starting material in the reactions described below to further convert oligomers to desired L_1E.

3.4.1. Hydrolysis via Batch Reactive Distillation. Hydrolysis of the oligomer residue was conducted at 80 °C (ethanol−water azeotrope temperature) in the stirred glass batch reactor equipped with a condenser and sampling port (Figure 3). A 37 g sample of oligomeric residue along with 37 g of water was added to the reactor, giving a water-to-L_2E molar ratio of 16. To these reactants, 2.3 g (dry basis) of Amberlyst 15 cation-exchange resin was added as a catalyst. The reactor was heated to reflux temperature, and ethanol, the volatile product of hydrolysis, was removed as the ethanol−water azeotrope and collected as a distillate product over the course of the reaction. Samples of the liquid phase were collected to follow the concentrations of reactants and products during reaction.

After 7 h of reaction, all L_2E, L_3E, and L_4E were consumed along with L_3 and L_4. The concentrations of L_1 and L_2 in the final solution were determined by direct titration with NaOH and by HPLC analysis to be 52 wt % L_1 and 6 wt % L_2. Water was determined by gas chromatograph to be 41 wt %. There was no L_1E in the reaction solution. The L_1 and L_2 concentrations are consistent with equilibrium concentrations of L_1 and L_2 in water as reported in the literature for this concentration range of lactic acid.[27] Thus, complete hydrolysis of the oligomer acids and esters to a mixture of L_1 and L_2 is possible.

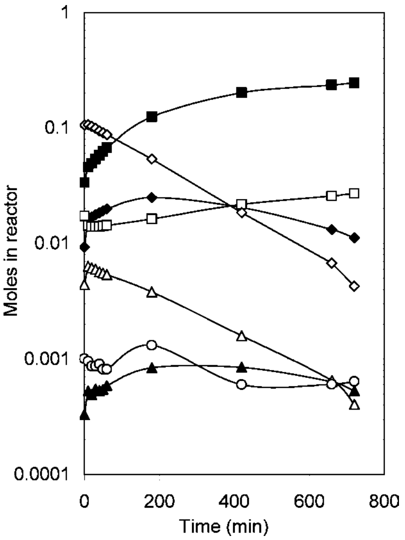

Figure 4. **Hydrolysis of byproduct acid and ester oligomer mixture. (■) L_1; (◆) L_2; (▲) L_3; (□) L_1E; (◇) L_2E; (△) L_3E; (○) L_4E. Initial mixture composition: $L_1 = 0.03$ mol; $L_2 = 0.01$ mol; $L_3 = 0.0005$ mol; $L_4 = 0.00005$ mol; $L_1E = 0.02$ mol; $L_2E = 0.1$ mol; $L_3E = 0.01$ mol; $L_4E = 0.001$ mol; water = 0.3 mol; temperature = 80 °C; catalyst = Amberlyst 15; catalyst loading = 2 g (2.5 wt % of total mass of reactant).**

3.4.2. Hydrolysis in Closed Batch Reactor. A second experiment was conducted with a 28.5 g sample of the oligomeric residue described above along with 54 g of water and 2.0 g of Amberlyst 15 resin (dry basis), giving a water/L_2E molar ratio of 28. Reaction products were not withdrawn from the reactor (except for analysis) during the 6 h of heating at a reflux temperature of 78 °C. The concentrations of key species over time are given in Figure 4. Substantial hydrolysis takes place as indicated by the decline in L_2E concentration over the course of the reaction and the increase in lactic acid concentration. Some L_1E is formed during the reaction as part of the product mixture. Even after 6 h, the hydrolysis reaction mixture was not at equilibrium, indicating that multiple reaction pathways are in effect and kinetics are relatively slow.

3.4.3. Transesterification in Closed Batch Reactor. As an alternative to hydrolysis to recover acid, we conducted transesterification of the oligomer mixture with ethanol to directly produce L_1E. Transesterification was performed at 80 °C in the stirred batch reactor by adding 38 g of the oligomeric residue and 27.6 g of ethanol along with 1.7 g (dry basis) of Amberlyst 15 cation-exchange resin, giving a molar ratio of ethanol-to-L_2E of 2.6. Samples were collected during reaction to follow the concentrations of reactants and products.

The concentrations of species in the batch reactor over the course of 24 h of experiment are given in Figure 5. The predominant product of reaction is L_1E; concentrations of all other species decline or remain constant over the course of the reaction. The acid oligomers undergo transesterification to form L_1E and L_1−L_3; L_1 also undergoes esterification to L_1E with liberation of water. L_2E−L_4E transesterify directly to L_1E. Based on the concentrations of all monomer

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(27) Holten, C. H. *Lactic acid: Properties and Chemistry of Lactic acid and Derivatives*; Verlag Chemie: Copenhagen, 1971; p 192.

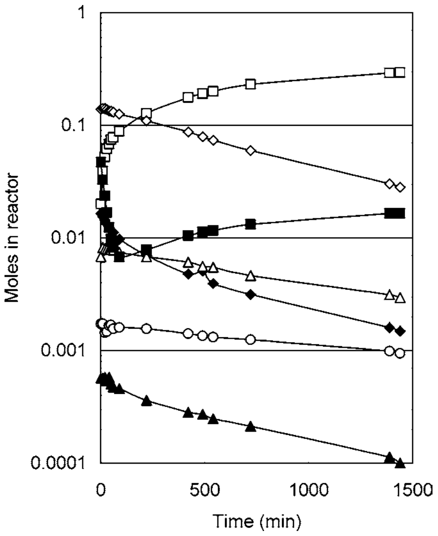

Figure 5. **Transesterification of byproduct acid and ester oligomer mixture. (■) L_1; (◆) L_2; (▲) L_3; (□) L_1E; (◇) L_2E; (△) L_3E; (○) L_4E. Initial mixture composition: $L_1 = 0.04$ mol; $L_2 = 0.01$ mol; $L_3 = 0.006$ mol; $L_4 = 0.0003$ mol; $L_1E = 0.02$ mol; $L_2E = 0.134$ mol; $L_3E = 0.009$ mol; $L_4E = 0.002$ mol; ethanol = 0.6 mol; temperature = 78 °C; catalyst = Amberlyst 15; catalyst loading = 1.7 g (2.5 wt % of total mass of reactants).**

and oligomeric species in the residual starting mixture, the overall conversion of lactate to L_1E in this experiment is 76%. It is interesting to note that the transesterification reactions are thermodynamically more favorable than the hydrolysis reactions presented above, but kinetically they are significantly slower. Even after 24 h of reaction, it is clear that concentrations of L_2E−L_4E continue to decline and L_1E concentration increases; thus the reaction is not close to equilibrium.

Based on this result in a single stage batch reactor, it is apparent that a continuous, multistage reactive separation column for transesterification would lead directly to secondary conversion of the residual oligomer stream to desired L_1E.

4. Process Concept for Ethyl Lactate Formation

A process concept for producing L_1E continuously is given in Figure 6. The process contains three major columns: the primary reactive separation column for L_1E and oligomers production, a vacuum distillation column to separate product L_1E from the oligomers, and a second reactive separation column in which transesterification of the oligomeric mixture is carried out. A fourth separation unit (A in Figure 6) is required for recycling ethanol; this unit may be dedicated to the proposed esterification process or it may be part of a fuel ethanol production facility with which the esterification process is associated. Ethanol recycling is very simple if azeotropic ethanol is used for esterification and somewhat more complex if absolute ethanol is required.

5. Conclusions

Ethyl lactate (L_1E) can be synthesized from aqueous lactic acid solution using a continuous reactive separation column. Although L_1E yield in a reactive distillation column per pass is comparable to that obtained at equilibrium in a simple batch reaction, complete lactic acid conversion is possible to L_1E and a mixture of oligomer acids and esters. Concentrated (88 wt %) lactic acid is the preferred feedstock for the reaction because it contains relatively little water; efficient conversion is achieved with as little as 40% excess ethanol fed to the column along with the acid. Good column performance is also observed (1) with 50 wt % lactic acid solution in water, although more alcohol and feed preheating is required, and (2) with an azeotropic ethanol−water mixture as the alcohol feed.

The oligomeric byproduct mixture of esterification can be either hydrolyzed to monomer acid or transesterified to form L_1E in near-theoretical yields. The process thus has potential advantages over current methods for L_1E production from biorenewable feedstocks.

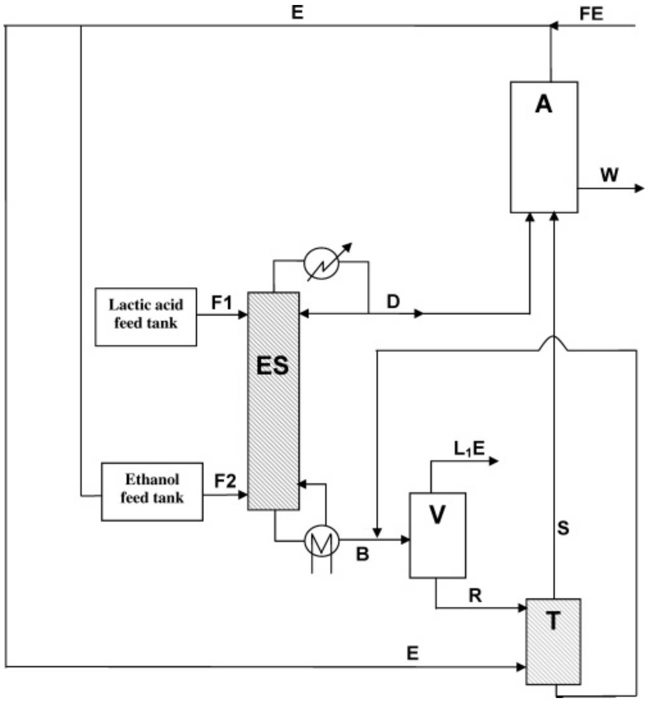

Figure 6. **Process concept for ethyl lactate production. F1: Lactic acid feed. F2: Ethanol feed to column. FE: Ethanol process feed. ES: Primary esterification column. B: Bottom stream from ES. V: Vacuum distillation column for L_1E recovery. L_1E: Ethyl lactate product. R: Oligomer residue from V. T: Transesterification column. S and D: Mixture of ethanol and water. A: Absolute ethanol recovery unit. E: Ethanol stream. W: Water.**

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