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by

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ABSTRACT

Lactic acid has been an intermediate-volume specialty chemical (world production ~50,000 tons/yr) used in a wide range of food-processing and industrial applications. Potentially, it can become a very large-volume, commodity-chemical intermediate produced from carbohydrates for feedstocks of biodegradable polymers, oxygenated chemicals, environmentally friendly "green" solvents, and other intermediates. In the past, efficient and economical technologies for the recovery and purification of lactic acid from fermentation broths and its conversion to the chemical or polymer intermediates had been the key technology impediments and main process cost centers. Development and deployment of novel separations technologies, such as electrodialysis with bipolar membranes, extractive and catalytic distillations, and chemical conversion, can enable low-cost production with continuous processes in large-scale operations. The emerging technologies can use environmentally sound lactic acid processes to produce environmentally useful products, with attractive process economics. These technology advances and recent product and process commercialization strategies are reviewed and assessed.

Keywords: lactic acid products, technologies, commercialization.

BACKGROUND

Lactic acid (2-hydroxypropionic acid), $\text{CH}_3\text{CHOHCOOH}$, is the most widely occurring hydroxycarboxylic acid. Although it has been ubiquitous in nature and has been produced as a fermentation product for many years, it has not been a large-volume chemical. Its worldwide production volume by 1990 had grown to approximately 40,000 tons/yr with two major producers - CCA biochem b.v. of Netherlands and its subsidiaries in Brazil and Spain, and Sterling Chemicals, Inc., in Texas City, U.S.A., as the primary manufacturers. Musashino in Japan has been a smaller manufacturer. Recently ADM has entered the market with production for captive use and sales. Cargill has also announced demonstration-scale production for polymer development and commercialization. The estimated current worldwide production is ~50,000 tons/yr. Thus, lactic acid was considered a relatively mature fine chemical in that only its use in new applications (such as a monomer in plastics or as an intermediate in synthesis of high-volume oxygenated chemicals and products) would cause a significant increase in its anticipated demand.

Lactic acid can be manufactured by either (1) chemical synthesis or (2) carbohydrate fermentation — both are used for commercial production. In the U.S., lactic acid is manufactured synthetically by means of the lactonitrile route by Sterling Chemicals, Inc. In Japan, Musashino Chemical Co. used this technology for all of Japan's production. Carbohydrate fermentation technology is used by CCA and the new entrants ADM and Cargill.

(1) Chemical Synthesis. The chemical-synthesis routes produce only the racemic lactic acid. The commercial process is based on lactonitrile, which used to be a by-product from acrylonitrile synthesis. It involves base catalyzed addition of hydrogen cyanide to acetaldehyde to produce lactonitrile. This is a liquid-phase reaction and occurs at atmospheric pressures. The crude lactonitrile is then recovered and purified by distillation and is hydrolyzed to lactic acid by using either concentrated hydrochloric or sulfuric acid, producing the corresponding ammonium salt as a by-product. This crude lactic acid is esterified with methanol, producing methyl lactate, which is recovered and purified by distillation and hydrolyzed by water under acid catalysts to produce lactic acid, which is further concentrated, purified, and shipped under different product classifications. The raw materials and processing costs do not lend support to this chemical synthesis approach for large-scale, low-cost manufacturing in the future.

(2) Carbohydrate Fermentation. The fermentation technology can make a desired stereoisomer of lactic acid. The existing commercial production processes use homolactic organisms, such as *Lactobacillus delbrueckii*, *L. bulgaricus*, *L. leichmanii*. A wide variety of carbohydrate sources can be used (molasses, corn syrup, whey, dextrose, cane, or beet sugar). The use of a specific carbohydrate feedstock depends on its price, availability, and purity. Proteinaceous and other complex nutrients required by the organisms are provided by corn steep liquor, yeast extract, and soy hydrolysate, for example. Excess calcium carbonate is added to the fermenters to neutralize the acid produced and produce a calcium salt of the acid in the broth. The fermentation is conducted as a batch process, requiring 4 to 6 days to complete. Lactate yields of approximately 90% (w/w) from a dextrose equivalent of carbohydrate are obtained. Keeping the calcium lactate in solution is desirable so that it can be easily separated from the cell biomass and other insolubles, and this limits the concentration of carbohydrates that can be fed in the fermentation and the concentration of lactate in the fermentation broth, which is usually around 10% (w/v). The broth containing calcium lactate is filtered to remove cells, carbon treated, evaporated, and acidified with sulfuric acid to convert the salt into lactic acid and insoluble calcium sulfate, which is removed by filtration. The filtrate is further purified by carbon columns and ion exchange and evaporated to produce technical and food-grade lactic acid, but not a heat-stable product, which is required for the stearoyl lactylates, polymers, and other value-added applications. The technical-grade lactic acid can be esterified with methanol or ethanol, and the ester is recovered by

distillation, hydrolyzed by water, evaporated, and the alcohol is recycled. This separation process produces a highly pure product, which, like the synthetic product, is water white and heat stable.

Some of the major economic hurdles and process cost centers of this conventional carbohydrate fermentation process are in the complex separation steps that are needed to recover and purify the product from the crude fermentation broths. Furthermore, approximately one ton of gypsum by-product is produced and needs to be disposed of for every ton of lactic acid produced by the conventional fermentation and recovery process. These factors had made large-scale production by this conventional route economically and environmentally unattractive.

POTENTIAL PRODUCTS AND MARKETS

The future growth opportunities for lactic acid are in its use as a feedstock for potentially large-volume applications. These applications can be classified into four categories - biodegradable polymers, oxygenated chemicals, "Green" chemicals/solvents, and specialty derivatives. The overall size of this opportunity, both in terms of mass/volume and product sales value, is substantial. For the U.S. markets, this could be approximately 5.5-7.5 billion lb/yr (2.5-3.4 million tons/yr), with sales volume between approximately \$3.1-4.4 billion/yr. The volume and selling price projections for the new products are made on the basis of several published studies. It should be noted that the high volumes can be reached only when the prices are within the acceptable ranges and vice versa. The projections of these possibilities are by no means comprehensive nor would all these products (particularly the oxychemicals) be derived from lactic acid in the near future. It should be noted, however, that recently large U.S. companies either alone or in joint ventures have been involved in product and process development with lactic acid, with some of these opportunities as targets.

RECENT TECHNOLOGICAL ADVANCES

Technological advances in the major process components - fermentation, primary purification, and secondary purification and polymerization/chemical conversion of lactic acid and its derivatives - have recently occurred. These and other advances would enable low-cost, large-volume, and environmentally sound production of lactic acid and its derivative products.

In fermentation, high (>90%) yield from carbohydrate, such as starch, is feasible, together with high product concentration (90 g/L, 1 M). Stable strains with good productivity (>2 g/L h) that utilize low-cost nutrients (such as corn steep liquor) are available. Furthermore, the fermentation is anaerobic and thus has low power and cooling needs. All of these make the fermentation step very facile and inexpensive.

Recent advances in membrane-based separation and purification technologies, particularly in micro and ultrafiltration and electrodialysis, have led to the inception of new processes for lactic acid production. These processes would, when developed and commercialized, lead to low-cost production of lactic acid, with a reduction of nutrient needs and without creating the problem of by-product gypsum. In recently issued patents, an efficient and potentially economical process for lactic acid production and purification is described. By using an osmotolerant strain of lactic acid bacteria and a configuration of desalting electrodialysis, water-splitting electrodialysis, and ion-exchange purification steps, a concentrated lactic acid product containing less than 0.1% of proteinaceous impurities could be produced from a carbohydrate fermentation. The electric power requirement for the electrodialysis steps was approximately 0.5 kWh/lb (~1 kWh/kg) lactic acid. Such a process can be operated in a continuous manner, can be scaled up for large-volume production, and forms the basis for several commercial development projects. Another recent entrant, Ecochem, a DuPont-ConAgra partnership, has tried to develop a recovery and purification process that produces a by-product ammonium salt instead of insoluble gypsum cake and intends to sell this as a low-cost fertilizer.

The utilization of the purified lactic acid to produce polymers and other chemical intermediates requires the development of secondary purification and integration of catalytic chemical conversion process steps with the lactic acid production processes. Examples of such process steps would be dilactide production for polymerization to make high-molecular-weight polymers or copolymers and hydrogenolysis to make propylene glycol - a large-volume intermediate chemical. In the past, very little effort was devoted to develop efficient and potentially economical processes for such integrations, because only small-volume, high-margin specialty polymers for biomedical applications or specialty chemicals were the target products.

Recently, several advances in catalysts and process improvements have occurred and proprietary technologies have been developed that may enable the commercialization of integrated processes for large-scale production in the future. Recent patents have been issued to Cargill, DuPont, and Chronopol, which has consolidated the DuPont technology with its own technology portfolio. Both Cargill and DuPont have very active projects for commercial development and deployment of biodegradable polymeric products from lactic acid.

Hydrogenolysis reaction technology to produce alcohol from organic acids or esters has also advanced recently - new catalysts and processes yield high selectivity and rates and operate at moderate pressures. This technology has been commercialized to produce 1,4 butanediol, tetrahydrofuran, and other four-carbon chemical intermediates from maleic anhydride. In the future, such technologies could be integrated with low-cost processes for the

production of lactic acid to make propylene glycol and other intermediate chemicals.

The opportunities for commercialization of lactic acid based products and processes are very bright for those organizations that target the right products, including the non-polymeric products, and, select and deploy the right process technologies.

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