# 8 Life Cycle Thinking Informs Catalysis Choice and Green Chemistry

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> Let us not demand more of the Earth.
> Let us do more with what the Earth provides.
>
> **Gunter Pauli**

## 8.1 INTRODUCTION

Since the late eighteenth century, humans have been altering the earth at an unprecedented and unsustainable rate and scale.[1] Our economies are based on global resource use with modern man consuming between 30 and 75 tons of material per person per year in their companies and households.[2] Of the materials consumed, an estimated 90% of all biomass inputs and more than 90% of the nonrenewable materials used are wasted on the way to providing products to the end-user.[3] Resource extraction can result in serious environmental damages through the extraction and refining processes itself, and also due to the increasing transport distances between extraction, processing and final consumption. The chemical and petrochemical industry is a large user of chemical feedstock and energy (10% of total final energy demand) and contributes approximately 7% to global greenhouse gas (GHG) emissions.[4] However,

chemical products and technologies are also used in a wide variety of applications (e.g., insulation or lighter and advanced materials for transport) that help conserve resources and energy, thereby reducing environmental pressures. With the goal to develop more cost-effective and environmentally benign processes, the chemicals industry is increasingly seeking to replace stoichiometric reagents with catalytic routes. Today, an estimated 60% of chemical products and 90% of chemical processes employ catalysts,[5] as do nearly all petroleum-refining processes.[6] Their role in chemical synthesis is to facilitate reaction pathways with lower activation energies and to avoid the production of unwanted by-products. Because catalysis allows for easier-to-control process conditions (e.g., operation at lower temperatures and pressures or increased yields), it finds use in a wide range of applications including the production of commodity and petrochemicals, fine chemicals, pharmaceuticals, and food products.[7,8] Catalysis can be divided into heterogeneous (acting in a different phase than the reactants) and homogeneous (acting in the same phase as the reactants) catalysts. The use of enzymes for chemical transformations is referred to as biocatalysis. In the future, the use for catalysis is expected to further increase, especially in environmental catalysis (e.g., for the reduction of sulfur and $NO_x$ emissions), alternative fuel and energy systems (e.g., hydrogen cells and biofuels), and water purification and recycling.[9,10]

Because catalysis allows for more efficient, less energy-intensive, and more selective chemical reactions, it is regarded by many as an enabling technology to promote overall sustainability.[11–14] The concept of "sustainability" was defined in 1987 by the Brundtland Commission as "Sustainable development meets present needs without compromising the ability of future generations to meet their needs."[15]

Following this widely accepted definition of sustainable development, Christensen[16] defines sustainable chemistry as "chemistry that contributes to securing the needs of the present without compromising the ability of future generations to meet their own needs." Consequently, sustainable chemistry should consider the three dimensions of sustainability displayed schematically in Figure 8.1.[17]

Because chemistry is pervasive in so many aspects of our societal goals (e.g., improved materials, healthcare, agrochemicals, and energy), catalysis possesses the potential to reduce environmental pressures and enhance overall sustainability. Indeed, the International Energy Agency estimates that catalytic and related process improvements in the chemical industry could reduce energy consumption by 13 exajoules (EJ) (equivalent to the current annual primary energy use of Germany) and 1 gigatonne (Gt) of carbon dioxide equivalent ($CO_2$-eq) per year by 2050.[4] However, a systematic assessment taking into account various environmental pressures, and ideally the various aspects of sustainability, is required to avoid burden shifting and improve system-wide performance.

This book chapter first introduces a number of system analysis tools (e.g., material flow analysis [MFA] and life cycle assessment [LCA]) used to quantify material stocks and flows and associated environmental effects along a product's life cycle. Sustainable development requires not only the piecemeal improvements of separate parts of production, consumption, and waste management but must also make sure that, for example, environmental impacts or anthropogenic material flows, are reduced from a system-wide perspective. The term *system* or *life cycle*
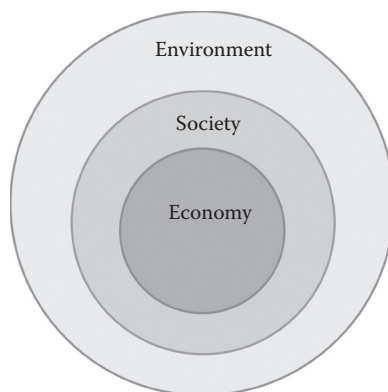
**FIGURE 8.1**   A diagram showing the three spheres of sustainability. Economy and society are constrained by environmental limits, and the economy is a construct of society. (Adapted from Mebratu, D., *Environ. Impact Assess. Rev.*, 18, 493–520, 1998.)

refers to the major activities across the life span of a material, product, process, or service beginning with resource extraction (mining, logging, and raw material extraction) to materials processing, to manufacturing and fabrication, to use, and then to collection, processing, and ultimate end-of-life management. Our focus is on environmental impacts, but a few references regarding social and economic approaches in the system analysis toolbox are also provided in the next section. We then continue to discuss the use of these tools in the context of sustainable (green) chemistry and catalysis. The chapter concludes with a case study applying LCA to bioacrylics.

## 8.2   LIFE CYCLE THINKING INFORMS GREENER PRODUCTS

Lack of availability or consideration of life cycle data in product design and decision-making has created unintended environmental consequences, some of which have only been recognized in recent years, such as indirect land use change in first-generation biofuels production.[18] Today, a number of tools are available to assess the life cycle–wide performance of a new process or product chain. These include, for example, MFA,[19] environmental LCA,[20,21] environmentally extended input/output (EIO) analysis,[22] life cycle cost (LCC) analysis,[23] social life cycle assessment (SLCA),[24] and resource criticality assessments.[25–27] Life cycle thinking reflects the considerations of cradle-to-grave implications of any action, and common to all these concepts is that they are taking a systems approach, considering upstream and downstream processes.[28]

### 8.2.1   Material Flow Analysis

MFA aims at quantifying the stocks and flows of materials at different temporal and spatial scales (e.g., an economy, country, region, community, business, company, or

household[19,29] to study their role in the industrial metabolism*.[30] Materials can refer to bulk materials (e.g., steel, wood, and total mass), but also to single substances (e.g., a metal) or group of substances (e.g., the rare earth elements).[†] In the case of metals, the material cycles are expressed through four principal processes: production, fabrication and manufacturing, use, and waste management and recycling. A cycle is characterized by processes that are linked through markets,[31] each market indicating trade with other regions at the respective life stages. The scrap market plays a central role in that it connects manufacturing and waste management and recycling with production and fabrication. The cycle is surrounded by entities lying outside the system boundary: trade partners (other regions), Earth's crust from which ore extraction takes place, and repositories for metals in production waste deposits and landfills. Understanding the whole system of material flows can help quantify potential primary and secondary source strengths, manage resource use more wisely, and protect the environment.

In the context of catalysis, the platinum group metals (PGMs) consisting of ruthenium, rhodium, palladium, osmium, iridium, and platinum present an interesting case in which MFA elucidates potential burden shifting.[‡] The PGMs are among the rarest elements in Earth's upper continental crust[32] and their production is resource-intensive and energy-intensive.[33] Major PGM end-use applications include autocatalysts (for the automobile industry), chemical processes (e.g., use in the chemical and petroleum industries), dentistry, jewelry, electronics, investment, the glass industry, and others.[34] Their role in automobile catalysts is to reduce emissions, for example, of nitrous oxides ($NO_x$), during the vehicle driving phase. However, because their production is resource-intensive, obtaining PGMs may also result in environmental pressures in the major mining countries of Russia, South Africa, and North America. Indeed, a MFA study by Saurat and Bringezu[35] showed that using PGM catalysts in European cars results in a significant overall reduction of acidifying emissions ($SO_2$-eq) when compared with cars without using a catalytic converter, whereas life cycle–wide effects to global warming potential (GWP expressed in $CO_2$-equivalents) are slightly lower for gasoline cars and significantly higher for diesel cars (Figure 8.2). The analysis also indicates that the use of car catalysts leads to a drastic increase in resource extraction and mining waste (expressed in total material requirement [TMR]; Figure 8.2).

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* The term *metabolism*, applied to plants or animals, includes the transformations of inputs (sunlight, chemical energy, nutrients, water, air) required by an organism to function and associated waste products. "Industrial metabolism," by analogy, refers to the flows of materials, energy, and waste in industrial systems.

† A group of metals including lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), lutetium (Lu), and yttrium (Y) used increasingly in modern technology.

‡ In the context of this chapter, burden shifting refers to attempts to improve the environmental performance or material efficiencies in one part of a product system at the expense of increasing the effects elsewhere. Only if the full life cycle (from "cradle-to-grave") is taken into consideration can burden shifting be elucidated and addressed. Burden shifting can take place in various ways, for example, between different media, between geographical regions, between life cycle stages, between generation, or between different effect categories (see, e.g., Wrisberg and de Haes[28] for a summary).
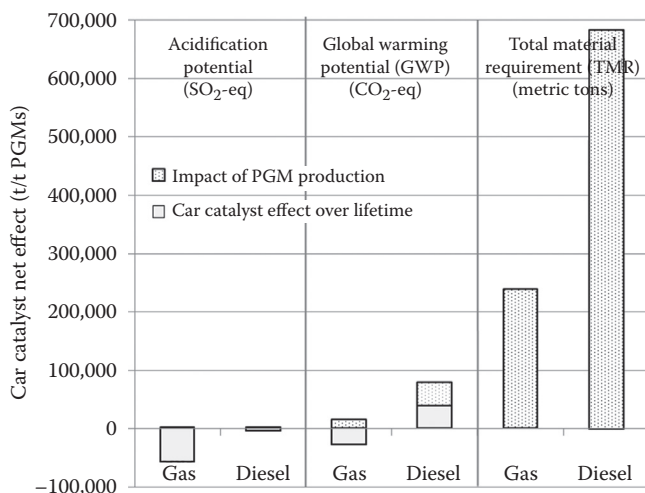
**FIGURE 8.2**  Net effect of gas or diesel car catalysts over their service lifetime (i.e., in comparison to cars without a catalytic converter). The negative effects are due to the emissions avoided from cars using a PGM catalyst when compared with cars without a catalytic converter. eq = equivalents. (Data from Saurat, M., Bringezu, S., *J. Ind. Ecol.*, 12, 754–767, 2008.)

**Key point:** Use of car catalysts in Europe can result in shifting emissions to other locations.
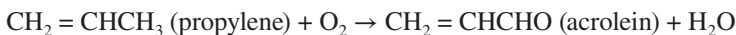
Although the intention of the catalytic converter is to reduce tailpipe emissions and associated human health and ecosystem damages, a more system-wide examination shows that the use of catalytic converters in automobiles in Europe simply shifts some of the environmental pressures to the PGM-producing countries.[35] In addition, the data indicate a shift from emissions-related effects (acidification potential and GWP) toward potential effects due to raw materials movement (TMR).[36] One possible strategy to enhance the positive effect of catalytic converters and avoid shifting environmental effects to other locations is to increase recycling rates for PGMs to replace primary by secondary production.[35] However, to date, the growing stock of cars cannot be matched by secondary production.

## 8.2.2  LIFE CYCLE ASSESSMENT

LCA is a tool to systematically evaluate the potential cradle-to-grave environmental impacts of products, technologies, and services. The LCA concept can be traced back to the 1960s, when its forerunners (i.e., resource and environmental profile analysis and net energy analysis) were developed. Today, LCA as broadly defined by the International Organization for Standardization[20,21] consists of four steps: first, the goal and scope explains the study context and system boundaries, and defines a (quantifiable) functional unit to describe the primary function(s) fulfilled by the product or service system. Second, a life cycle inventory (LCI) comprising all environmentally

relevant flows, such as material and energy inputs and outputs and emissions to air, soil, and water, is compiled. Third, the LCI is translated into potential effects including damage to human health, ecosystems, and depletion of resources, using life cycle impact assessment (LCIA) models. Finally, during the interpretation stage, results of the LCA and their wider implications are critically assessed. Recent efforts have been focused on broadening the traditional LCA framework to integrate environmental, social,[24] and economic[23,37] aspects at varying spatial levels, also referred to as life cycle sustainability assessment (LCSA).[38] A concise overview of LCA is given, for example, in Hellweg and Canals[39] and a more detailed explanation provided elsewhere.[40,41]

In the context of catalysis, LCA has been applied to compare environmental impacts of different catalytic reaction processes.[42–44] For example, Holman et al.[42] investigated the environmental impacts of acrylic acid (2-propenoic acid) production from propylene in a two-step reaction via acrolein with the use of propane as a potential starting material in a one-step process through a selective oxidation reaction (see the following equation).

$$CH_2 = CHCH_3 \text{ (propylene)} + O_2 \rightarrow CH_2 = CHCHO \text{ (acrolein)} + H_2O$$

$$CH_2 = CHCHO + 1/2\ O_2 \rightarrow CH_2 = CHCO_2H \text{ (acrylic acid)}$$

Acrylic acid is a commodity chemical with a market that reached approximately 3.2 million tons by the end of 2005.[45] Acrylic acid finds application, for example, in superabsorbent materials (e.g., for diapers) and as a replacement for phosphates in detergents. However, the propane process has not been commercialized and current work focuses on the development of catalysts to increase the conversion of propane and the selectivity toward acrylic acid. The use of LCA showed that even at low yields exceeding 33%, the propane process may have a lower GWP than the current propylene process (compared with a yield of 87% of the current commercial propylene process). This is mostly due to the upstream environmental burdens associated with propylene production, which are higher than those of propane production. Thus, from an environmental standpoint, the propane process may already present a viable option even at low conversion rates using current catalysts.

**Key point:** LCA can help to illustrate the environmental impacts of alternative catalyst-based processing routes, even when one of these routes has not yet been fully developed.

### 8.2.3 Metal Catalysis and Environmental Impacts

Organometallic catalysts are important in both fine and bulk chemicals production. However, most of the catalysts employed today rely on rare and expensive transition metals with potentially high toxicity and life cycle–wide environmental impacts.[11,46] Furthermore, because these metals cannot be metabolized by biological systems, any resulting catalyst waste may cause environmental problems in the long-term.[11]

As a result, researchers are increasingly looking into alternatives including (a) biocatalysis, (b) organocatalysis, and (c) sustainable metal catalysis. The term "sustainable metal catalysis" refers to the use of metals that are nontoxic, abundant, and biologically relevant, for example, magnesium, calcium, manganese, iron, cobalt, nickel, copper, zinc, and molybdenum.[11] An example is metal-catalyzed olefin hydrosilation, in which silicon–hydrogen bonds are added across a carbon–carbon double bond—a process used in the commercial production of silicone-based surfactants, fluids, molding products, coatings, and additives.[47] For many years, platinum-based compounds such as Karstedt's and Speier's catalysts were used by industry, whereas iron catalysts were introduced only recently as a potential alternative.[48] Indeed, a review of metal LCAs showed that on a per kilogram basis, iron production results in a much lower GWP (1.5 kg $CO_2$-eq/kg) when compared with platinum production (~12,500 kg $CO_2$-eq/kg; Figure 8.3).[49]

**Key point:** LCA can provide interesting insights into the environmental implications of the choice of catalytic metals already in the design phase.

Using such LCA-based information can guide metal catalyst developers in choosing a metal with the lowest environmental impact when designing new metal catalytic compounds. However, only one effect category is shown in Figure 8.3, and ideally, the catalysts' designer should also look at additional effect categories such as toxicity, cumulative energy demand, water use, acidification, and eutrophication, and carry out a cost analysis[50] when making the choice of using one metal over another. In some cases, the ligands surrounding the metal in homogeneous catalysis are expensive[51] and might also contribute to environmental impacts, for example, if a very resource-intensive chemical is used to produce them. A clear limitation of a cradle-to-gate LCA, as shown in Figure 8.3, is that the use and end-of-life phases are not included within the system boundary. For example, a catalyst may have a high environmental impact in the production phase but display only minor loss rates during the use phase and high recycling rates at end-of-life. This would only be captured by doing a cradle-to-grave assessment. For example, it is estimated that in 2007, the silicone industry consumed approximately 5.6 metric tons of platinum catalyst with most of this not being recovered.[52] Taking the result from Figure 8.3, this equals 70,000 metric tons $CO_2$-eq in 2007 (the per kilogram effect reported for platinum in Figure 8.3 already includes secondary production of the global supply mix). This figure could be drastically reduced if platinum catalysts were recycled at end-of-life. Nevertheless, if used together with cost and detailed energy analysis,[50] detailed information on the cradle-to-gate environmental impacts can provide a first indication of environmental impacts already in the design phase of a new metal catalyst as well as how an alternative option might compare with the metals currently used.

### 8.2.4 CRITICALITY ASSESSMENT

However, LCA only accounts for environmental impacts and does not yet cover other important issues such as social and regulatory and geopolitical factors of

Global warming potential (kg $CO_2$-eq/kg)

Lowest — Highest

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| H | | | | | | | | | | | | | | | | | He 0.9 |
| Li 7.1 | Be 122 | | | | | | | | | | | B 1.5 | C | N | O | F | Ne |
| Na | Mg 5.4 | | | | | | | | | | | Al 8.2 | Si | P | S | Cl | Ar |
| K | Ca 1.0 | Sc 5710 | Ti 8.1 | V 33.1 | Cr 2.4 | Mn 1.0 | Fe 1.5 | Co 8.3 | Ni 6.5 | Cu 2.8 | Zn 3.1 | Ga 205 | Ge 170 | As 0.3 | Se 3.6 | Br | Kr |
| Rb | Sr 3.2 | Y 15.1 | Zr 1.1 | Nb 12.5 | Mo 5.7 | Tc | Ru 2110 | Rh 35,100 | Pd 3880 | Ag 196 | Cd 3.0 | In 102 | Sn 17.1 | Sb 12.9 | Te 21.9 | I | Xe |
| Cs | Ba 0.2 | La-Lu* | Hf 131 | Ta 260 | W 12.6 | Re 450 | Os 4560 | Ir 8860 | Pt 12,500 | Au 12,500 | Hg 12.1 | Tl 376 | Pb 1.3 | Bi 58.9 | Po | At | Rn |
| Fr | Ra | Ac-Lr** | Rf | Db | Sg | Bh | Hs | Mt | | | | | | | | | |

| *Group of lanthanide | La 11.0 | Ce 12.9 | Pr 19.2 | Nd 17.6 | Pm | Sm 59.1 | Eu 395 | Gd 46.6 | Tb 297 | Dy 59.6 | Ho 226 | Er 48.7 | Tm 649 | Yb 125 | Lu 896 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Group of actinide | Ac | Th 74.9 | Pa | U 90.7 | Np | Pu | Am | Cm | Bk | Cf | Es | Fm | Md | No | Lr |

**FIGURE 8.3** Cradle-to-gate GWP of various elements compared on a per kilogram basis. Data are representative of metal end-uses in 2008 using 2006 to 2010 price averages to allocate environmental impacts. Please see Nuss and Eckelman[49] for more details and additional effect categories. (From Nuss, P., Eckelman, M.J. Life cycle assessment of metals: A scientific synthesis. *PLoS ONE*, 9, e101298, 2014. Copyright: © 2014 Nuss, Eckelman. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.)

metal use, or issues related to the vulnerability to supply restriction (e.g., competing end-use applications and metal substitution). These issues are important because many of the transition metals used in today's catalysts may not be available in quantities that guarantee sufficient supplies in the coming decades. Issues of resource availability are covered in depth in criticality assessments,[25–27] with outcomes for some of the metals used in sustainable metal catalysis (see above) reported at the global level and for the United States in Figure 8.4. The issue of critical materials in catalysts is further discussed in a study by the US National Research Council.[51]

**Key point:** Resource criticality assessments enable issues of resource concerns (of geological, geopolitical, and regulatory nature) to be identified and provide information about possible options to reduce resource constraints, for example, via substitution or alternative sourcing.

Figure 8.4 presents four metals of potential use in sustainable catalysis and their supply risk (SR) and vulnerability to supply restriction (VSR) scores. Iron and copper display low to moderate SR in the long-term VSR and medium VSR. Manganese indicates potential VSR issues, mostly related to issues of substitutability in some of its end-uses (e.g., steel making).[53] Zinc shows a slightly elevated SR (global level and national level) because its depletion time (i.e., the time until the geological reserve

Lower risk                                    Higher risk

Color key

| Metal | Iron (Fe) | Manganese (Mn) | Copper (Cu) | Zinc (Zn) |
|---|---|---|---|---|
| SR (Global)[a] (0–100 axis) | 0 | 2 | 5 | 41 |
| SR (USA)[1] (0–100 axis) | 45 | 61 | 52 | 57 |
| VSR (Global)[2] (0–100 axis) | 58 | 66 | 53 | 52 |
| VSR (USA)[2b] (0–100 axis) | 48 | 73 | 54 | 51 |
| Reference | Nuss et al.[53] | Nuss et al.[53] | Nassar et al.[54] | Harper et al.[55] |

**FIGURE 8.4** Criticality results reported in the literature for some metals of interest in sustainable catalysis. The criticality methodology applied to derive these is given in Graedel et al.[27] All results are converted to a 0 to 100 (low–high) gray scale bar. [a]SR at the global scale consists of depletion time and companion metal fraction. At the national scale (United States), additional social and regulatory and geopolitical aspects of producing countries such as the policy potential index, human development index, political stability, and global supply concentration are included.[27] All scores are transformed to a 0 to 100 scale with 0 representing the lowest and 100 the highest SR. [b]VSR looks at issues such as importance, substitutability, and susceptibility of the metal under investigation.[27] All scores are transformed to a 0 to 100 scale with 0 representing the lowest and 100 the highest VSR.

base is exhausted taking into account current production figures, in-use lifetimes, and end-of-life recycling rates) is shorter than for any of the other elements in Figure 8.4.[55] Overall, any of these elements might be used in catalysis so long as a watchful eye is kept on the zinc and manganese situation.

## 8.3  LCA EXAMPLE: BIOBASED ACRYLIC ACID

As mentioned throughout this chapter, LCA is a useful tool to examine the environmental impacts of existing chemical routes as well as of processes still in their early stages of development. Here, we use literature data to investigate the life cycle–wide GHG emissions of biobased acrylic acid production and illustrate potential "hot spots" along the production chain. This process has not yet been developed commercially and therefore process data are scarce. However, the goal of this LCA is to illustrate how a streamlined LCA model can be developed even at an early stage of process development using best available literature data to obtain interesting insights, for example, into major contributors to environmental impacts. Such a basic LCA model, once developed, can be updated as better process data become available. It may be used internally within a company or research group when investigating the environmental performance of a novel synthesis route. Given the data limitations, we only focus on GWP as an effect category (in a full LCA, other impact categories should also be included).

Acrylic acid (2-propenoic acid) is commercially produced from petrochemicals, with the majority of it being generated by partial oxidation of propylene. Yields range between 50% and 60% for the single-step process and up to 90% for the two-step process via acrolein.[56] The major use of acrylic acid, and its derivatives, is in polymeric flocculants, dispersants, coatings, paints, adhesives, and binders for leather and textiles.[56] Currently, a variety of alternative routes from biomass to acrylic acid are under investigation. The biotechnological production from either 3-hydroxypropionic acid (3-HPA) or lactic acid is explored in the United States.[57] A number of companies and academic research groups are pursuing routes toward acrylic acid utilizing renewable feedstock. In a joint project, HTE (High Throughput Experimentation Company) and Arkema are working on the development of suitable catalysts for the conversion of biodiesel-derived glycerol to acrolein and acrylic acid.* The companies Cargill and Novozymes announced a joint $1.5 million agreement funded by the US Department of Energy to investigate technologies for the production of acrylic acid via 3-HPA from renewable biomass.† 3-HPA could act as precursor for acrylate production. Different hypothetical pathways for converting sugars into acrylate are summarized in the literature.[56] Each route may have particular advantages in terms of yield, productivity, ease of product separation, economy, and environmental impact. The most direct route is via lactate.

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* See news article on http://biopol.free.fr/?p=597 (accessed March 17, 2010).
† See *Biomass Magazine* article on http://www.biomassmagazine.com/article.jsp?article_id=1407 (accessed March 17, 2010).

### 8.3.1 Life Cycle Inventory Data

The conversion process studied here is based on a hypothetical process flow diagram by Straathof et al.[56] In their study, a 100,000 tons/year fermentation process for acrylic acid production, including product recovery, was conceptually designed based on the assumption that an efficient host organism for acrylic acid production could be developed. It is assumed that conversion of the sugars toward acrylate can be achieved in a single step. A possible route that could be undertaken in this processing facility would be the fermentation of sugars through *S. cerevisiae* via pyruvate and lactate toward acrylic acid.[56,58] The production system considered in this study consists of (1) glucose production via corn wet milling, (2) fermentation in which the microorganism produces acrylic acid from fermentable sugars, (3) disk stack centrifuge for cell removal, (4) filtration system consisting of microfiltration and ultrafiltration, (5) liquid-liquid extraction of the product using an organic solvent, and (6) distillation of the solvent to obtain pure acrylic acid as the product.

Glucose production is based on a combination of data describing corn production in the United States (including farm equipment use)[59,60] and glucose production via corn wet milling[61–64] as described elsewhere.[65] The transportation distance and price data for allocation of environmental burden between glucose, corn meal and feed, and corn oil are based on the LCA model of Nuss and Gardner.[65] Data for the fermentation process is based on a yield of 0.72 g acrylic acid per gram glucose and a broth concentration of 50 g/L[66] to calculate the amount of fermentable sugars required and waste water produced (assuming no recirculation). Due to a lack of data on the detailed composition of wastewater generated, we use typical numbers from commercial polylactic acid (PLA) production according to the ecoinvent database[67,68] and Vink et al.[69,70] Approximately 0.10 g dry cells per gram of glucose are produced[58] and removed via filtration. Allocation of environmental burdens is based on the dry weight of product outputs. We do not include biogenic $CO_2$ emissions, for example, from cellular respiration during fermentation, and the uptake of biogenic $CO_2$ in the final product's effects on GWP. A liquid–liquid extraction process was chosen for the separation of acrylic acid from the mixture formed after fermentation and centrifugation. Alvarez et al.[71] found diisopropyl ether to be the most suitable solvent for acrylic acid from a water mixture. A diisopropyl ether requirement of 7.8 kg per kilogram of acrylic acid[71] and a solvent recovery rate of 0.95 kg per kilogram of waste solvent[72] are used in this assessment. Because no LCI data on diisopropyl ether are available in commercial LCI databases,[59] data for isopropyl acetate are used as a proxy.* Waste solvent not recovered is assumed to be treated in a hazardous waste incinerator.[73] The energy requirements of 3 kWh/m³ feed for agitation and aeration and 7 kWh/m³ feed for the centrifuge are taken from Patel et al.[74] Energy requirements for distillation (1.21 kg steam and 0.03 kWh electricity per kg waste solvent) and nitrogen requirements ($0.24 \times 10^{-3}$ Nm³ per kg waste solvent) are obtained from Capello et al.[75] No data were available on the amount of sodium carbonate (used to adjust the pH) and the upstream environmental burden of biocatalyst

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* Alvarez et al. state that, even though in their study, diisopropyl ether was used as a solvent, previous studies indicated the possibility of also using isopropyl acetate as a solvent for acrylic acid recovery.

production, and they are therefore excluded from the analysis. No infrastructure processes are included in this assessment. Electricity mixes of the background system represent the United States and all inputs and waste treatment processes are linked to respective unit processes from the US EI database.* The functional unit for this study is 1 kg of acrylic acid at the factory gate and the results are compared with conventional acrylic acid production using data from Althaus et al.[67] SimaPro8 LCA software is used to create the LCA model and effects on GWP are calculated using the IPCC 2013 GWP LCIA method with a 100-year timeframe.[76]

### 8.3.2 Results

The Sankey diagram for the production of bioacrylic acid from corn feedstock is shown in Figure 8.5. In the figure, the width of the arrows indicates the contributions of each unit process to total GWP. Unit processes located upstream or downstream of biobased acrylic acid production are shown as separate boxes in Figure 8.5 and represent conversion processes contributing to varying degree to GWP.

**Key point:** LCA allows a contribution analysis already in the design phase of a new chemical route or catalytic process. Based on this information, approaches can be developed to improve life cycle–wide performance.

Producing 1 kg of acrylic acid from corn feedstock is estimated to result in a GWP of approximately 4.9 kg $CO_2$-eq. The largest contributors to this are steam consumption during the distillation process (32% of total GWP) and corn wet milling during which glucose is produced (30%). This is mostly due to a combination of electricity, natural gas, and heavy fuel oil consumption associated with both processes. GHG emissions during corn production also contribute to the effects of corn wet milling. In addition, the use and subsequent disposal of solvents results in 22% and 10% of overall GWP, respectively. On-site electricity demand during fermentation contributes to 5%, only a small share to overall GWP. This compares with an estimated 2.4 kg $CO_2$-eq per kilogram of fossil-based acrylic acid (produced via a two-step oxidation process from propylene).[67]

However, large uncertainties are associated with many of the input parameters used in this streamlined LCA model. For example, the solvent/acrylic acid ratio and solvent recovery rate are based on simulation or laboratory-scale data and may not represent a commercial process in the future. The amount of solvent eventually required for the extraction process will vary with reaction conditions and the design of the fermenter (continuous or batch process, total throughput, type of waste solvent, size of the distillation equipment, etc.). For example, by decreasing the amount of waste solvent from 7.78 kg to 5 kg per kilogram of acrylic acid, the GWP would decrease to 4.3 kg $CO_2$-eq per kilogram of acrylic acid. Using a different solvent with a lower carbon footprint would further reduce these effects. Furthermore, steam generation is another major contributor to GHG emissions in this LCA. The amount required depends, among others, on the enthalpy of vaporization of the solvent and

* Using Ecoinvent 2.2.[59] with United States electricity mixes (www.earthshift.com/software/USEI -database).
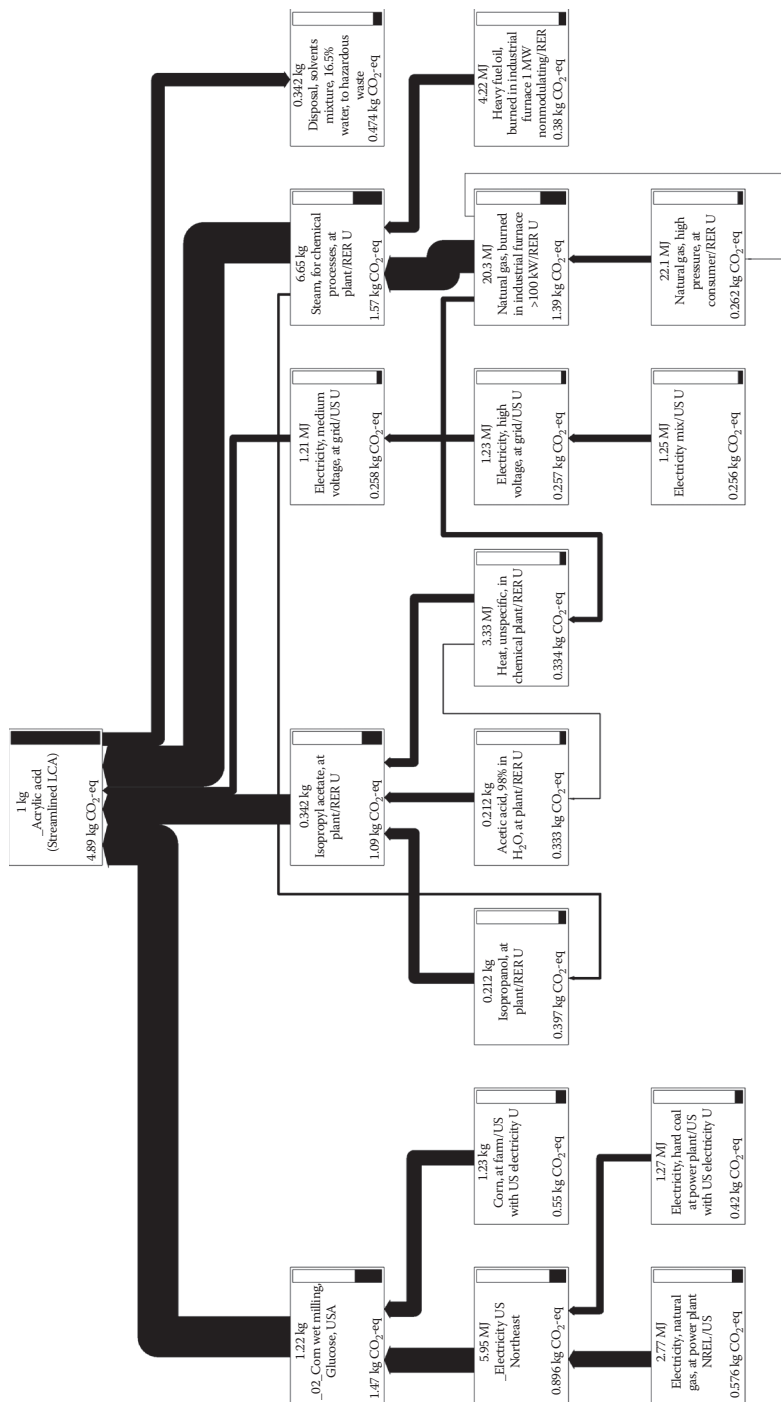
**FIGURE 8.5**  Sankey diagram showing the GWP associated with 1 kg corn-based acrylic acid production. Each box represents a unit process along the production chain of acrylic acid production and the width of the arrows indicates the contributions of each unit process to total GWP. For example, glucose provision via corn wet milling shown on the left hand side of the Sankey diagram contributes 1.47 kg $CO_2$-eq (~30% of total GWP).

may be significantly lower depending on the final solvent used in a commercial process. For example, cutting steam inputs by half would lower GWP to 4.15 kg $CO_2$-eq per kilogram of acrylic acid. Finally, switching to an alternative feedstock for fermentable sugar production (e.g., sugars obtained from lignocellulose feedstock) may help to further reduce environmental impacts.

Nevertheless, despite the issues of data availability discussed previously, this simple exercise demonstrates the capability of LCA to point toward potential "hot spots" in the life cycle of a chemical process, and it shows how various process settings may be examined early on in the design of a new chemical route. Furthermore, creating a first LCA model based on literature data usually takes no more than a few hours to perhaps a few days. If done in conjunction with process development in the laboratory, it can help the chemist to make more informed decisions and improve the life cycle–wide environmental performance of chemical synthesis.

## 8.4 CONCLUSIONS

Catalysis is an enabling technology that can help promote significant energy savings in the chemical industry and provide products of crucial importance for sustainable development in the future. However, several studies within the area of green chemistry and sustainable catalysis promote new techniques and products as "sustainable" or "more environmentally benign" without taking a life cycle–wide perspective and quantifying their benefits and tradeoffs. Life cycle approaches such as LCA and MFA can be used (oftentimes even during process development) to quantify environmental impacts and resource flows, and thereby help to elucidate improvement options and avoid shifting of (environmental) burdens to other parts of the life cycle. Resource criticality assessments can provide additional information with regard to possible resource constraints. It is hoped that these tools and approaches find increasing application in catalyst and chemical process design to help avoid unintended consequences and decrease our environmental impact on the earth.

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