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Title: Bio- and Photodegradable Copolymers Derived from Low-Cost Feedstocks

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Introduction

Agricultural and industrial waste streams have become an economic burden as well as a serious environmental problem. In the United States, billions of pounds of cheese-whey permeate and approximately 10 billion pounds of potatoes processed each year are typically discarded or sold as cattle feed at $3-6/ton, sometimes requiring expensive transportation. As a potential solution to this economic and environmental problem, Argonne National Laboratory is developing technology that:

- Bioconverts existing food-processing waste streams into lactic acid, and
- Uses lactic acid to make environmentally safe, degradable plastics.

An Argonne process for bioconverting high-carbohydrate food wastes into lactic acid will not only help to solve a waste problem for the food industry, but also will save energy and is economically attractive.

Interest in bio- and photodegradable plastics is rapidly expanding. Major environmental concerns such as litter, waste materials on beaches and in the ocean, and burgeoning landfills are directly affected by plastics that can remain for hundreds of years. Stimulated by public demand, strong legislative action in state legislatures and the U.S. Congress is forcing industry to explore the development and use of degradable and recyclable plastics. These plastics should degrade to innocuous compounds, have suitable physical and mechanical properties, and be cost effective. Few, if any, of the degradable plastics currently available, including plastics containing starch, meet these criteria. However, polymers and copolymers with excellent mechanical properties and degradability characteristics can be made from lactic acid. The availability of a low-cost feedstock (i.e., starch and lactose from potato waste streams and cheese-whey permeate, respectively) and cost-effective bioconversion and recovery processes should greatly stimulate the development of lactic acid as a commodity compound and its use in making bio- and/or photodegradable plastics.

Prototype System

Although the initial substrate for Argonne's process development is potato waste, the process will be applied to convert other food wastes to lactic acid and other products. Proprietary technology for bioconverting more than 90% of the starch in potato wastes to glucose has been developed (Fig. 1), and the process involves a substantial reduction in processing time (less than 10 hrs vs. more than 100 hrs) over conventional technology. Therefore, the entire process of converting a batch of potato wastes into glucose can be completed in one day. The dextrose and other products of starch hydrolysis are subsequently fermented by bacteria that produce lactic acid (Fig. 2). The lactic acid will be continuously recovered, concentrated, and then further purified into a polymer-grade product. Although excellent plastics containing lactic acid have been made elsewhere, Argonne has designed and is constructing polymers and copolymers that will be environmentally safe and have improved use characteristics, i.e., both bio- and photodegradability.

The bioconversion of food wastes into higher-priced products of broader utility is very promising. For example, two (solid potato waste and primary peel effluent) of the three major wastes from french-fry production are highly enriched with carbohydrates, quite clean, and available in large volumes (more than 80,000 gal at 12% starch per day per large processing plant). Other foods that are 70-75% starch (dry weight), such as corn, sorghum, and wheat, also are sources of wastes that are excellent candidates for direct enzymatic or microbial conversions.

Argonne has determined that lactic acid has several major advantages over other products that could be made from such wastes:

- Accepted by Federal Drug Administration (FDA), biocompatible, non-allergenic,
- Made by fermentation of inexpensive feedstocks,
- Promising technology is being developed for its recovery that will likely result in major reductions in costs to make lactic acid,

- Many uses in industry including use as a major precursor for the expanding degradable plastics market,
- Excellent degradable plastics containing lactic acid are used for biomedical applications, and
- Plastics' mechanical, physical properties, and rates of degradation can be adjusted.

Research Focus

Several areas of research and development at Argonne are considered significant to the success of this project; these include:

1. Major improvements in liquefaction and saccharification protocols have been achieved to bioconvert starch in potato waste to glucose.
   - processing times have been reduced by 90% while still achieving high efficiencies (greater than 90%) of starch hydrolysis;
   - two steps of processing have been combined;
   - minimal pH adjustment is necessary; and
   - no microbial contamination is present in saccharified samples.
2. The use of high-performance strains of lactic acid-producing bacteria with enhanced thermophilic properties and increased tolerance to lactate. Various homofermentative strains are first screened for their ability to produce either the D- or L-isomer of lactic acid, followed by strain acclimation to growth at above 45°C and tolerance to 10-12% sodium lactate.
3. The development of cell-recycle bioreactors for continuous operation and minimal generation of waste streams.
4. The modification of membrane separation and liquid-liquid extraction systems for improved product recovery and low energy consumption. Electrodialysis and liquid-liquid extraction systems, as well as esterification, are being examined.
5. The design, construction, and testing of degradable plastics made from lactic acid including bio- and photodegradable plastics. Several monomers as

additives (less than 10%) to polylactate are being tested for the their ability to effect an increased sensitivity to water hydrolysis and/or photodegradation.

Market Opportunities

Although lactic acid has always had wide utility in industry as an acidulant, flavor ingredient, emulsifier, stabilizer, and antimicrobial agent, its real potential in making plastics is receiving increased attention. Public and legislative action has prompted a demand for degradable products such as grocery, trash, and composting bags; beverage o-rings; fast food packaging; agricultural mulch films; and diaper backings and has created a large potential need for many new plastic products. The superior properties of polymers and copolymers containing lactic acid and other FDA-approved monomers, such as glycolic acid, are well known. These properties include biocompatible/non-allergenic and varying degrees of degradability and mechanical strength. Their use as a replacement for petrochemicals in both photo- and biodegradable plastics could create the need for billions of pounds per year of new materials.

We believe there are several attractive end uses for degradable plastics. One area is sustained or programmable delivery systems for pesticides and fertilizers. Approximately 1 billion pounds of pesticides are used every year in the United States, but a high proportion is vastly underutilized and can often contaminate subsurface aquifers. A "time-released" pesticide eluting from a degradable plastic matrix could greatly improve the efficiency of pesticide use (less wasteful, more cost-effective) and minimize pollution of groundwaters. Other potential markets include mulch films (125,000,000 lb/yr), compost, and trash bags, requiring nearly 1 billion pounds of plastic for 1989 in the United States.

Funding

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Conventional		Argonne*
Corn Starch (from corn wet milling)	**Substrate**	Potato Starch (Solid Potato Waste)
Jet Cooking (105°C, 5–10 min)	**Gelatinization**	Combined Processing Step (20–30 min)
Liquefaction: α amylase (95–98°C, 90 min, pH 6)	**Enzyme Hydrolysis**	
<u>Saccharification</u>: glucoamylase (60°C, 100–120 hrs, pH 4.5)	**Enzyme Hydrolysis**	Enzyme Digest (4–8 hrs)
94–96% glucose	**Product**	> 90% glucose
Unknown	**Bacterial Contamination**	None

*proprietary

Figure 1

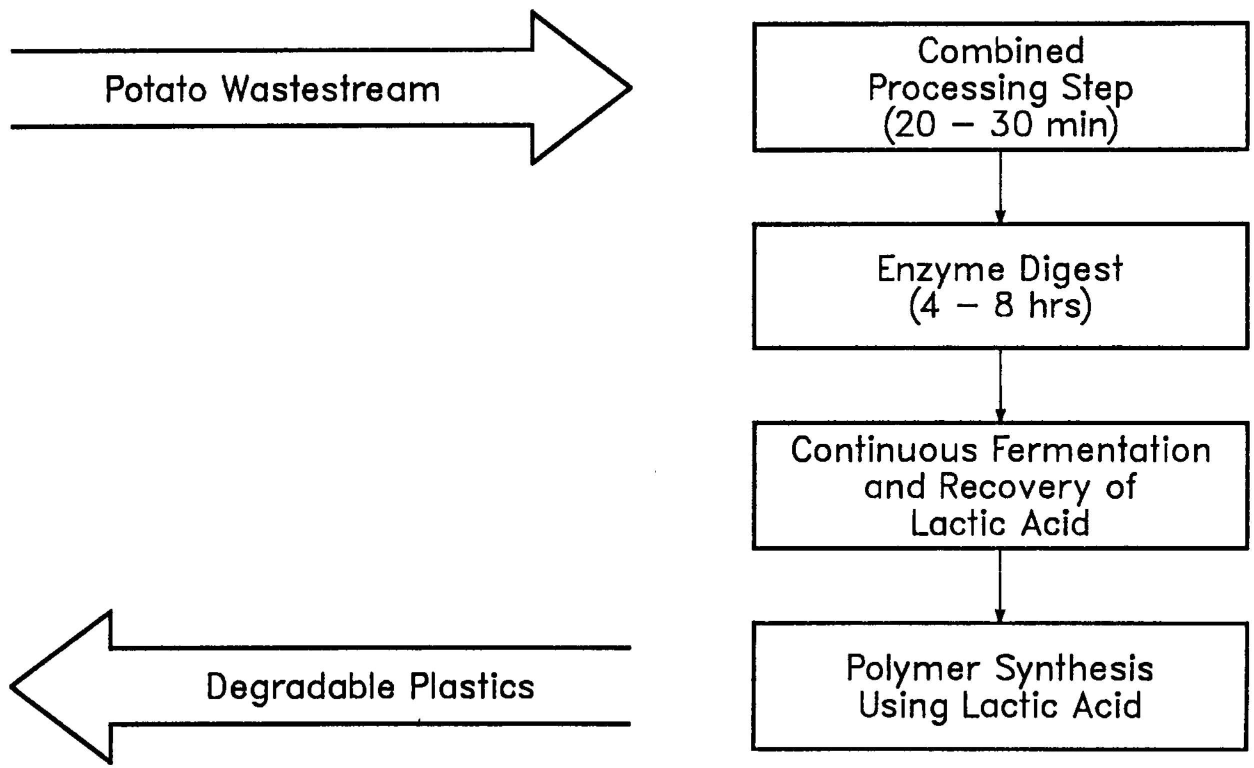
Potato Wastestream
Combined
Processing Step
(20 – 30 min)
Enzyme Digest
(4 – 8 hrs)
Continuous Fermentation
and Recovery of
Lactic Acid
Polymer Synthesis
Using Lactic Acid
Degradable Plastics

Figure 2