The Sustainability of NatureWorks™ Polylactide Polymers and Ingeo™ Polylactide Fibers\textsuperscript{a}: an Update of the Future

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Introduction

Cargill Dow LLC produces a new packaging and fiber material – polylactide (PLA) – from annually renewable resources. The presence of the company and the PLA polymer on the industrial scene signals the emergence of a new model for industrial development in the twenty-first century. During the nineteenth century people relied predominantly on a wide range of natural materials, such as wood, hides, wool and starch, to provide the essentials of then-modern life. This picture changed significantly during the twentieth century, when people in developed countries experiencing the industrial revolution became almost totally dependent on fossil materials to produce the fuels, polymers and chemicals required for modern life. With exponential growth in the demand for fossil raw materials in both developing and developed countries today, the question increasingly posed is how we will derive the materials we will need in the twenty-first century. An increasingly broad range of experts and analysts have concluded that new – or in some very important ways, “old” – raw materials will become the foundation of packaging materials and fibers in a world challenged by the interrelated problems of depletion of fossil resources and of proliferation of global climate changing emissions, pollutants and solid wastes. A consensus remains that fossil resources will be required and used for quite some time, but it is also hardly doubted that maintaining and enhancing quality of life for a growing population around the globe compels the development of new technologies to produce packaging materials and fibers from new “old” resources like traditional agricultural crops (e.g., corn, wheat, sugar beets) and other grown biomass materials.

It is in this new and renewed reality of renewable raw-materials reliance that Cargill Dow LLC emerges.

The objective of this paper is to answer the question: “What makes NatureWorks\textsuperscript{TM} PLA a more sustainable polymer?” To answer this question the article addresses applications and marketing of PLA, costs, today’s and future renewable raw material resources, reduction of fossil fuels and the associated emissions of green house gases, waste management options, and manufacturing processes.

About Cargill Dow

Cargill Dow LLC is leading the world in its effort to convert, through the application of new science and technology, annually renewable plant matter into a full range of useful products such as food packaging materials, films and fibers.

Cargill Dow LLC was founded in 1997 as a joint venture between Cargill Incorporated and The Dow Chemical Company. It is a new business dedicated to building a platform of sustainable polymers and chemicals with competitive performance and entirely made from annually renewable resources. The company’s efforts focus on using and optimizing a combination of agriculture (crop growing), biological processes (fermentation), and chemical technologies (polymerization). Cargill Dow has its headquarters in Minneapolis, Minnesota, USA. It also operates offices in Naarden, The Netherlands, and Tokyo, Japan. Today Cargill Dow is a stand-alone organization employing more than 250 people worldwide. To date, more than US$750 million has been invested in the development of the technology, as well as in the construction and commissioning of the world’s first commercial scale production facility.
for a polymer with broad practical application derived entirely from annually renewable resources. Squarely based on a foundation of research and development spanning many years, Cargill Dow researchers are titled in hundreds of patents worldwide.

Cargill Dow has increased its manufacturing capacity for PLA polymer from 4000 to 140,000 metric tons per year with the completion of its Blair, Nebraska polylactide manufacturing facility. This facility began operating in November 2001, was producing prime material by the end of December 2001 and had gone through a complete product production cycle by February 2002. The associated lactic acid facility, with a capacity of 180,000 metric tons, is located adjacent to the polymer facility and was started up in October 2002. Both plants are situated near a corn wet mill where the starchy component of corn kernels is converted into dextrose that Cargill Dow uses as a raw material for its lactic acid fermentation process. All these facilities are situated at one industrial “park” on the eastern edge of the state of Nebraska, one of the largest U.S. producers of corn. The proximate location of the facilities and the production of corn make it possible to build a very efficient integrated production operation.

**NatureWorks™ Polylactide Production Process**

Cargill Dow’s PLA is a versatile new compostable polymer that is made from 100% annually renewable resources. Today, the PLA life cycle starts with corn. The various steps in the production process, beginning with corn production and culminating in the production of PLA, are illustrated in Figure 1.

The basic building blocks for the PLA polymer chain are carbon dioxide and water. Both components are formed into sugars through photosynthesis driven by solar energy and occurring inside growing plants. Hundreds of years of hybridization and crop improvement have yielded modern varieties of corn that result in some 30% of the plant mass developing as sugars stored as starch in the kernels of the cob. After harvest, the corn is transported to a corn wet mill where the starch is separated from the other components of the corn kernel (proteins, fats, fibers, sugars and water) and converted via enzymatic hydrolysis into dextrose. Cargill Dow ferments dextrose into lactic acid at almost neutral pH. Via acidulation and a series of purification steps, the lactate salt fermentation broth is then purified to yield lactic acid.

Cargill Dow uses ring-opening polymerization through the lactide intermediate. In the first step of the process, water is removed under mild conditions (and without the use of a solvent) to produce a low-molecular-weight prepolymer. This prepolymer is then catalytically depolymerized to form a cyclic intermediate dimer, referred to as lactide, which is then purified to polymer grade using distillation. The purified lactide is polymerized in a solvent-free ring-opening polymerization and processed into PLA pellets. By controlling the purity of the lactide it is possible to produce a wide range of molecular weights. Because there are four unique groups attached to the central carbon atom, lactic acid is a chiral molecule. Chiral molecules exist as ‘mirror images’ or stereoisomers. The optically active lactic acid has both left-handed (“L” or “S”) and right-handed (“D” or “R”) stereoisomers. Chemically synthesized lactic acid gives the racemic mixture (50% D and 50% L). Fermentation-derived lactic acid typically consists of 99.5% of the L-isomer and 0.5% of the D-isomer. Production of the cyclic lactide dimer results in three potential forms: the D, D-lactide (called d-lactide), L, L-lactide (called L-Lactide) and L, D or D, L lactide called meso lactide. Meso lactide has different properties from D and L lactide. The D and L lactide are optically active, but the meso is not. Before polymerization, the lactide stream is split into a low D lactide stream and a high D/meso lactide stream. Ring-opening polymerization of the optically active types of lactide can yield a ‘family’ of polymers characterized by the molecular weight distribution and by the amount and the sequence of the D-lactide in the polymer backbone. Polymers with high L-lactide levels can be used to produce crystalline polymers while the higher D-lactide materials are more amorphous. More details about the PLA production process are given by Gruber[11] and Vink.[12]

**Today’s and Future Products from NatureWorks™ Polylactide**

**NatureWorks™ Packaging**

NatureWorks™ PLA is the foundation of a new, versatile, bulk polymer family and can be used in a wide range of applications. An overview of Cargill Dow’s business segment opportunities and examples of commercially available products is provided in Table 1.

Some specific final product examples merit further discussion, and are illustrated in Figure 2–4.

- Figure 2 shows a rigid thermoformed food container. These food containers have various valuable attributes.
They are made of renewable resources, have high stress crack resistance, exhibit high ductility (if hinges are applied), have high gloss and clarity, are easy to process, may require less material because down-gauging is possible due to PLA’s inherent higher stiffness, and are compostable. They are made of renewable resources, have high stress crack resistance, exhibit high ductility (if hinges are applied), have high gloss and clarity, are easy to process, may require less material because down-gauging is possible due to PLA’s inherent higher stiffness, and are compostable.

- Figure 3 shows cold drink cups. Together with the thermoformed food containers and disposable articles such as plates, forks, knives and spoons, these materials can be used during large events such as open festivals and sport events. After using PLA in food service, event organizers have only one organic waste stream to manage – via composting. The economic benefits of this model can be quite attractive, since the costs for composting are about half of incineration.

![Figure 3. "Disposable" cold drink cups.](image)

- Figure 4 depicts transparent bread bag windows made from PLA. Some typical valuable attributes of this application include the low barrier for moisture – so the warm bread can be put in the bag and the moisture leaves through the film and high gloss and clarity – so customers can view the product. Again, the product is made of renewable resources and can be composted at the end of its useful life.

**Latest Developments Concerning NatureWorks™ PLA Packaging**

NatureWorks PLA represents a real breakthrough, and a significant step towards more sustainable packaging applications. PLA exhibits a balance of performance properties

![Figure 2. Rigid thermoforms suitable for food and nonfood packaging materials.](image)

![Figure 4. Window in bread bag.](image)

**Table 1. Business segments for products based on NatureWorks™ PLA.**

<table>
<thead>
<tr>
<th>Business segment</th>
<th>Commercially available applications</th>
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<tbody>
<tr>
<td>Rigid thermoforms</td>
<td>- Clear fresh fruit and vegetable clamshells</td>
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<tr>
<td></td>
<td>- Deli meat trays</td>
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<tr>
<td></td>
<td>- Opaque dairy (yogurt) containers</td>
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<tr>
<td></td>
<td>- Bakery, fresh herb and candy containers</td>
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<tr>
<td></td>
<td>- Consumer displays &amp; electronics packaging</td>
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<tr>
<td></td>
<td>- Disposable articles and cold drink cups</td>
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<tr>
<td>Biaxially-oriented</td>
<td>- Candy twist and flow wrap</td>
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<tr>
<td>films</td>
<td>- Envelope and display carton windows</td>
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<tr>
<td></td>
<td>- Lamination film</td>
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<tr>
<td></td>
<td>- Product (gift basket) overwrap</td>
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<tr>
<td></td>
<td>- Lidding stock</td>
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<tr>
<td></td>
<td>- Die cut labels</td>
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<tr>
<td></td>
<td>- Floral wrap</td>
</tr>
<tr>
<td></td>
<td>- Tapes</td>
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<tr>
<td></td>
<td>- Shrink sleeves</td>
</tr>
<tr>
<td></td>
<td>- Stand-up pouches</td>
</tr>
<tr>
<td></td>
<td>- Cake mix, cereal and bread bags</td>
</tr>
<tr>
<td>Bottles</td>
<td>- Short shelf-life milk</td>
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<tr>
<td></td>
<td>- Edible oils</td>
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<tr>
<td></td>
<td>- Bottled water</td>
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![Figure 2. Rigid thermoforms suitable for food and nonfood packaging materials.](image)
that are comparable to those of traditional thermoplastics. PLA can be fabricated in a variety of familiar processes and brings a new combination of attributes to packaging, including stiffness, clarity, deadfold and twist retention, low-temperature heat sealability, as well as an interesting combination of barrier properties including flavor, aroma and grease resistance. These combined attributes of this new thermoplastic make PLA a performance polymer that is environmentally and economically appealing.

NatureWorks PLA is more than just a new thermoplastic for packaging. Cargill Dow’s marketing staff has also demonstrated, working with customers championing the use of PLA, a new category of competitive benefit. With well-structured marketing support, NatureWorks PLA packaging can transform packaging from a commodity cost item to a differentiable marketing feature at the point of sale. Using NatureWorks PLA for packaging offers a unique opportunity for retailers and brand owners to demonstrate their commitment to protection of the environment and to the commercialization of more sustainable packaging from annually renewable resources. Extensive research and real-world application has demonstrated that when retailers communicate these concepts and commitments to their customers, a positive connection between the customer, the product and the retailer is established.

NatureWorks PLA packaging offers product differentiation for the retailer or brand owner. It gives consumers the opportunity to “do the right thing.” Consumers value that opportunity and are willing to pay more for it. Consumers like the option of purchasing naturally fresh foods in “natural” packaging, for example, and NatureWorks PLA has been demonstrated to create and support customer perceptions of product freshness and safety. The result for the retailer or brand owner is reinforcement of their own brand and increased consumer loyalty. More importantly, experience shows that product differentiation with NatureWorks PLA packaging will drive sales.

A consumer study[3] was conducted this year in the US and Europe by Grapentine Company, a leading market research firm for major consumer product companies. The study use conjoint analysis techniques with more than 3,000 retail food store customers in the US and Europe. The study tested the product position statement “Use new packaging material for bakery, produce, and deli items. This new packaging, called NatureWorks, is made 100% from corn, the food contained in this packaging is fresh and safe for my family, and the packaging can be composted.”

A substantial segment consisting of a majority of respondents (59%) find the NatureWorks concept very desirable. Of that majority, customers expressed a willingness to pay more for the concept, though this willingness was inversely proportional to price. Specifically, it was found that one third of the surveyed consumers would be willing to pay $0.20 more per package of food and 40% would be likely to pay $0.10 more per package.

Two case studies actually support a conclusion that there exists a real market opportunity in packaging-differentiated fresh foods. The first is Finiper in Italy, a major food retailer, who launched a fresh pasta product line using NatureWorks PLA packaging in 2002.[3] Finiper educated their employees and consumers that they were offering fresh products in natural packages from annually renewable resources. Early success in in-store trials led to the expansion of the NatureWorks packaging concept to other fresh products and to twenty-one additional Finiper stores in Italy.

A second case study is underway with Wild Oats Markets, a specialty retail food chain with stores located primarily in the western United States.[3] In 2003, Wild Oats launched in eleven locations in the Pacific northwest region of the U.S. Results were impressive. Employees found that customer interest in NatureWorks packaging created an interactive teaching and discussion opportunity, thus building brand loyalty. Wild Oats also introduced a collection “green” bin so customers could return their NatureWorks packaging for organic recycling. Wild Oats committed to ensure that the returns were composted at a local facility and then began offering bags of compost for sale at their stores. This strategic merchandising program demonstrated to their customers the “closed loop” product cycle achievable with NatureWorks packaging. Wild Oats found that the program increased sales and attracted new customers. Not surprisingly and ahead of schedule, Wild Oats announced in October 2003 that it would incorporate NatureWorks™ packaging at all of its 77 Wild Oats stores.

NatureWorks packaging creates impact at the point of sale by making packaging a meaningful aspect of a food product purchase. As the case studies show, NatureWorks packaging will positively impact sales by improving consumer perception of the food products packaged in it. NatureWorks packaging has been found suitable for food packaging in every country where NatureWorks PLA is sold.

Other Applications of NatureWorks™ PLA

In addition to traditional food packaging applications, several leading companies are exploring an exciting array of non-food packaging applications for PLA, including:[4]

- Sony Walkman body (Figure 5)
- Mitsui-Chemical telephone cards
- Sanyo compact disc
- Matsushita (Panasonic) battery packaging (Figure 6)
- Fujitsu PC body components.

These new products demonstrate the versatile character of PLA polymers. The sustainability “strength” of NatureWorks PLA is that it combines valuable emotional, performance and environmental attributes with a competitive price. A summary of these valuable attributes is given in Figure 7.
Ingeo™ fibers are the world’s first man-made (synthetic) fibers made from 100% annually renewable resources and were publicly launched by Cargill Dow in early 2003 in New York, New York. An overview of Cargill Dow’s fiber platforms and examples of commercially available products is provided in Table 2.

Figure 8–10 show three applications of Ingeo™ fibers made from PLA. These are pillows, mattresses and duvets; apparel; and floor, wall, and furniture textiles. Ingeo fibers combine the qualities of natural and synthetic fibers in a new way. Strength and resilience are balanced with comfort, softness and drape in textiles. In addition, Ingeo fiber is naturally flame retardant and has good moisture management characteristics. This means that Ingeo is ideally suited to fabrics from fashion to furnishings. In fiberfill, for products such as pillows, duvets and comforters, Ingeo fibers’ superior loft means that they feel more like down than conventional synthetics. In nonwovens, a new family of

Table 2. Fiber Platforms for products based on Ingeo™ fibers.

<table>
<thead>
<tr>
<th>Business segment</th>
<th>Commercially available applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Apparel</td>
<td>Casual (sports-), active- and underwear and fashion</td>
</tr>
<tr>
<td>Non-wovens</td>
<td>Wipes, hygiene products, diapers, shoe liners, automotive head and door liners and paper reinforcement</td>
</tr>
<tr>
<td>Furnishings</td>
<td>Blankets and panel, upholstery and decorative fabrics</td>
</tr>
<tr>
<td>Industrial</td>
<td>Agricultural and geo textiles</td>
</tr>
<tr>
<td>Carpet</td>
<td>Residential/institutional broadloom and carpet tiles</td>
</tr>
<tr>
<td>Fiberfill</td>
<td>Pillows, comforters, mattresses, duvets and furniture</td>
</tr>
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compostable products can be produced. Finally, Ingeo fiber stain resistance properties make it an ideal carpet fiber for home, office, and transportation applications.

The sustainability “strength” of Ingeo™ fiber is that it combines valuable emotional, performance, and environmental attributes with a competitive price. A summary of these valuable attributes appears in Figure 11.

Other Materials from Lactic Acid

As explained above, lactic acid can be used to produce the versatile polymer polylactide. Other products, such as chiral synthons and a range of lactate ester solvents may also be produced. One of these solvents, ethyl lactate, is a high-purity solvent used in the microelectronics industry and is already commercially available. As the production costs of lactic acid are further reduced, basic chemical building blocks such as propylene glycol, propylene oxide and acrylic acid can be produced. This means that one day traditional polymers might also be made from renewable resources. The many potential pathways for intermediate product development are illustrated in Figure 12.

Cargill Dow and the Pursuit of Sustainability

The pace of human demand for resources is growing due to increased population and increasing average wealth per capita. In many ways, this increase in demand now outpaces
The ability of Earth’s natural systems to replenish and restore natural resources. It is becoming increasingly clear that these trends are not sustainable. That is, they cannot continue unabated without risking severe consequences in terms of human and ecosystem health and welfare. The concept of sustainable development was first articulated as an approach to allow improvements in both human welfare and natural health, both today and in the future.

Cargill Dow seeks to be sustainable in its processes and activities, and to sell products that contribute to sustainability wherever they are used. Cargill Dow’s commitment to sustainability is reflected in its statement of business philosophy: “Cargill Dow is the leader in producing plastics from renewable resources, and is dedicated to meeting the world’s needs today without compromising the Earth’s ability to meet the needs of tomorrow.” Cargill Dow’s focus on sustainability entails a commitment to meeting the simultaneous objectives embodied in the concept of the “triple bottom line.” This means that Cargill Dow continuously seeks improvements in economic, social and environmental sustainability through PLA production processes and product applications. Although full realization of this concept is challenging in practice, explaining it is relatively simple.

- **Economic sustainability** is about building and growing an economically successful business, and producing economic benefits up and down the value chain. Economic sustainability for Cargill Dow, therefore, entails supporting new markets for agricultural products, new career opportunities for researchers and staff, and other economic benefits to investors and society.

- **Environmental sustainability** is about making products that serve useful market and societal functions with less environmental impact than currently available alternatives. Moreover, environmental sustainability necessarily implies a commitment to continuous improvement in environmental performance. The key measurement tool for environmental sustainability is Life Cycle Assessment.

- **Social sustainability** is reflected in social responsibility, and involves concepts of equitable opportunity for all participants in the value chain as well as strong bias against business and operational practices that take unfair advantage of particular segments of society. From Cargill Dow’s perspective, social sustainability implies that business success must not disadvantage, for example, feedstock and materials suppliers.

The “best” performance traits and business practices simultaneously serve more than one triple bottom line objective. Optimal ones serve all three. For example, environmentally friendly production processes and compostability and recyclability of PLA products help ensure that production, use and ultimate disposal of products do not impose disproportionate burdens on any particular segment of society, while simultaneously increasing economic opportunities and reducing adverse environmental impacts.

### The “Ideal” Sustainable Material

We can project our vision of triple bottom line sustainability onto any and all aspects of society. New materials that seek to be more sustainable should:

- have an equivalent function to the material replaced. This means that the material must “meet the world’s needs today.” For example, if one wants to replace a PET bottle with a PLA bottle, the technical performance of the PLA bottle should be better or at least the same.

- be available at lower total cost and at a competitive price. More sustainable materials deliver additional value-added benefits, including reduced total societal cost. To succeed in the market place, these benefits must come at a competitive price to ultimate consumers. Competitive pricing also facilitates more comprehensive distribution of the material’s benefits.

- have a minimum environmental footprint for all processes involved, including those up- and down-stream.

- be made from renewable resources.
• be completely recyclable on carbon level or material level (also termed, chemical recycling and mechanical recycling).
• use only ingredients that are safe for both humans and the environment.
• not use or include any environmentally dangerous persistent substance or compound.
• not have any negative impact on food supply.
• not have any negative impact on water.

The next level of strategic development involves applying the ideal to the specific task at hand. With the principles for a sustainable “ideal” material in mind, Cargill Dow adopted a set of design rules to guide both development and commercialization of PLA. The objectives reflect both the ideals and the unique issues associated with PLA. Because of the major role that fossil-based packaging and fibers materials play in contributing to anthropogenic greenhouse emissions, a first priority for PLA is to accomplish a reduction in the use of fossil resources and their related air emissions (e.g., carbon dioxide, heavy metals, hydrocarbons, oxides of nitrogen, sulfur dioxide). Similarly, the ideal packaging and fiber material is produced of safe, natural raw materials, and importantly, does not compromise that fundamental nature. As mentioned above, reliance on environmentally friendly processes for manufacturing, conversion, and finishing contributes to triple bottom line performance. In the same fashion, avoiding chemicals that could adversely impact health, safety or the environment also supports progress toward sustainability. In manufacturing, the material must “drop into” existing polymer processes, so as to avoid expensive retooling. From a process perspective, ideal packaging and fibers materials should also fit into any existing waste management system, and, if possible, offer a benefit in final disposal.

Again, while it is relatively easy to paint a picture of sustainability, getting there involves a long and challenging journey. Success will require determination, feedback and correction, enlightened governance and public policy, and the concerted efforts of every member of the value chain.

Biomass Utilization and Biorefineries

Cargill Dow utilizes dextrose corn syrup as the key raw material for its PLA plant today, as described above. The dextrose is produced from the wet milling of corn grain. Other (food-crop) raw materials could be potatoes, cassava, sugar, rice or wheat. Dextrose syrup is an excellent feedstock for fermentation, available at a relatively low cost and efficiently manufactured. However, Cargill Dow has worldwide expansion plans for the manufacture of PLA, a goal to eliminate fossil energy use and greenhouse gas emissions from the PLA life cycle inventory (LCI), and a goal of reducing manufacturing costs in order to make PLA competitive with dominant incumbent commodity plastics.

Therefore, Cargill Dow has evaluated options for improvements throughout its manufacturing processes. Cargill Dow has found that the processing of plant materials such as agricultural residues (e.g., corn stover, cereal straws, sugar cane bagasse) offers an opportunity to reduce costs, reduce fossil energy use, reduce greenhouse gas emissions, and provide a worldwide non-food feedstock for PLA manufacture. Other advantages of using agricultural residues are a more efficient use of land, additional revenues for farmers and less dependence of fossil resources. These agricultural residues, along with trees and other plant material, are generally referred to as “biomass.” The processing of biomass for the production of materials, chemicals and fuels will likely occur in an industrial facility known as a biorefinery, reflecting both the source of the feedstocks and the nature of the multi-product conversion processes that will be undertaken at the facility. Modern grain processing facilities and pulp and paper mills are the best current examples of biorefineries. Cargill Dow expects to help pioneer a new type of biorefinery for the production of materials, chemicals and fuels displacing products produced from petroleum crude oil and natural gas.

The potential cost benefits of sugars from biorefinery processing of agricultural residues has been evaluated and reported by Wooley[6,7] and Aden.[8] These studies are supported by commercial engineering firm evaluations of key process designs and equipment as well as by research data. A few key variables and assumptions form the basis for the various costs reported. Depending on the realization of these key assumptions, mainly cellulase enzyme performance and efficiency of biomass conversion to sugar, the cost of sugar is expected to range from four to eight U.S. cents per pound of sugar. Cargill Dow expects to achieve costs in the low end of the range.

One important cost assumption is the cost of cellulase enzyme required for the hydrolysis of cellulose to glucose. Recognizing this critical need, the U.S. Department of Energy commissioned a study by Hettenhaus[9] in late 1996 to determine the likely cost of cellulase enzymes and the course of action to make them commercially available for use in biorefineries. The results of the study suggested that utilizing biotechnology tools emerging at the time would allow a ten-fold cost reduction for cellulase enzymes to be achieved. Competitive solicitations resulted in the award of contracts to develop low-cost cellulase enzymes to Genencor and Novozymes in 2001. The contracts were for a period of three years and approximately $15 million each was provided to both companies over the study period (there is a 20% cost share requirement from the companies counted in that total). The fruits of this research are expected to help Cargill Dow and others achieve biorefinery commercialization.

Several studies[10,11] on ethanol production from biomass and other sources show the impact of biomass processing on the LCI for PLA relating to fossil energy use and
greenhouse gas emissions. Although the references generally report on ethanol production, translation back to the sugars is a relatively easy calculation. Cargill Dow has used U.S. National Renewable Energy Laboratory (NREL) design data in its evaluations. Figure 13 and 14 summarize the positive impact on PLA fossil energy use and greenhouse gas emissions expected from the use of biomass sugars. The details about PLA1 and PLA B/WP are described by Vink et al.\(^\text{[2]}\) Biomass processing is shown to be a key part of achieving the goal of net zero fossil energy use and net zero greenhouse gas emissions for the manufacture of PLA products.

The sustainability advantage lies in the phase out of non-renewable energy (fossil and nuclear), the use of renewable resources and the innovative processes. The significant reduction (86%) is due to the combined benefits of the utilization of biomass (corn stover as a feedstock), the use of an optimized fermentation process, and the use of wind power for electric energy. The contribution of each of these measures is described by Vink et al.\(^\text{[2]}\) A further reduction to eliminate the impacts of residual greenhouse gas and fossil fuel emissions can be achieved by offsetting these emissions with green energy certificates, as discussed below.

Cargill Dow is pursuing the conversion of agricultural residues and other biomass materials utilizing an enzymatic hydrolysis process. In order to achieve the fermentation of the resulting mixed sugars Cargill Dow is developing a biocatalyst to convert biomass sugars to lactic acid. Cargill Dow has partnered with the U.S. Department of Energy through a competitive solicitation process. Through several successful proposals, Cargill Dow has been awarded more than US$25 million to develop the required technology. The technology is expected to be ready to support the design of a commercial biorefinery by 2007.

A simplified schematic diagram for the current PLA production process (hereinafter referred to as “PLA1”) and the future one incorporating process improvements, biomass feedstocks and wind energy (referred to as “PLA B/ WP”) is provided in Figure 15.

The left-hand portion (PLA1) of Figure 15 illustrates the various steps involved in the production of PLA starting with corn growing and ending with the production of PLA granules (explained above). The right-hand portion of the Figure depicts the production process that Cargill Dow plans to use in the future. As a complement or replacement to the use of fermentable sugars from starch, Cargill Dow is working, as described above, to develop technology to produce lactic acid from corn “biomass” or stover – stalks and leaves and other material from the corn plant. In addition, this diagram contemplates the replacement of fossil and nuclear electricity currently used at the facility with wind energy. This next-generation PLA facility objective for Cargill Dow is labeled “PLA B/WP.” The ‘B’ stands for biomass and the ‘WP’ for wind power.

The facility and process will actually differ from PLA1 in five key ways:

- Instead of corn-derived dextrose, the primary feedstock is crop residue (stems, straw, husks, and leaves) from corn or, potentially, other crops;
- The cellulose and hemicellulose will be converted into fermentation sugars in a so-called biorefinery. The remaining lignin-rich fraction will be combusted or gasified to produce steam which will in turn provide thermal energy for the various conversion processes;
- The lactic acid production process will be adapted to ferment the biomass (corn residue) sugars and further optimized to increase yield and reduce raw material use among other improvements;
- Instead of electricity from the Nebraska grid, the additional required electricity inputs will be derived from wind power; and
- Further optimization of the energy efficiency of the lactide and polymer facilities.

All these improvements and changes will lead to lower fossil fuel and raw material use as well as lower air emissions, water emissions and solid waste production.

The biorefinery concept is still under development and therefore the process configuration and resultant calculations will change to some extent as the process is developed and optimized. Alternative uses for the lignin fraction will also be examined, including use as a feed supplement, roadway material additive, and others.\(^\text{[12]}\)
Figure 16 provides an overview of potential products coming from a biorefinery fed with corn residue. One of the secondary products is lactic acid. Potential products of lactic acid are given in Figure 12.

**PLA LCI Impacts of Wind Power RECs to Offset Net (Residual) GHG Emissions**

The life cycle inventory (LCI) for NatureWorks™ polylactide shows very clearly that even though the product is made from annually renewable resources there is still a significant use of fossil fuels and an associated net release of greenhouse gases (Figure 13 and 14). Closer inspection of the LCI reveals that the majority of this fossil fuel use and greenhouse gases (GHG) release is associated with the production of process energy, either from the production of steam or from the production of electricity. This process energy is used in dextrose production, lactic acid production, and in polymer production. It includes the energy needed to run pumps, evaporators, distillation columns, and other process equipment.
improvements are a direct method of reducing process energy associated emissions. Throughout process industries it has become a truism that negawatts (energy savings gained by installing energy efficiency measures) are generally the best first tool for reducing emissions. That is, reducing consumption of energy is the first step in making a more sustainable product. Efficiency improvements have the multiple benefits of reducing demand on strained infrastructure, reducing emissions, and generally reducing costs. However, even when all of the technically and/or economically achievable energy conservation projects have been implemented there will be a need for power to run the process.

The next step in the mission to continuously improve the PLA LCI is to find a ‘green’ source of energy. Cargill Dow LLC joined in the formation of the Green Power Market Development Group (GPMDG), in May 2000. The GPMDG is a collaboration of twelve companies with the World Resources Institute, and is dedicated to building corporate markets for green power. The group goal is to develop corporate markets for 1,000 MW of new, cost competitive green power by 2010. GPMDG’s website[13] offers background information on various technologies and a collection of tools and publications developed by the group to help others in their search for cost effective green power solutions. As of September 2003, the group had achieved an aggregate of 112 MW toward their goal, including very significant programs in landfill gas-derived energy, fuel cells, wind energy, and the use of renewable energy certificates (RECs), described below.

After evaluating various technologies, Cargill Dow determined that electricity derived from wind and steam derived from biomass fuel are the most attractive sources of green energy for our facilities. The biomass work has been described above, and is part of a long-term, next-generation process for PLA production. The wind energy is more readily available now and is being pursued in two ways as described below.

Cargill Dow’s plant is located in Blair, Nebraska, in the mid-central portion of the United States. The greater Midwest region contains significant amounts of high quality wind resources and is currently seeing the development of several new wind farms, especially in Minnesota and Iowa. At this time, Nebraska has not had significant development of its wind resource for the production of electricity, and Cargill Dow is unable to directly purchase wind energy for its facility there. We continue to work toward a future where that will be possible. In the meantime, renewable energy certificates (RECs) allow us to encourage the development of renewable energy and to offset the emissions associated with the production of the electricity we use.

As described in the World Resource Institute “Corporate Guide to Green Power Markets, Installment 5”:[14] RECs are a renewable energy product that companies can purchase to reduce the environmental impact of their business activities. A REC represents the environmental attributes -for example, avoided CO₂ emissions – that are created when electricity is generated using renewable resources instead of using fossil fuel sources such as coal, oil, and natural gas. RECs can be sold separately from their associated electricity and thus enable customers to purchase the environmental attributes of renewable power generation independently of their retail power supply. Purchasing RECs, therefore, can be an effective means for a company to “green” the electricity it consumes.

A significant benefit of the RECs is that the company can shop among various providers and various renewable power options, such as selecting RECs derived from wind-generated electricity. As of October 2003, Cargill Dow has committed to using RECs from wind energy to offset 100% of the electricity used in our corporate headquarters building in Minnetonka, Minnesota.

As mentioned above, Cargill Dow is exploring the option to buy RECs to offset the net or residual GHG emissions associated with PLA production. “Net” or “residual” emissions are carbon dioxide-equivalent greenhouse gas emissions calculated as total emissions from the cradle to the factory gate minus carbon dioxide uptake that occurs during corn production. Preliminary analysis suggests that the use of wind power RECs to offset GHG emissions also yields other significant emissions offsets benefits. Results of this preliminary analysis are summarized in Figure 17. The calculation procedure is explained in Footnote.³

Note that carbon-equivalent greenhouse gas emissions are derived from CO₂, N₂O, and CH₄ emissions. As a result, the table shows use of RECs sufficient to offset 141% of CO₂ emissions in order achieve CO₂-equivalent neutrality.

³ Calculation procedure for estimated effects on LCI due to offsetting the net cradle to factory gate GHG emissions of PLA1 production with renewable energy certificates (RECs). According to Vink[2] and corrected with the latest available corn growing data, the net PLA1 cradle-to-pellet carbon dioxide equivalent GHG emissions are 1,642 MT CO₂ eq./MT PLA. In order to offset these emissions equivalents, it is assumed that RECs are derived from 100% wind energy. This avoids (offsets) all the fossil-fuel consumption-related emissions as well as emissions attributed in another way to the manufacture of PLA. As a result, in addition to the offsetting the carbon-equivalent GHG emissions, other non-GHG emissions are also reduced in the PLA1 LCI. The first step in the calculation involved determining total electricity use reflected in the GHG emissions of 1,642 MT CO₂. Electricity production data of the local electricity provider (OPPD – Omaha Public Power District) was used as a reference. According to data obtained from the OPPD (the electricity service provider for the Blair facility) about 240,766 mg CO₂ is emitted per MJ electricity produced. This equals 0.867 MT CO₂/MWhr. In order to offset the 1,642 MT CO₂ eq. emissions associated with PLA, then, 1.642/0.867 = 1.894 MWhr of non-emitting electricity/MT PLA must be obtained.

Actual \( N_2O \) emissions are not offset – only the GHG equivalent impact of the \( N_2O \) emissions (these emissions are entirely associated with corn production).

### Future Price Trends on PLA

Cargill Dow plans for increasing price competitiveness against commodity polymers like PET. PLA prices will fall as a result of improvements in technology, economies of manufacturing scale, new technology developments, and amortization of capital investments. The rate of this decline in prices will therefore be dependent on the rate of growth in markets for PLA among other factors. PLA represents a superior value in polymers even today, and it is cost-competitive in a wide range of specialty applications.

### Waste Management Options

The most common waste management options for the fossil fuel based polymers are incineration, landfill and mechanical recycling. For PET, chemical recycling is also used in very limited applications. In addition to these traditional processing routes, PLA waste streams can also be processed using composting, chemical recycling and anaerobic digestion. These additional waste management options give rise to greater flexibility for waste stream managers – a more sustainable solution set from an environmental, economic and social perspective. The optimal choice for a specific waste management route depends on various parameters such as the local availability of infrastructure for collection and processing; the requirements laid down in national, state or local legislation; the composition of the waste stream; and public perceptions about waste management options. For example, convention and festival food packaging might best be disposed of with other organic wastes, like food scraps. Large volume wastes might best be targeted for chemical recycling.

### Composting

Composting is a method of waste disposal that allows organic materials to be recycled into a product that can be used as a valuable soil amendment. PLA undergoes a two-step degradation process. First, the moisture and heat in the compost pile attacks the PLA polymer chains and splits them apart, creating smaller polymer fragments, and finally, lactic acid. Microorganisms found in active compost piles consume the smaller polymer fragments and lactic acid as energy source. Since lactic acid is widely found in nature, a large number of naturally occurring organisms metabolize lactic acid. At a minimum, fungi and bacteria are involved in PLA degradation. The end result of the process is carbon dioxide, water and some humus. In summary, via composting the carbon dioxide, which has been harnessed during corn growing, flows back into the atmosphere and the short cycle carbon dioxide loop has been closed. The degradation process is temperature- and humidity-dependent. PLA is compostable at industrial composting facilities, but will not degrade sufficiently fast in residential composting piles since the minimum required conditions are typically not present.[1,15]

Regulatory guidelines and standards for composting revolve around four basic criteria: material characteristics, biodegradability, disintegration, and ecotoxicity. Descriptions of the requirements of these testing can be found in the appropriate geographical area: DIN 54900-1 (Germany), EN13432 (EU), ASTM D 6400 (ASTM) and GreenPla (Japan). After submitting the required testing data NatureWorks™ PLA received listing on Din Certco’s (German registration body), BPS’s (Biodegradable Plastics Society – Japan) and BPI’s (Biodegradable Products Institute – USA) positive lists for compostable materials.

### Chemical Recycling

The PLA polyester polymer is formed from reversible polycondensation reactions and can be depolymerized by hydrolysis. This equilibrium results in a recycling advantage for polyesters such as PLA. Manufacturing-waste, converter-waste, or post-consumer PLA materials can be recycled by chemical means to produce lactic acid monomer and oligomers. These materials can then be fed to the front end of a manufacturing process for making PLA, lactide, ethyl lactate, or other lactic derivatives. Depending on the quality of the recycled feedstock and the economics relative to fermentation-derived lactic acid, chemical recycling can be highly attractive.

The recycling can be carried out with water at a wide range of temperatures (100–250 °C). The reaction rate is enhanced by the addition of a catalyst. A typical catalyst would be a strong inorganic acid, such as nitric acid or sulfuric acid, as is common in the PET recycling industry. Reactor residence times for PLA hydrolysis are on the order of hours and depend on reactor temperature and catalyst...
level. Generally, reactor conditions are tailored for the desired molecular weight and \( \delta \)-lactic acid level of the product.

Reactor-engineering issues include interphase mass transfer, the mixing flow pattern in the reactor, heat distribution, and racemization rates relative to molecular-weight reduction. Where racemization rates need to be tightly controlled, batch or plug-flow configurations are preferred. However, if racemization of the lactic acid product is less important, then continuous stirred-tank reactors may be preferable due to lower cost. In any case, there will likely need to be clean-up operations after the hydrolysis unit, to purify the lactic acid. Examples include ion exchange and carbon columns to remove impurities that cause polymerization problems.

Chemical recycling should be considered in any waste-management scheme for PLA, since from a life-cycle perspective, it represents a relatively small amount of net chemistry compared to the CO\(_2\)-to-PLA cycles for incineration or composting. Simple hydrolysis can turn waste PLA back into fully functional lactic acid, at potentially low economic and environmental costs, contributing to the total sustainability of PLA production. There exist many ways to implement chemical recycling of PLA, and the choice ultimately depends on the process scale, product quality requirements, and overall capital and operating economics.

What Makes NatureWorks\textsuperscript{TM} PLA a More Sustainable Polymer?

First, it is important to remember that sustainability is not an endpoint, but a journey. Still, at Cargill Dow, we believe we are headed in the right direction toward sustainable products. A review of the features of PLA and Cargill Dow’s activities will help solidify understanding of the company’s commitment to sustainability.

1. NatureWorks\textsuperscript{TM} PLA is competitive from a performance point of view

A product is more sustainable only when it has an at least equivalent function as the products it is replacing. NatureWorks\textsuperscript{TM} PLA meets and often exceeds the requirements for a wide range of applications. From the list of applications shown and discussed in this paper it is clear that NatureWorks\textsuperscript{TM} polymers are becoming a real alternative from a performance point of view in many applications in food and non-food packaging, films and fibers. Cargill Dow believes this is just a start and that the future will bring more and exciting new applications.

2. NatureWorks\textsuperscript{TM} PLA is becoming available against competitive costs

For a long period of time the “biopolymers” were only available against relatively high prices, but the industry is also leaving its infancy phase from this perspective and prices are coming down. Of course it will take considerably more time to compete on price with the cheapest mature, traditional bulk polymers.

3. NatureWorks\textsuperscript{TM} PLA is made from annually renewable resources

The first generation of PLA will be produced from the annually renewable resource corn (or maize), the cheapest and most widely available starch-rich source in the USA. In other parts of the world, locally available crops such as rice, sugar beets, sugarcane, wheat or sweet potatoes can be used as starch/sugar feedstock. However, Cargill Dow will carefully evaluate the social impact of use of these human food sources prior to manufacturing PLA. Cargill Dow is also working to develop new conversion technologies to facilitate the use of lignocellulosic biomass feedstocks, such as corn stover (the residue left in the field), grasses, wheat and rice straws, and bagasse (the residue of sugar cane production). There are various drivers to move away from agricultural crops to agricultural waste streams, including cost, long-term supply availability, more efficient land use, and additional revenue opportunities for farmers.

4. NatureWorks\textsuperscript{TM} PLA reduces fossil fuel resource use

The conventional hydrocarbon polymers use limited reserves of oil and natural gas as their feedstock source. Fossil fuels take tens of millions of years to regenerate. In contrast, the monomer for NatureWorks\textsuperscript{TM} PLA is derived from annually renewable resources such as corn. Energy from the sun and carbon dioxide from the atmosphere are harnessed in agricultural crops. About one third of the energy required of PLA is derived from these renewable resources, resulting in PLA utilizing 25–55 percent less fossil fuel than other polymers derived directly from hydrocarbons. This percentage is valid for the “cradle to the factory gate” part of the polymers life cycle.

5. NatureWorks\textsuperscript{TM} PLA emits less carbon dioxide

Carbon dioxide is believed to be the most important contributor to global climate change. Because carbon dioxide is removed from the air when corn is grown, the use of NatureWorks\textsuperscript{TM} PLA has the potential to emit fewer green house gases compared to competitive hydrocarbon-based polymers.

6. NatureWorks\textsuperscript{TM} PLA fits into any waste management system with a benefit

At the end of their useful life, NatureWorks\textsuperscript{TM} PLA products can be disposed of by all traditional waste management methods such as incineration, landfill and mechanical recycling. In addition, PLA products can be composted in
industrial composting facilities, thereby providing an alternative means of managing municipal solid waste. Chemical recycling (recycling back to the monomer stage) and anaerobic digestion followed by a composting step are possible future routes. More options mean more flexibility in use of PLA compared to other materials. Materials management issues vary from community to community, and are influenced by issues such as local infrastructure, waste stream composition, public perceptions, and differences in economic situations. A material that adapts more easily to a wide range of local conditions is, by definition, more sustainable.

7. NatureWorks™ PLA is produced in environmentally friendly manufacturing processes

Sustainability is a journey. While we are not ready to declare victory, PLA is a good start along the road to sustainability in man-made packaging and fiber materials. Cargill Dow’s program to improve the manufacturing processes is described in the section ‘Biomass utilization and Biorefineries’.

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