Green Chemistry and Green Engineering:

An Essential Task for Chemists and Chemical Engineers

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Abstract

Chemists and chemical engineers design chemical products and chemical processes that serve the needs and wishes of society. Every decision in this design activity must be in accord with laws concerning health and the environmental. The purpose of these laws is to promote the principles of Green Chemistry and Green Engineering for producing products and designing processes that do no harm to human health or to the environment. To illustrate, we consider here some features of polylactic-acid production and the significant advantages of a "green" polymer relative to other polymers made from petroleum.

Introduction

The basic goal of a chemical process is to convert raw materials into a desired product. However, because it is almost always impossible to achieve 100 % conversion in any process, waste streams are also produced; the waste streams are often disposed in the environment (air, water and/or soil). Regrettably, animal and human populations are exposed to these waste streams that may be harmful to health or that may lead to environmental degradation.

Typical environmental issues include global warming, due to production of greenhouse-gas (CO_2, CH_4, N_2O) emissions; ozone depletion in the stratosphere, due to chlorofluorocarbons (CFCs); photochemical *smog* (a word derived from "smoke" and "fog"), due to emissions of volatile organic compounds (VOCs) and nitrogen oxides (NOx); incomplete combustion, emitting carbon monoxide and particulates; and emissions of lead to the atmosphere and to rivers and lakes. (Allen and Shonnard, 2002)

Legislation concerning environmental protection and human safety has become increasingly strict. Public awareness of the impact of the chemical industry on daily life has grown, reflected in increasing pressure from government and from non-governmental organizations (NGOs), such as churches, clubs and public-interest groups. (Clark, 2007)

Green Chemistry and Green Engineering provide a paradigm to overcome environmental degradation. Green Chemistry and Green Engineering concern the design and use of processes and products that are feasible and economic while (1) reducing generation of pollution at the source and (2) minimizing risk to human health and to the environment.

Although the history of Green Chemistry and Green Engineering is short (twenty years maximum), the literature is rich in pertinent textbooks, academic publications, and computer software. An early important reference for Green Engineering is the Environmental Protection Agency's (EPA's) Green Engineering website, http://www.epa.gov/oppt/greenengineering/index.html. For Green Chemistry, the corresponding reference is EPA's Green Chemistry website, http://www.epa.gov/gcc/.

When designing a new chemical process or a new chemical product, chemists and chemical engineers must take into consideration environmental-impact issues that may follow from toxicological properties of all pertinent components. These issues pertain, for example, to the design of boilers, reactors, separators, storage tanks, heat exchangers etc., and also to selection of alternative feedstocks and solvents. (Allen and Shonnard, 2002)

Case Study

To illustrate Green Chemistry and Green Engineering, the case study in the following section concerns the production of polylactic acid (PLA), a thermoplastic polymer obtained via bacterial fermentation. PLA can replace similar products that are often obtained from petroleum-based processes that are not environment-friendly.

Polylactic Acid (PLA) Production and Its Benefits

Production of PLA is in accord with at least three of the twelve principles of Green Chemistry, shown in Table 1: it is a *more energy-efficient* process, requiring only 20 – 50 % fossil-fuel resources compared to those used in the production of similar petroleum-based plastics such as polyethylene and polypropylene; PLA uses *renewable feedstocks* such as corn and sugar beets; because PLA is *biodegradable*, when it is discarded, it turns into innocuous products, such as PLA oligomers and L-lactic acid (Jarerat, Tokiwa and Tanaka, 2004), that do not persist in the environment.

Figure 1 shows the production of PLA from renewable resources (Jarerat and Tokiwa, 2005). Some renewable sources, such as sugar cane and sugar beets, contain fermentable sugars, i.e. they can be directly fermented by selected microorganisms, e.g. *Rhizopus oryzae*, into L-lactic acid. However, other sources, such as non-fermentable corn, cassava and rice, must be “broken” into smaller and directly fermentable polymers, i.e. a saccharification process, by enzymatic hydrolysis to be converted to L-lactic acid and subsequent polymerization.

Figure 2 shows two routes for the conversion of monomer lactic acid into PLA: route (1) uses direct condensation of lactic acid while route (2) produces a cyclic intermediate dimer (lactide), followed by a ring-opening process (Farrington *et al*., 2005). Polymerization via polycondensation, route (1), is carried out by the removal of water by condensing the lactic acid monomers using a solvent under high-vacuum and high-temperature conditions, yielding low to intermediate-molecular-weight PLA. On the other hand, ring-opening polymerization, route (2), produces high-molecular-weight PLA through removal of water under moderate conditions, without a solvent, to obtain a cyclic intermediate dimer that is purified under vacuum distillation; finally, ring-opening polymerization of the dimer is accomplished by heating without a solvent. PLA from this technology will probably replace some conventional plastics, such as polyethylene (PE) and polypropylene (PP), that are made from monomers obtained from petroleum.

Table 1: Twelve Principles of Green Chemistry

1	Prevent waste
2	Design safer chemicals and products
3	Design less hazardous chemical syntheses
4	Use renewable feedstocks
5	To accelerate reactions, use catalysts, not stoichiometric reagents
6	Avoid chemical derivatives
7	Maximize atom economy
8	Use safer solvents and safer reaction conditions
9	Increase energy efficiency
10	Design chemicals and products to degrade after use
11	Perform chemical analyses in real time to prevent pollution
12	Minimize the potential for accidents

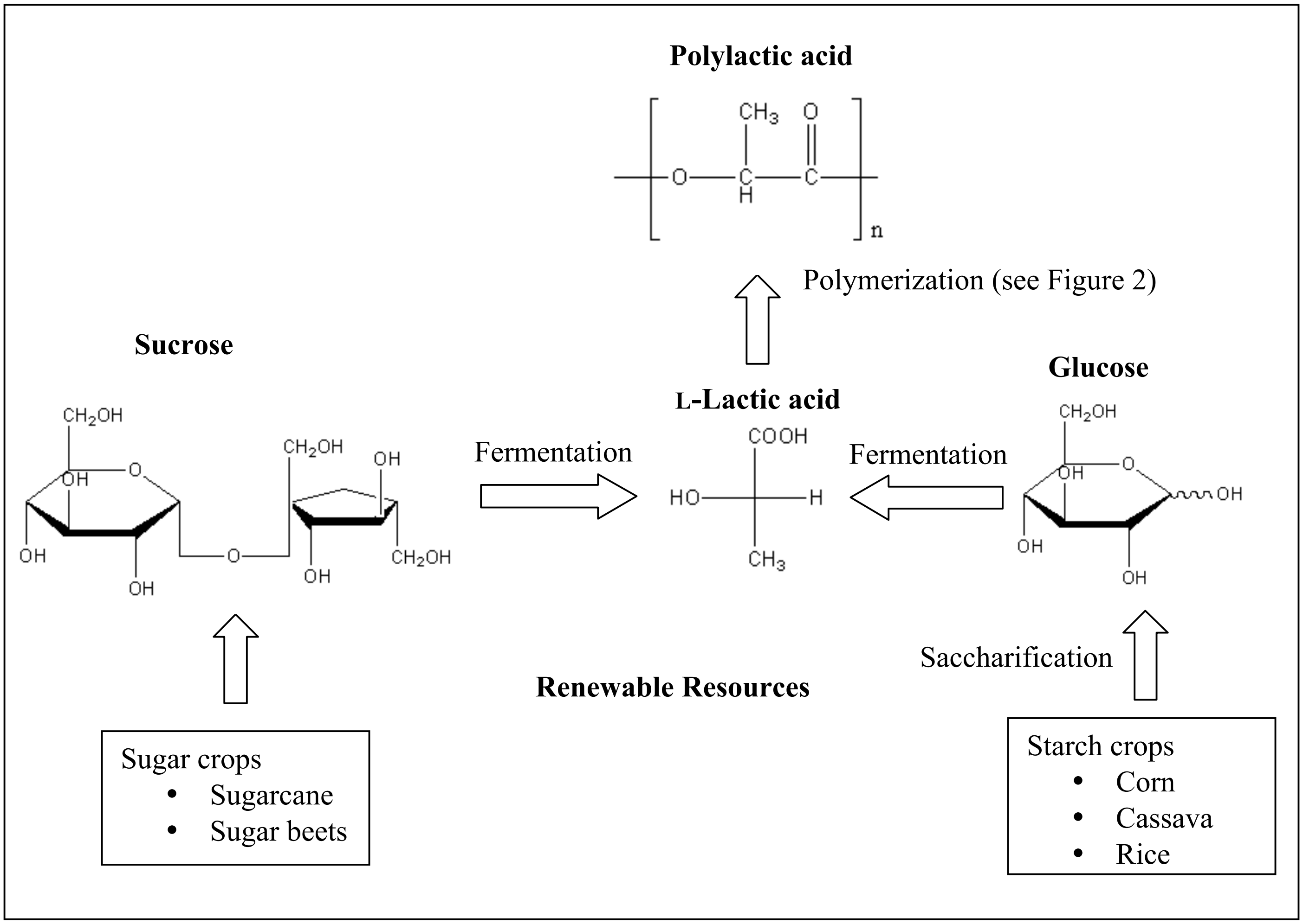

Figure 1: Production of PLA from renewable resources

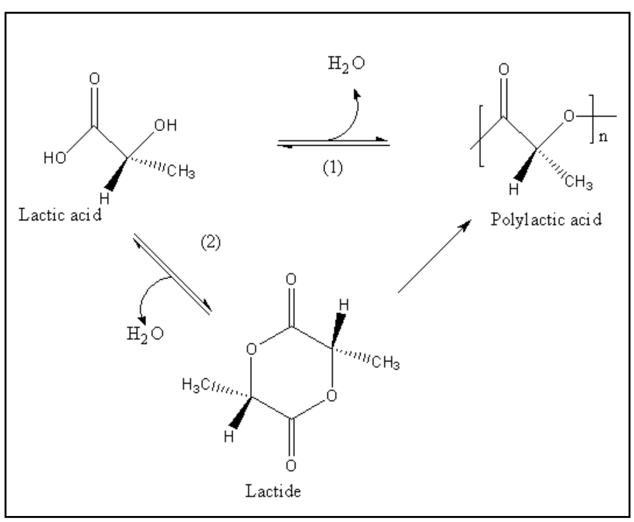

Figure 2: Two polymerization routes to PLA

Common applications of PLA are: plastic cups, clothing, food packaging, bottles, surgical sutures, stents, dialysis media and drug-delivery devices. At present, most stents used in angioplasty are made of metals that can lead to undesirable reactions in the patient. (Doble and Kruthiventi, 2007)

Cargill-Dow owns NatureWorks LLC, a company dedicated to produce biopolymers from renewable resources. Production of NatureWorks® PLA is characterized by the following desirable features (NatureWorks LLC website):

(1) *Renewable Resources*: field corn is decomposed into various foods and animal-feed components; one of these is corn sugar, or dextrose.

(2) *Fermentation*: the dextrose is fermented to give lactic acid that is distilled.

(3) *Production*: lactic acid is polymerized into NatureWorks® PLA.

(4) *Disposal*: articles such as packaging and service ware (plates, bowls, cups and cutlery) can be broken down into compost that can be used to grow more corn.

(5) *Reduced Fossil-Fuel Use*: because it is made from a renewable resource, NatureWorks® PLA uses up to 55 % less fossil-fuel energy than that used for manufacturing traditional plastics.

(6) *Reduced CO_2 emissions*: NatureWorks® PLA is the world's first greenhouse-gas-neutral polymer, i.e. CO_2 is fixed by plants into corn starch; when the PLA polymer subsequently degrades, the same CO_2 is released into the atmosphere.

NatureWorks LLC can produce PLA from biomass (B) and wind power (WP) as energy sources (PLA B/WP). Engineering estimates (Farrington *et al*., 2005) allege that:

- The first-generation polylactide-production system (PLA1) uses 25 to 55 % less fossil energy than that required for petroleum-based polymers such as nylon 66, nylon 6, polycarbonate (PC), high-impact polystyrene (HIPS), general-purpose polystyrene (GPPS), low-density polyethylene (LDPE), polyethylene terepthalate made by solid-state polymerization (bottle grade) (PET SSP), amorphous polyethylene terepthalate (fibers and film grade) (PET AM) and polypropylene (PP);
- The production of PLA B/WP requires less than 90 % of the fossil energy needed for the petroleum-based polymers above;
- Figure 3 shows the contributions to global climate change for PLA1, PLA B/WP and some petroleum-based polymers. In this comparison, all emissions are converted to CO_2 equivalents. The PLA1 production process has significant advantages relative to production processes for other polymers. The PLA B/WP production process, based on biomass feedstocks and wind energy, shows a negative greenhouse impact; this estimate takes into account utilization of the lignin fraction of lignocellulosic feedstocks for process-heat generation.

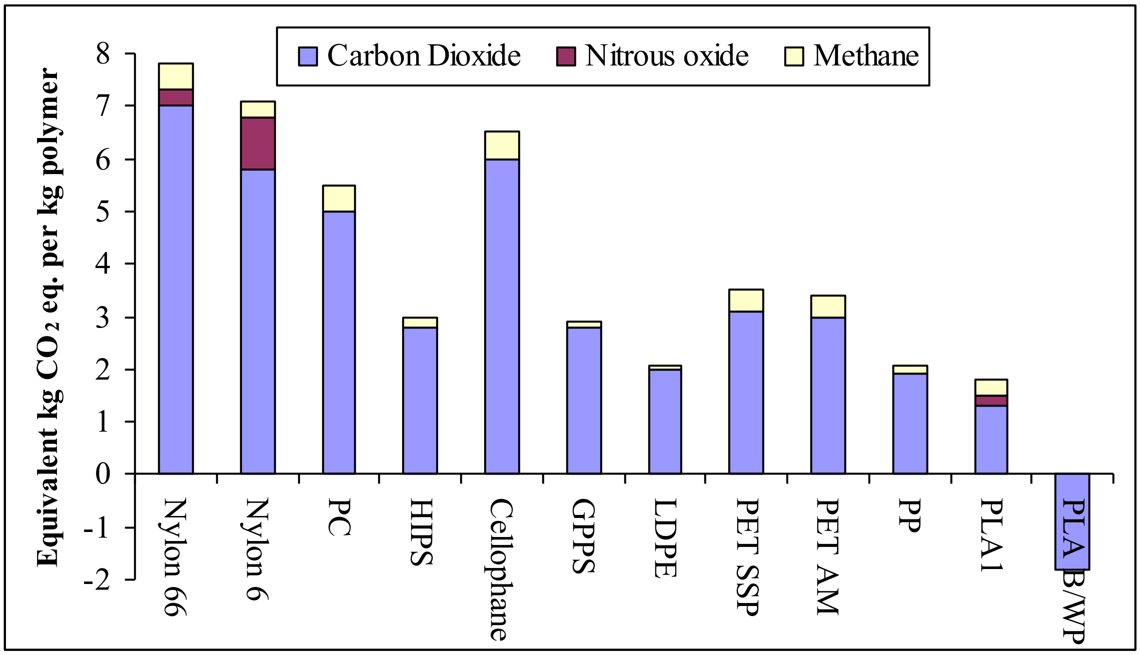

Figure 3: Contributions to global climate change for PLA1, PLA B/WP and some petroleum-based polymers. Adapted from Farrington *et al*., 2005.

Conclusions

Polylactic-acid production provides a case study for application of Green Chemistry and Green Engineering principles for reducing pollution. A few other case studies can be found in the literature; for example, advances in reactive distillation (Doherty and Malone, 1999), minimize production of side-product hazardous chemicals in the paper industry (Weinstock *et al*., 1997); and use of hydrogen-peroxide activators (called TetraAmidoMacrocyclicLigand, TAML®) as multi-effect catalysts for degradation in water of phenols, mitigation of pulp and paper effluent color and mill smells; rapid destruction of biological warfare agents, detoxification of chemical warfare agents and inhibition of dye transfer from laundries (Collins, 2002).

In the design of chemical products and processes, chemists and chemical engineers must take into account environmental effects. Because the main goal of the chemical profession is to manufacture chemical products for society, it is essential that these products and their method of manufacture minimize harm to the environment.

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