

**ADVANCED ELECTRODIALYSIS AND PERVAPORATION FOR
FERMENTATION-DERIVED ORGANIC ACIDS PRODUCTION**

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ADVANCED ELECTRODIALYSIS AND PERVAPORATION FOR FERMENTATION-DERIVED ORGANIC ACIDS PRODUCTION

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Lactate esters produced from carbohydrate have potential markets as nontoxic replacements for halogenated and toxic solvents and as feedstocks for large-volume chemicals and polymers. Argonne National Laboratory has developed a novel process for the production of high-purity lactate esters from carbohydrate. The process uses advanced electrodialysis and pervaporation technologies to overcome major technical barriers in product separation; more specifically, the process involves cation elimination without the generation of salt waste and efficient esterification for final purification. This patented process requires little energy input, is highly efficient and selective, eliminates the large volumes of salt waste produced by conventional processes, and significantly reduces manufacturing costs. The enabling membrane separation technologies make it technically and commercially feasible for lactate esters to penetrate the potential markets.

Introduction

Many organic acids can be produced from carbohydrates via fermentation [1]. The existing uses of these fermentation-derived organic acids are primarily in food applications. There are also industrial applications, especially for citric acid and sodium gluconate. Some of these organic acids, particularly lactic and succinic acids, are also known to have significant market potential as a feedstock for large-volume chemicals and polymers [2-4]. However, there are significant technoeconomical barriers that need to be overcome for these fermentation-derived organic acids to capture these large-volume potential markets. Argonne National Laboratory (ANL) has developed a novel process for the production of lactic acid and its derivatives, particularly lactate ester, from carbohydrate. In this process, two advanced membrane-separation technologies — electrodialysis and pervaporation — are successfully applied to overcome the major challenges in product purification and enable the low-cost production of ethyl lactate for large-volume markets as industrial solvents and chemical feedstocks.

Commercial lactic acid fermentation was practiced as early as 1881. The conventional fermentation process typically involves fermenting suitable carbohydrates to lactic acid, which is neutralized to form calcium lactate, followed by purification of calcium lactate and addition of sulfuric acid to form free lactic acid and calcium sulfate. Chemical synthesis of lactic acid involves reacting hydrogen cyanide with acetaldehyde to form lactonitrile, followed by hydrolysis and purification to obtain a purified lactic acid [2]. Compared with the fermentation route, the synthetic process has a much higher raw material cost and is no longer competitive, because of the new technologies developed in recent years for the fermentation route.

Program Strategy, Opportunities, and Technical Challenges

The ANL program of chemicals and polymer feedstocks from carbohydrate-derived lactic acid has adopted a platform strategy based on lactate ester as the intermediate, which has immediate market potential itself and leads to other products (see Figure 1).

Lactate esters have excellent solvent properties; are nontoxic (approved for food use); are completely degradable; and have the potential to be a major "green" solvent for widespread use in industrial, commercial, and consumer applications. Ethyl lactate is also a very versatile building-block molecule that can be used to derive a wide variety of chemical products — such as degradable plastic polymers; three-carbon oxygenated chemicals, such as propylene glycol, acrylates, and propylene oxide; and specialty product derivatives — by using certain basic chemical and catalytic conversion processes. The potential volume and dollar value of the platform of products that are derivable exceeds 7 billion lb/yr and \$5 billion/yr in the United States alone (see Table 1). Thus, this platform strategy for these key chemical intermediates can lead to a major opportunity for United States industry to make environmentally friendly chemicals and products from renewable carbohydrate feedstocks.

A lot of published information is available regarding the formulation and efficacy of lactate ester solvent applications. These applications range from major industrial segments (such as semiconductor manufacturing, paints and coatings, metal cleaning, printing, and adhesives) to commercial segments (such as paint stripping and degreasing) and consumer uses (such as general-purpose degreasers and cleaners) [5, 6]. Therefore, the solvent markets for lactate ester can be captured immediately, thereby eliminating the long lead-time required to develop new product applications.

To succeed with such a strategy, the energy use, the waste production, and the manufacturing cost has to become very low. The innovative technologies developed at ANL have addressed and overcome these barriers for lactate ester so that it can be cost competitive and serve as a “platform chemical” of the future.

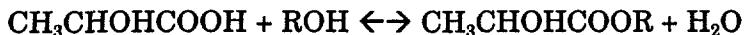
Commercial lactic acid fermentation processes use bacteria (e.g., *Lactobacillus delbrueckii*) or fungi (e.g., *Rhizopus oryzae*) to convert carbohydrate into lactate [1]. The key technical issues in the fermentation step (such as product concentration, yield, productivity, nutrient requirements, strain stability, and product isomer) have been adequately addressed by many research groups to develop efficient fermentation processes [1, 7]. The most significant technical barriers for the production of lactic acid and lactate ester are in product separation and purification steps and include the following:

1. Cation elimination without generating salt waste: The lactic acid fermentation process produces a salt of the organic acid (e.g., calcium lactate or ammonium lactate), rather than the acid, in a crude, impure broth. However, it is usually the purified acid that is required for conversion into esters or other lactic acid derivatives. The question of how to convert this lactate salt into the acid without consuming an equivalent quantity of another acid and generating an equivalent quantity of waste salt has been the major technical challenge of cation elimination. Conventional lactic acid recovery technologies, such as mineral acid addition or ion-exchange, produce waste calcium sulfate or other waste salts.
2. Efficient esterification for final purification: For the lactic acid or lactate ester to be suitable for solvent applications or as a feedstock for polymerization or chemical conversion, a very high purity is required. Lactic acid fermentation broth contains high concentrations of impurities; therefore, product purification to meet the required specification is a very significant challenge. Although many different approaches have been attempted, esterification has been known to be the only effective, reliable method to obtain the high purity needed for lactic acid to be a feedstock for the chemical conversion and polymerization processes. However, the conventional processes for lactic acid esterification are inefficient and costly because of the contacting and equilibrium conversion issues.

The Membrane-Based ANL Approach

The ANL process uses advanced electrodialysis and pervaporation for product separation and esterification and overcomes the aforementioned technical barriers. This process requires little energy input, is highly efficient and selective, and eliminates the large volumes of salt waste produced by conventional processes. The ANL process uses a double-electrodialysis approach to recover lactate from the crude fermentation broth and convert the lactate into lactic acid without generating a salt waste. As shown in Figure 2, the desalting electrodialysis step purifies and concentrates the lactate, and conversion of lactate into lactic acid is accomplished by water-splitting electrodialysis, which employs the bipolar water-splitting membrane. The use of water-splitting for fermentation product separation is technically challenging because of the low conductivities of the process streams and the potential interference of soluble impurities to electrodialysis operation. In ANL’s double-electrodialysis process, the desalting electrodialysis step improves the operability and efficiency of water-splitting electrodialysis to make such an application feasible and economical.

Esterification is a reversible reaction. The ethyl esterification of lactic acid as shown below has a low equilibrium constant (about 2).



Therefore, a high conversion yield cannot be achieved unless the product (ester or water) is removed. However, the relative volatility of the components of this system is as follows:

Ethanol > Water > Ethyl Lactate > Lactic Acid,

and so distillation, including reactive distillation, cannot be used to efficiently remove water or ester and achieve a high conversion. In addition, the high volatility of ethanol creates problems in terms of retaining the alcohol in the reaction mixture, and the existence of the alcohol/water azeotrope makes removing the water from the system difficult. As a result, conventional processes for lactic acid esterification with volatile alcohols are inefficient and costly because of intensive energy consumption, low conversion, and high lactate and alcohol losses.

As shown in Figure 3, the ANL esterification process uses selective pervaporation membranes to efficiently remove water during esterification, whereas alcohol, acid, and ester are retained in the esterification reactor [8]. Commercially available pervaporation membranes have been found to give very good performance for this process, with good membrane stability, economically attractive flux, and a less than 1% loss of alcohol. This pervaporation-assisted esterification process makes it possible to use a small excess of alcohol to achieve very high conversions and fast reaction rates. Because of the high conversions and low levels of undesirable by-products in the reaction mixture, purification of lactate ester from the reaction mixture becomes very easy. Highly pure ethyl lactate is readily produced at high yields in the subsequent distillations. This lactate ester production process has been successfully demonstrated in the pilot scale, and the ethyl lactate product has been shown to meet the purity requirements of target market applications.

This patented ANL pervaporation-assisted esterification process also allows for a potential breakthrough in the direct esterification of ammonium lactate to ethyl lactate. In this process, the pervaporation membranes pass ammonia and water and yet retain other reactants. By directly esterifying ammonium lactate, this process can potentially eliminate multiple process steps and costs associated with water-splitting electrodialysis or any other acidification process and become the lowest cost lactate-ester process.

By overcoming these technical barriers, this novel ANL process uses approximately one-tenth of the energy of the conventional process, eliminates the production of waste salt, and will enable the selling price of lactate esters to be lowered, from about \$1.60-\$2.00/lb to less than \$1.00/lb. At such prices, it would be technically and commercially viable to replace a wide range of environment-damaging halogenated and toxic solvents with lactate esters.

During the course of developing this membrane-based ANL process for lactate ester production, it was recognized that successful development of new applications for membrane separation technologies requires the following:

- Proper integration of the enabling membrane separation steps with other processing steps that use conventional technologies (i.e., ion-exchange and distillation).

- A system's approach to the performance of the membrane systems, including all components (e.g., gaskets and adhesive), instead of focusing only on the membranes.
- Close collaborations between the equipment supplier and the application developer to ensure proper use of the membranes and equipment and to develop novel applications.

Conclusions

Ethyl lactate and other lactate esters produced from carbohydrate have potential markets as nontoxic replacements for halogenated and toxic solvents and as feedstocks for large-volume chemicals and polymers. The total volume and dollar of these potential markets exceed 7 billion lb/yr and \$5 billion/yr in the United States. Argonne National Laboratory has developed a novel process for the production of high-purity ethyl lactate and other lactate esters from carbohydrate. The process uses advanced electrodialysis and pervaporation technologies to overcome major technical barriers in product separation; more specifically, the process involves cation elimination without the generation of salt waste and efficient esterification for final purification. This patented process requires little energy input, is highly efficient and selective, eliminates the large volumes of salt waste produced by conventional processes, and significantly reduces the manufacturing cost. The enabling membrane separation technologies make it technically and commercially feasible for lactate esters to penetrate these large-volume potential markets.

Acknowledgment

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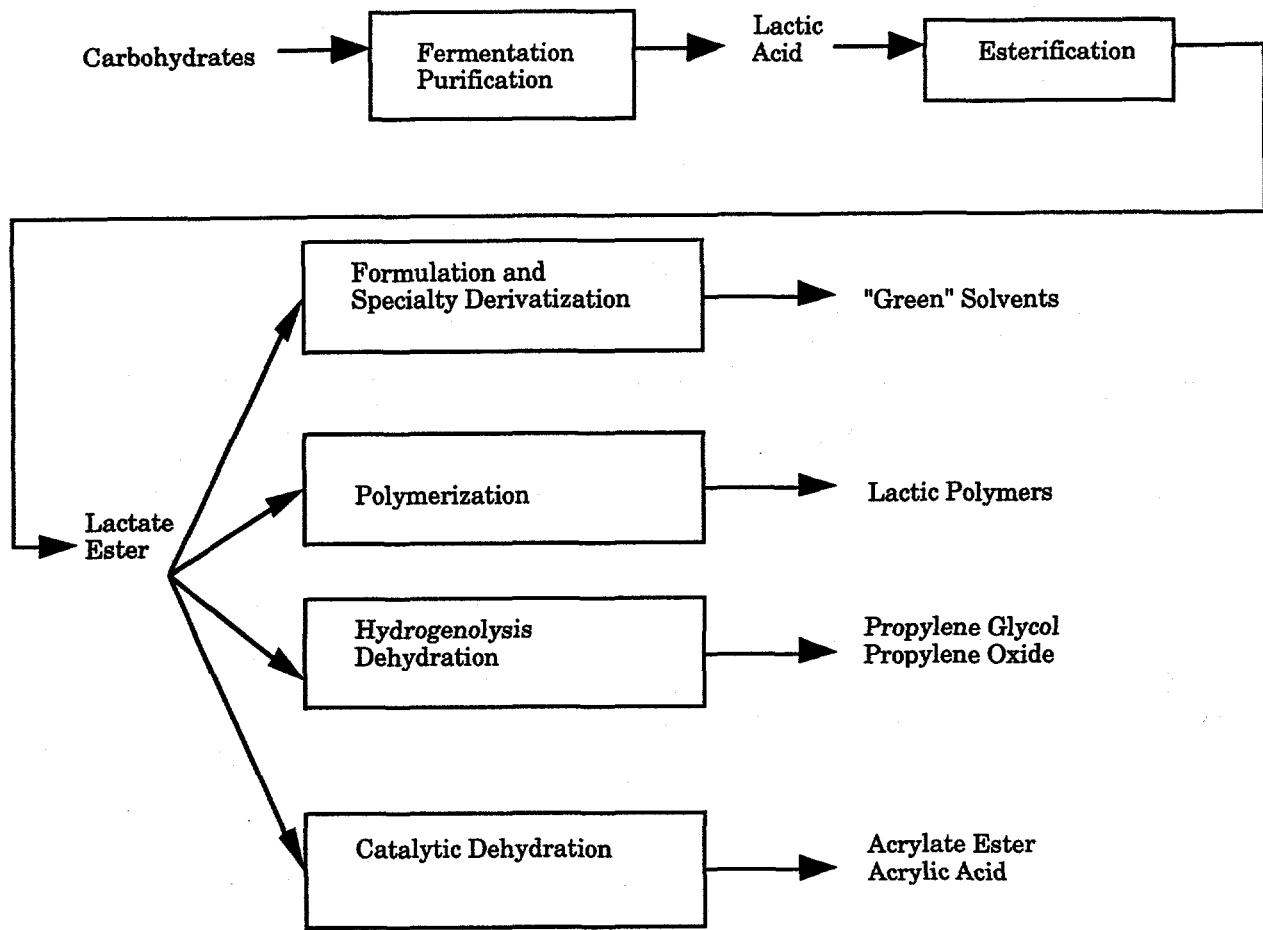


Figure 1. Solvents, Oxychemicals, and Polymer Feedstock Production from Carbohydrate-Derived Lactate Ester

Table 1. Solvents, Chemicals, and Polymers Derivable from Lactate Ester

Product	Uses	U.S. Market ^a (billion lb/yr)	Selling Price ^a (\$/lb)	Total Value (million \$/yr)
"Green" Solvents				
Esters	Industrial, commercial, consumer applications	0.5–1.0 ^b	0.8–1.0 ^b	500–800
Ester Derivatives and Blends	Same as above	0.1–0.2 ^b	1.0 ^b	100–200
Polymers				
Degradable Plastics	Packaging, films, molded articles	0.3–2.5 ^c	0.40–0.60 ^c	180–1,000
Oxychemicals				
Propylene Glycol	Polymers, food, deicers, humectants	0.9	0.65	585
Acrylic Acid (Acrylates)	Polymers, plastics, films, coatings	1.7	0.80	1,360
Propylene Oxide	Polymers, plastics, solvents	3.6 ^d	0.64	2,300
Specialty Products				
Various	Various	0.05–0.1	1.00	50–100
TOTALS		7.1–10.0		5,075–6,345

^aQuantities and prices are for 1998 (C&EN and Chemical Marketing Reporter) unless otherwise noted.

^bArgonne National Laboratory and NTEC estimates.

^cEstimates from Battelle and 1993 Cargill announcement.

^dExcludes propylene oxide (PO) used for propylene glycol (PG) manufacture.

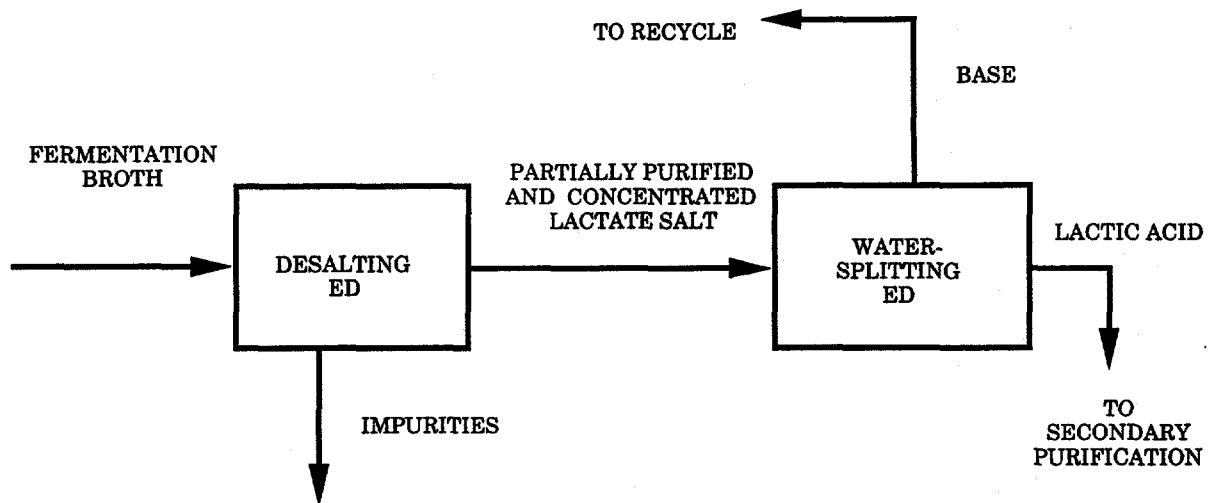


Figure 2. Schematic of the Double Electrodialysis Process for Lactic Acid Separation

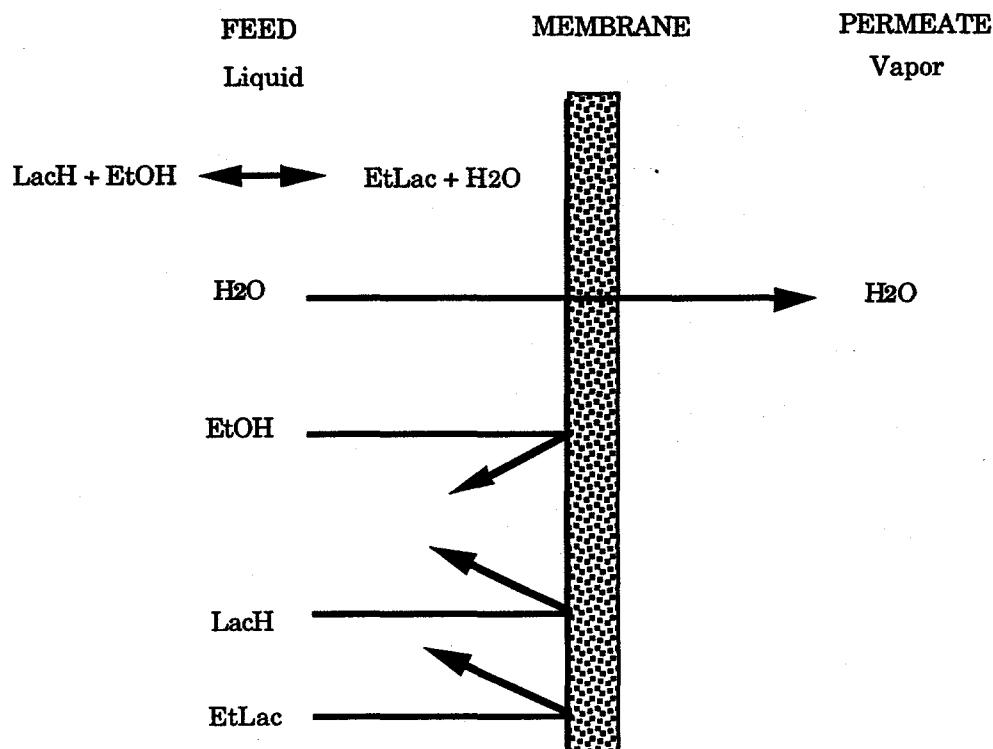


Figure 3. Schematic of the Pervaporation-Assisted Esterification Process