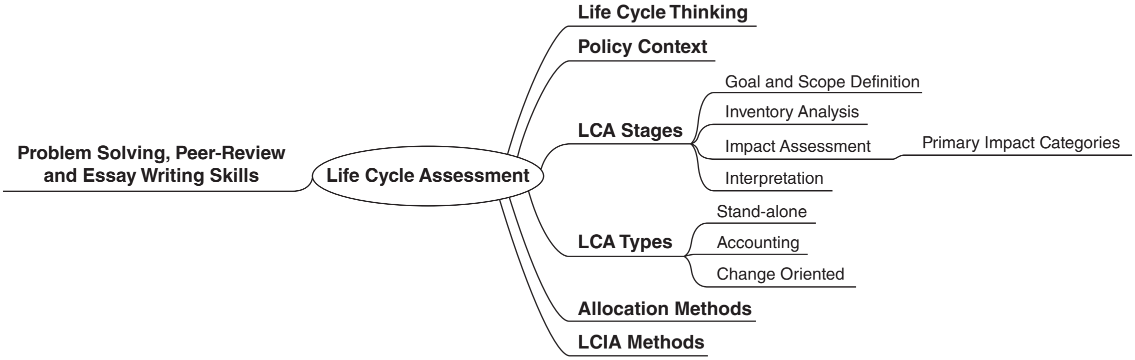
4

Life Cycle Assessment



Structure for Lecture Planning

4.1 Life Cycle Thinking

Life cycle thinking (*LCT*) includes analysis of whole system environmental impacts from primary material and energy resource extraction to end of life (*cradle to grave*), much beyond a chemical plant's material and energy efficiency. A system that includes primary resource extraction to manufacturing of products or *upto the plant gate* is called a *cradle to gate* system. If one part of a system has positive impacts, other parts of the system are likely to have negative impacts. System thinking is imperative for environmental sustainability. Environmental sustainability relates to the impact assessments due to emissions to air, water and land and avoidance of emissions by improved process configurations, feedstocks, products and supply chain distributions.

An example is whether a particular nuclear power generation plant can give more energy than it consumes; there is a need to go beyond the generation facilities and consider impacts of other aspects involved such as uranium mining, transportation, associated research and even the marketing services. The systematic process design and development study for one single step can be extended to the formulation of all steps in a product life cycle, raw material acquisition, manufacturing, logistics and, after consumption, reuse, recycling and landfill, etc. Figure 4.1 shows the basic building stages for the production of a product, from raw material extraction through manufacturing to end of life reuse and recycling. However, Figure 4.1 does not include life cycle impacts associated with the construction materials of the

Biorefineries and Chemical Processes: Design, Integration and Sustainability Analysis, First Edition.
Jhuma Sadhukhan, Kok Siew Ng and Elias Martinez Hernandez.

Companion Website: http://www.wiley.com/go/sadhukhan/biorefineries

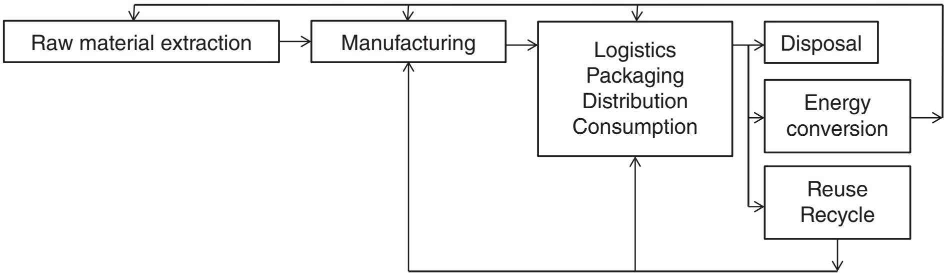


Figure 4.1 *Basic building stages for the production of a product.*

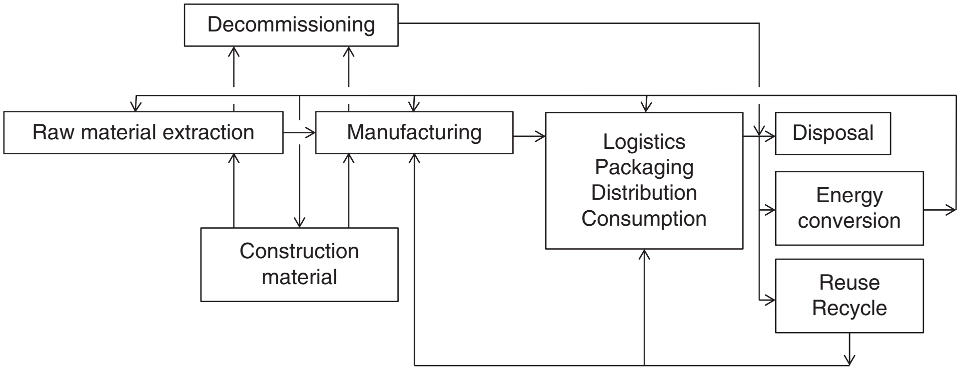


Figure 4.2 *Life cycle stages of a cradle to grave system.*

manufacturing plants. Figure 4.2 shows the complete life cycle stages of a system. Figure 4.2 shows that the emissions from the construction materials life cycles should be included in a life cycle assessment (LCA) study of a manufactured product.

The LCA is a holistic environmental impact assessment tool for cradle to grave systems that systematizes the assessment in a standardized way and format. LCA studies are data intensive. A whole system in Figure 4.2 can be divided into two parts, foreground and background systems, such as in Figure 4.3. This division is primarily applied to minimize the data

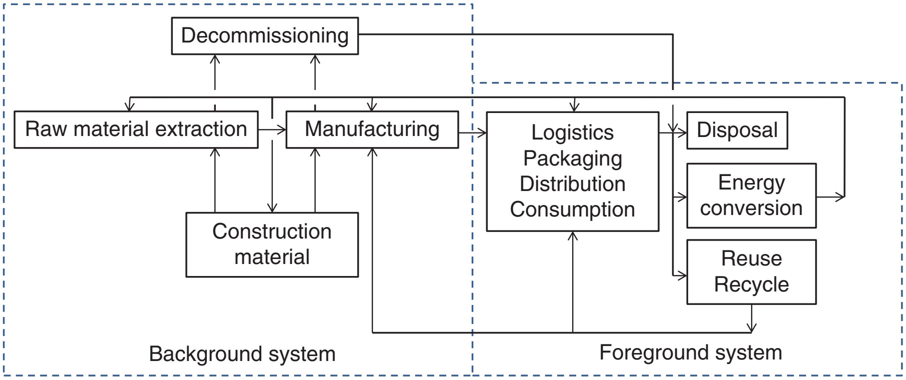


Figure 4.3 *Foreground and background systems.*

need. A decision maker primarily deals with one or some parts of a system, known as *foreground* system. The rest of the cradle to grave system is the *background* system for the decision maker. For the background system the life cycle inventory analysis data may be collected, compared and reconciled for incorporation into the foreground system. The foreground system is of central focus in terms of design, optimization and decision making.

Figure 4.3 shows an example of the foreground system with the rest presented as the background system. Which part of the system is the foreground system depends on the concerned decision maker. In this case, the decision maker is primarily dealing with the product logistics, such as a local authority trying to influence waste recycling as a better policy than landfilling, by taking the LCA approach. Whilst the foreground and the background systems are highly interactive and influenced by each other in terms of environmental impacts, the decision maker may just be concerned with the detailed evaluation of the foreground system, which can include raw material extraction and manufacturing, instead.

Uncertainties in data exist all the way in entire value chains; henceforth, structured approaches are recommended and guidelines are provided for making the most of LCA tools and for the best use of LCA results. Here, the focus is to first get familiar with the LCA approach generically followed by specific practical examples to help in applying LCA to biorefinery problems. The LCT spans not only across the whole lifetime of a process or product but also how the product or process is connected with other networks of products and processes. The networks may span across different geographic regions and hence value or supply chain analysis becomes part of the problem. Thus LCT-inspired problem formulation may take account of interacting products and process network design and decision making across supply chains in different geographic regions as well as time scale. Figure 4.4 shows an example of interacting networks of products and processes[1]. The primary raw material and energy for all kinds of products or processes under consideration come from reserves of coal, crude oil, natural gas and minerals from soil. Soil or land and water are also important resources. These resources contribute to the development of any product shown for cement, iron, electricity and heat, interdependent on each other by the constraints on resource availability. There are also demand side constraints for various products. Policies need to be in place to ensure that supply and demand are constantly balanced without damage to the environment, so as to retain resource reserves and reduce pollutant emissions to land, water and air. In this chapter, the

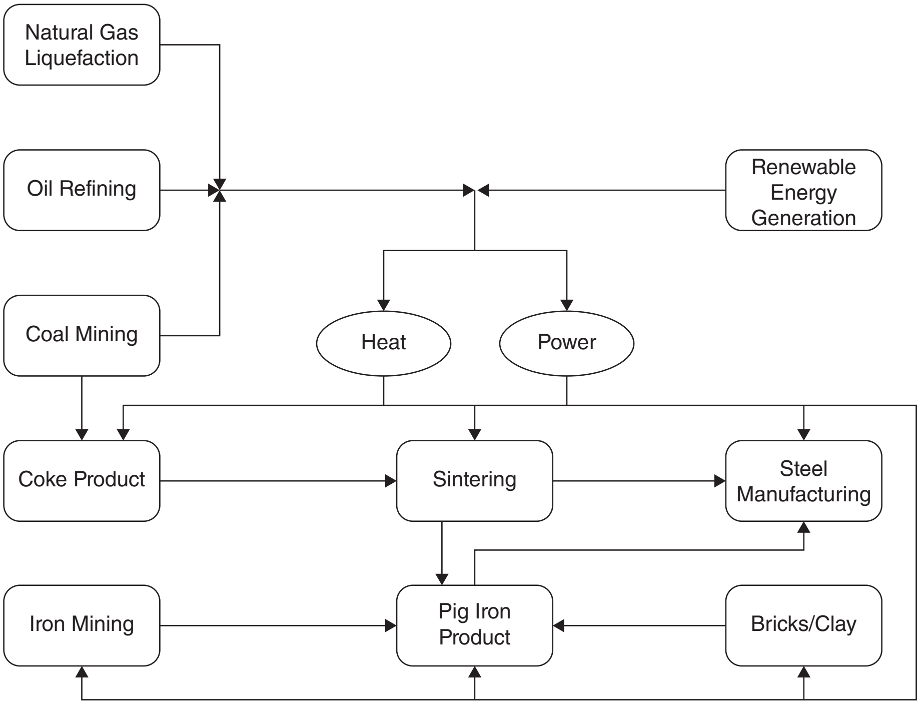


Figure 4.4 *Interacting networks of products and processes.*

focus is to discuss LCA for analyzing interactions between engineering systems and the environment through assessments of resource depletion and pollutant emissions. The learning objectives can be subdivided as follows.

1. Find the likely environmental impacts.
2. Structure pollutants under various impact characterizations.
3. Impact assessments.
4. Compare impacts between materials.

4.2 Policy Context

The policy landscapes are fast evolving by being more concerned about whole system impacts, such as the extended producer policy in which a producer's responsibility for a product is extended to the postconsumer stage of a product's life cycle, defined by OECD (2005)[2]. In this context, the decision maker must also systematically present the whole system impacts; hence the knock-on effects in the background system due to any changes in the foreground system and vice versa must be analyzed for any product or process development.

Modern lifestyle is chemical dependent. Chemicals contribute to household activities (energy appliances, clothes, food, beverages, polymers), pharmaceutical, petrochemical, agrochemical, industrial, etc. Throughout life cycles, chemicals have environmental impacts under various categories. Chemicals may cause global warming, stratospheric ozone layer depletion, acid rain, leaching to soil and water bodies (eutrophication), etc. These various environmental impact categories are commonly known as environmental impact characterizations, which is used in this text. In a broad sense, chemicals contribute to land, atmosphere and water environmental impacts. One of the earliest recognitions of environmental pollutions was by Dangerous Substances Directives, as follows, to regulate discharges to water bodies[3]. Because the earth's water body is connected through rain and soil water absorption, pollutants spread very quickly by water.

The Environmental Protection Act 1990 – for discharges from severe pollutants from industrial processes.
The Water Resources Act 1991 – for discharges to water.
The Water Industry Act 1991 – for discharges to sewer.

These first set of Directives were to limit the concentration and/or the total amount of priority pollutant categories, also known as List I substances, given in Table 4.1.

4.3 Life Cycle Assessment (LCA)

In the 1960s, the life cycle assessment (LCA) technique was applied to energy analysis; however, a group of researchers were commissioned by Coca Cola Amatil around the same period to study the resources and environmental profile of the different packaging materials they used for their products[3]. The impacts of pollutants turned out to be more severe than estimated. The majority of chemicals is related to one or more categories of environmental pollutants. Understanding the impacts of chemicals under various environmental categories or characterizations can help identifying and eliminating them at their sources, if possible at the first instance. If not, chemicals must be treated and regulated before their discharge to the environment.

By the mid-1980s the multicriteria systematic analysis had spread to include many more products. Different terms were used to describe these studies, the term Life Cycle Assessment was proposed and agreed upon at a workshop held by the Society of Environmental Toxicology and Chemistry (SETAC) at Vermont, USA, in 1990. SETAC have since published various guides and advice material on LCA simplification and methods.

The definition of Life Cycle Assessment as given by the *International Organization for Standardization* (ISO) in 1997 is:

> Compilation and evaluation of the inputs, outputs and the potential environmental impacts of a product system throughout its life cycle.

According to *ISO standards 14040, 14041 and 14044*, the LCA is carried out in four phases: Goal and Scope definition, Inventory analysis, Impact Assessment and Interpretation[4–6]. All these phases are interdependent as a result of one phase

Table 4.1 *List I of priority pollutant categories.*

1. Organohalogen compounds	For example, CCl_4 used as refrigerant, fire extinguisher, degreasing and dry cleaning agent. Its use declined in recent times due to its effect on stratospheric ozone depletion.
2. Organophosphorous compounds	Phosphates in fertilizer (though insoluble in water) can adhere to soil particles and erode into water bodies.
3. Organotin compounds	Chemicals of hydrocarbons and tin (Sn) generally used as a heat stabilizer in polyvinyl chloride, biocide, wood preservative, antibiofouling agent. Their toxic effects are detrimental to marine lives (1 ng L^{-1})
4. Compounds with carcinogenic properties in aquatic environment	Polycyclic aromatic hydrocarbons have toxic and carcinogenic properties and occur by natural and anthropogenic activities.
5. Mercury and its compounds	Organic mercury is more harmful than inorganic mercury, for human body (brain, nervous system and kidney and more harmful for youngsters). Occurs from rain, rock, soil, thermochemical process of coal and smelting processes.
6. Cadmium and its compounds	Categorized as Category 2 carcinogen by National Occupational Health and Safety Commission. Exposure limit in work place 0.01 mg m^{-3} and 0.002 mg m^{-3} for drinking water. They are present in ores, coal and other fossil fuels and in products, tobacco, fertilizer, PVC, petrol, tires, electronic components, batteries, textile dyes and ceramic glazes.
7. Mineral oils and hydrocarbons of petroleum origin	Fossil hydrocarbons in oil and petrochemical products have environmental impacts in all categories.
8. Synthetic substance in water	Pesticides, solvents and water-borne chemicals are the biggest threat to the fresh water supply and damaging to human reproductive systems.

determining the execution of the next phase. Figure 4.5 shows the different phases involved in an LCA study. Figure 4.6 illustrates the documents published by the ISO and an example of a life cycle management framework developed by 3M, 1997, for the assessments of risks and opportunities throughout the various stages of a product's life cycle.

Life cycle stages include compiling inventories over the complete supply chain, providing a service or product extending from the "cradle" of primary resources – fossil and metal ores, for example – through to the "grave" of recycling or safe disposal; the term "life cycle" also includes the service life of the capital goods needed for a product or process. In the sequence of steps conventionally followed in carrying out an LCA, compiling the material and energy balance is termed

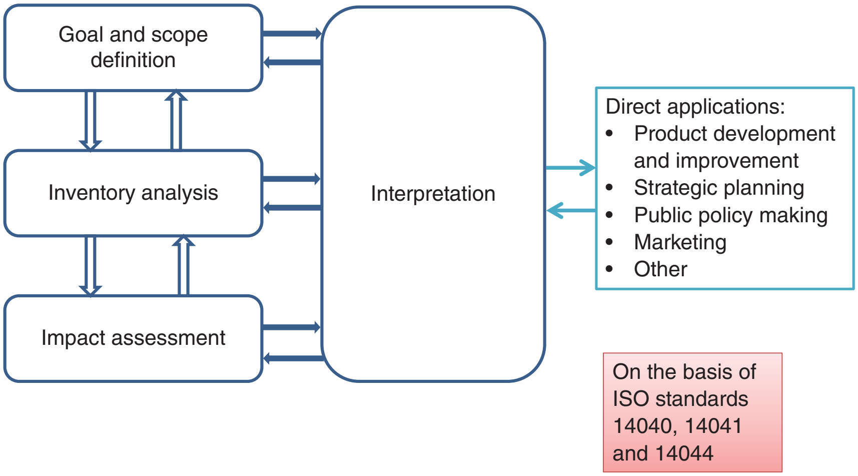


Figure 4.5 *LCA study stages*[4–6].

June 1997	ISO 14040 Life cycle assessment – principles and framework
October 1998	ISO14041 Life cycle assessment – goal and scope definition and inventory analysis
March 2000	ISO 14042 Life cycle assessment – life cycle impact assessment
March 2000	ISO 14043 Life cycle assessment – life cycle interpretation
2002	ISO/TS14048 Life cycle assessment – data documentation format

				Customer needs	
LCM stage impact	Material acquisition	R&D operations	Manufacturing operations	Use	Disposal
Environment					
Energy/Resources					
Health					
Safety					

Figure 4.6 *(above) LCA documents published by the International Organization for Standardization (ISO). (below) 3M, 1997, developed a Life Cycle Management framework for the assessment of risks and opportunities throughout the various stages of a product's life cycle.*

the *Inventory* phase. Apart from the extended system boundary, an inventory analysis differs from a conventional material and energy balance analysis by the need to include trace flows of species whose environmental significance is large, for example, because they have high human or ecotoxicity. There are two terminologies often used in LCA, LCI and LCIA. LCI refers to *Life Cycle Inventory* and LCIA refers to *Life Cycle Impact Assessment*. A study is not an LCA study when the study includes a goal and scope definition and inventory analysis, but not the impact assessment. This is then referred to as an LCI analysis. An LCIA includes an impact assessment, but not necessarily the interpretation. The LCA must include transparent and systematic discussions on all four stages.

It is more common to find chemicals with more profound (or primary) effects on one or more impact characterizations than others (secondary, tertiary, etc.), more commonly known as mid-point and end-point impacts. Pollutants with primary impacts are included in an impact characterization. Several pollutants have mid-point impacts on various characterizations. However, only primary effects of pollutants are considered to avoid double counting in most LCA studies. In Section 4.8, the various life cycle impact assessment (LCIA) methodologies are shown. A study can include a combination of primary, mid- and end-point impacts. Inclusion of mid- or end-point impacts in the LCIA methodology calls for robust reasons for doing so.

The effect of greenhouse gases (GHGs) such as CO_2, CH_4, N_2O, CFC (chlorofluorocarbon), etc., emissions on various levels is explained[3]. These gases absorb solar infrared radiation. Different gases have different abilities to absorb radiation. These gases create a GHG effect in sending the radiation to the earth's surface (Figure 4.7). Earth then absorbs some of this radiation energy and sends back the rest to the atmosphere. This exchange of radiative force between earth and GHGs in the atmosphere is regarded as a primary effect. The change in radiative force is expected to change the global temperature level, known as global warming and regarded as a secondary effect. The global warming effect is not uniform on the earth's surface, causing ice to melt, raised sea levels and severe weather patterns. These effects are known as tertiary effects. Once again, the consequences of tertiary effects on human health and ecological systems vary from place to place. The result may be changes in biodiversity in various ecosystems and impacts on food availability, agricultural patterns, society and economics. Having long chains of cause and effect, describing the environmental effects in a quantitative manner all the way through to the effects on the later stages in geographically segregated regions becomes impossible. As a result, LCIA is mostly done at a primary impact level or mid-point level (see Section 4.8: LCIA Methods).

The global warming potential (GWP) of a gas is determined by the infrared absorption capacity of the gas, which is related to the chemical structure and physicochemical properties of the gas. Similarly, all other impact characterizations depend on physicochemical properties of chemicals. Governed by molecular properties of chemicals, different chemicals have different levels of environmental impact characterizations. Over a 100 year period, methane gas has 25 times more GWP than carbon dioxide gas. Therefore, factors are used to provide an environmental impact characterization in relative

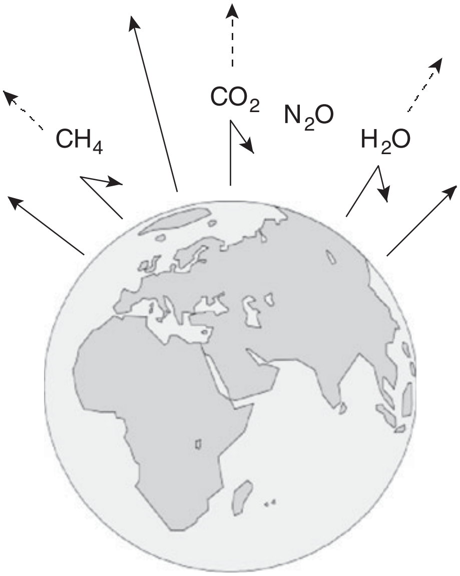


Figure 4.7 GWP impact of GHGs.

terms compared to a base chemical with an assumed value of 1 in the environmental impact characterization. Hence, methane gas has a global warming impact characterization factor of 25, over a 100 year period, implying that one unit mass of methane gas has 25 times more intensive global warming impact than the unit mass of carbon dioxide.

Quantities are then associated with each pollutant impacting on every category. These factors are called equivalence factors/equivalents/potentials/category indicators (according to the ISO standard)/characterization factors. Characterization factors are more commonly used in this text. The characterization factors depend on physicochemical properties of pollutants and are provided in relative terms compared to a base pollutant (assumed to have a value of 1 in an impact category). As shown, CO_2 is a base pollutant for the GWP impact category, that is, its GWP impact characterization factor is 1. All other pollutant GWPs are presented relative to CO_2. The GWP of CH_4 is 25 CO_2 equivalent and that of chlorofluorocarbons (CFCs) is 5000 CO_2 equivalent, over a 100 year lifespan.

Their units are represented in terms of: CO_2 equivalent, for example, kg CO_2 equivalent. Various notations used are CO_2 eq., CO_2-eq., etc.

The GHGs have different lifespans and therefore a basis of 25, 100 and 500 years is generally assumed over which the total GWP is predicted.

The volatile organic compounds (VOCs) are carbon containing compounds that take part in photochemical reactions. The VOCs do not include carbon dioxide, carbon monoxide, carbonic acid, metallic carbide, carbonates and ammonium carbonates. VOCs react with NO_x in the presence of sunlight to produce ozone and photochemical pollutants, such as peroxyacetyl nitrate (PAN), formaldehyde and acetic acid in the lower atmosphere. These pollutants and ozone in the lower atmosphere are responsible for urban smog and ground level ozone formation and are classified under photochemical oxidant creation potential.

NO_x (excluding N_2O) has primary effects on acidification and eutrophication potential impact categories. All these environmental impacts discussed are around ecological consequences. Most chemical pollutants also have primary impacts on human health. Depletion of quality and quantity of resources, for example, fossil energy, mineral and ores in earth, land and water, is also a reality and must be considered with due importance, in the context of growing population, energy demands and needs for sustainable lifestyles. Broadly, there are three classifications of environmental impacts of chemicals: resource use, human health and ecological consequences. Table 4.2 shows the most common impact characterizations responsible for environmental consequences that can be assessed. Table 4.3 shows the links between the various types of inventory stressors and their primary and secondary environmental impacts[3].

Table 4.2 Broad impact characterizations.

Resource Use	Human Health	Ecological Consequences
1. Energy (can also be subdivided into fossil and renewable) 2. Water 3. Land 4. Abiotic (ores) depletion	1. Toxicological impacts 2. Nontoxicological impacts 3. Work environment impacts	1. Global warming 2. Ozone depletion 3. Acidification 4. Eutrophication 5. Photochemical oxidant creation 6. Aquatic, human, terrestric ecotoxicity 7. Biodiversity

In evaluating the environmental impact characterization factors, no geographical segregation is considered. Henceforth, assessment of the environmental impact characterization factors, generally restricted up to the primary and mid-point levels of impacts can be applied to analyze life cycle impacts of any products or process systems, irrespective of geographic locations. The following sections explain the various calculation stages of the LCA.

4.4 LCA: Goal and Scope Definition

The goal and scope definition is the first step of LCA. A decision maker sets out objectives of interest for LCA study. The objectives need to be consistent with the intended application. The goal and scope definition involves identification of:

1. Functional unit
2. System definition
3. System boundaries

This phase also includes product definition, coproduct and waste utilization routes, any allocation method considered, LCIA methodology selected, database sources, year and geographic location.

> The functional unit is the unit of analysis for the study, and it provides a basis for comparison if more than one alternative is being studied. It should be defined in terms of the **service(s)** provided by any product, process, or activity under analysis.

An example often used to describe a *functional unit* is use of nappies by two babies. Nappies can be used up at various rates. In order to obtain average representative rates of use, the rates can be calculated based on uses over six months or longer. A functional unit can then be presented as the mass of nappies used in six months by each baby.

To compare between two or more washing liquids, the *functional unit* can be the mass of washing done per unit mass of a washing liquid. The functional unit of a system to be studied is associated with the service provided, for comparison

Table 4.3 Inventory stressors and environmental impacts.

Inventory Stressor	Initial Impact	Secondary Impact
Acid emission	Acid rain	Acidified lakes
Photochemical oxidants	Smog	Health impairment
Nutrients	Eutrophication	Bogs
Greenhouse gases	Global warming	Sea level rise
Ozone depletors	Ozone depletion	Skin cancer
Toxic chemicals	Toxic effect	Health impairment
Solid waste	Land consumption	Habitat destruction
Chemicals to groundwater	Groundwater impact	Health impairment
Fossil fuel use	Resource depletion	

Table 4.4 Transferable forms for comparison of LCA results between competing systems.

Item	Basis: 1	CPE (MJ)	GWP (g CO_2 eq.)
N fertilizer (urea)	kg	49.25	2940
P fertilizer (triple superphosphate)	kg	18.81	1160
K fertilizer	kg	5.6	380
Diesel	MJ	1.114	74.4
Electricity mix	MJ	2.597	173.4
Natural gas (NG)	MJ	1.016	61.2
Liquified petroleum gas (LPG)	MJ	1.06	76.4
Fuel oil	MJ	1.11	94.9
Hexane	kg	37.5	861
Methanol	kg	12.872	2836
Hydrogen	kg	183.2	11888
Soy meal	kg	4.13	726

with other systems. Issues of durability and maintenance should be taken into account for a realistic comparison between the same functional products.

In a goal and scope definition, system boundaries, LCIA methods and purpose must be defined with clear justifications. These will relate to audience and uses of a study. Assumptions, data availability, limitations and the quality of data are important to acknowledge for a system definition. It is important to recognize important impact categories for assessment at an early stage of an LCA. The supply of any component if changed from one region to another can affect impacts in accompanying categories. Thus, geographic regions need to be mentioned. System boundaries can show life cycle stages of productions and any transport involved.

Table 4.4 shows an example of *transferable form* for comparison. To compare between nitrogen fertilizers, a common basis of the mass of nitrogen in a fertilizer rather than the mass of the fertilizer should be selected. If the fertilizer (e.g., urea) is not in the pure form, then 1 kg of nitrogen can be selected as a basis for comparison between N based fertilizers. The unit that is highly dependent on the type of system or functionality to compare can be chosen to reflect the function or service for which a product has been produced. For example, 1 MJ of energy output from each of diesel, electricity, natural gas, LPG and fuel oil products may be compared in terms of the cumulative primary energy (CPE) use and GWP over 100 years. Likewise, if hydrogen rich gases produced from various flowcharts are to be compared for environmental impacts, the amounts of individual gas streams containing 1 kg of hydrogen can be taken as a basis. Thus, 1 kg of hydrogen production is the common basis (functional unit) for comparison of environmental impacts between various gas streams.

Figure 4.8 shows the boundary of an integrated crop and residue based biorefinery system. Assumptions, data availability, limitations and the quality of data are important to acknowledge for a system definition. It is important to recognize important impact categories for assessment in LCA that can be done at any stage and included in the goal and scope definition later. Assumptions and applicability of data over geographic regions and time scales must also be defined. The supply of any component if changed from one region to another may affect impacts in accompanying categories. Generally, 20 years and 100 years of time horizons are chosen for environmental impact assessment. In Figure 4.8, the system boundary shown considers the subsoil preparation outside the boundary, because the subsoil preparation occurs once before a given crop can be grown annually, when a steady state can be assumed, which is further explained in the section on land use.

Various cradle to grave system boundaries, such as for anaerobic digestion of sewage sludge for agricultural and energy generation applications, solar organic photovoltaic (OPV) glass manufacturing system and solar OPV cell manufacturing system, which can be considered within the goal and scope definition of the corresponding systems, are shown in Figures 4.9(a) to (c). The boundaries here are shown for the interactions between systems and the environment in terms of material and energy resource depletion and emissions to the environment. This is the convention followed in process engineering. However, in LCA, it is unnecessary to show such interactions between systems and the environment, because interactions are common: material resource (including land and water), primary energy resource and emissions to atmosphere, water and land.

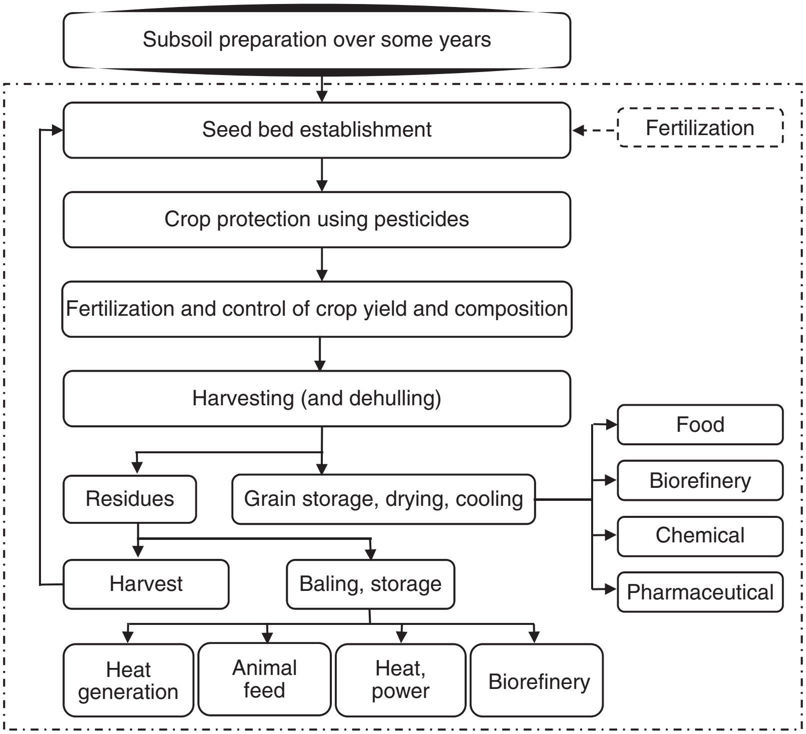


Figure 4.8 *Boundary of an integrated crop and residue based biorefinery system.*

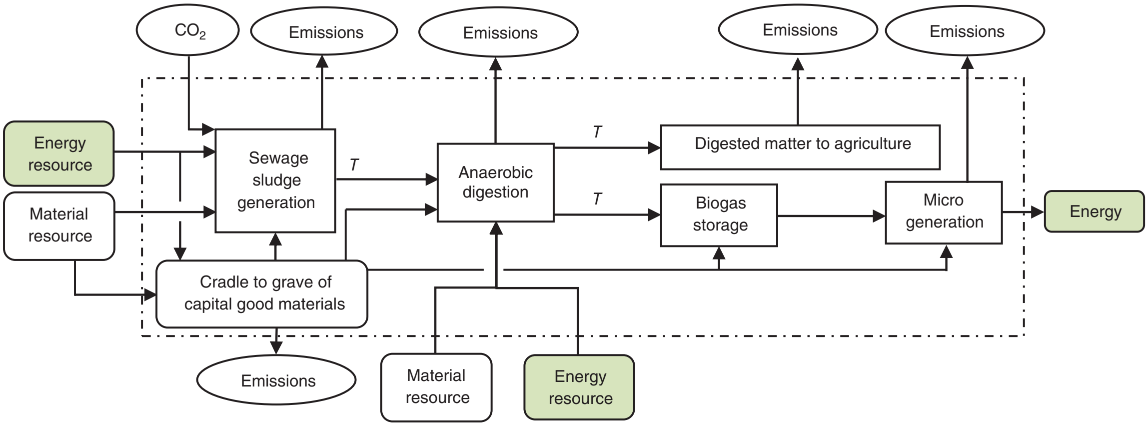


Figure 4.9(a) *Interactions between anaerobic digestion of sewage sludge system and the environment for LCA. T stands for transport.*

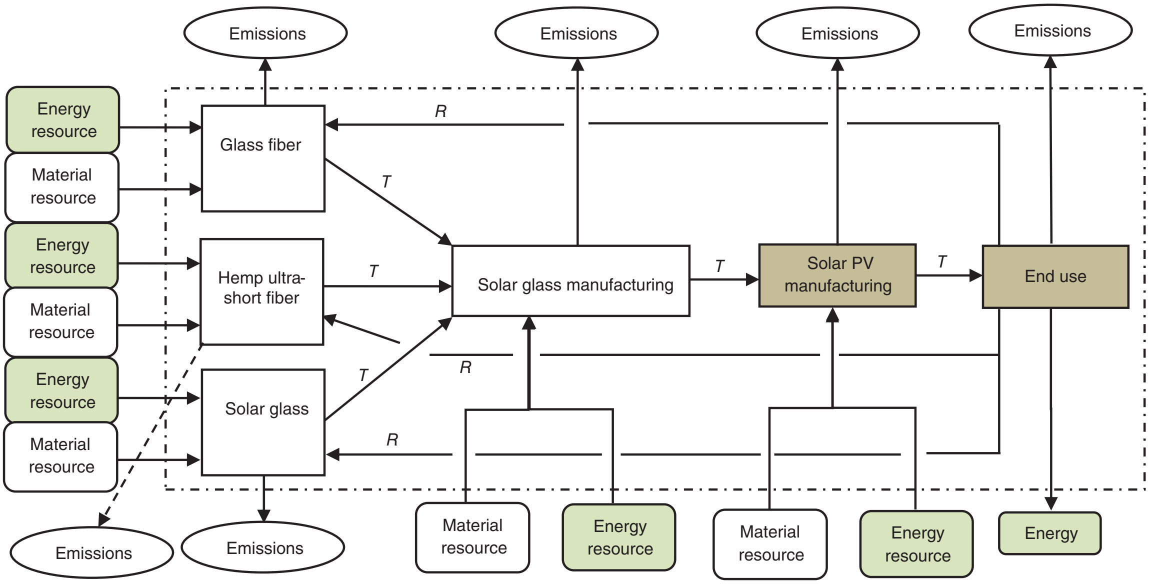


Figure 4.9(b) *Interactions between solar organic photovoltaic (OPV) glass manufacturing system and the environment for LCA. T stands for transport. R stands for recycle. T and R also cause resource depletion and environmental emissions. Only a part of the impacts from the "Solar PV manufacturing" and "End use" blocks that is due to solar glass manufacturing is considered within the system boundary.*

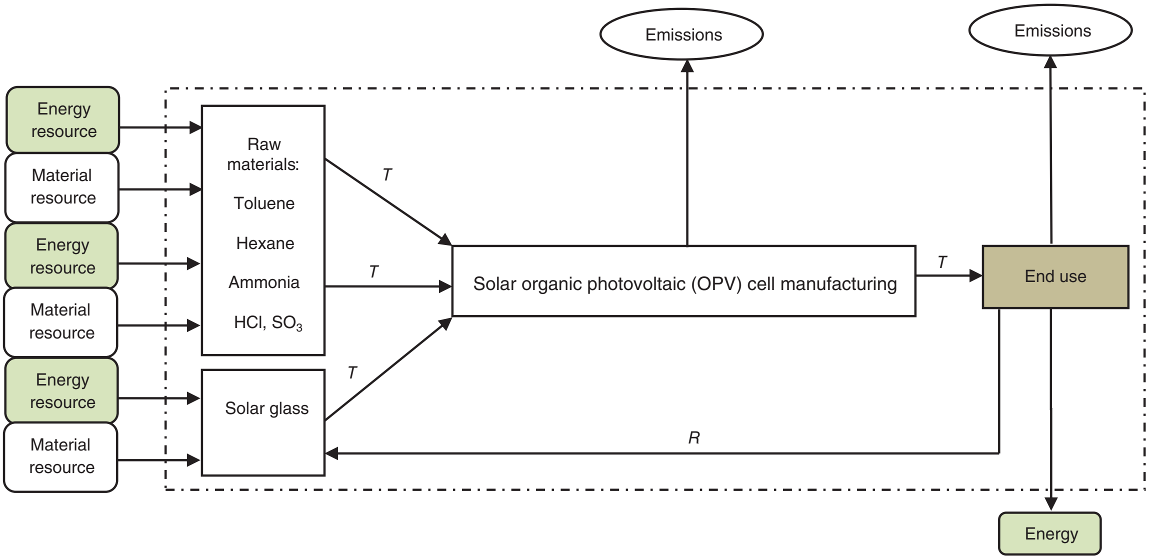


Figure 4.9(c) *Interactions between solar OPV cell manufacturing system and the environment for LCA. T stands for transport. R stands for recycle. T and R also cause resource depletion and environmental emissions.*

4.5 LCA: Inventory Analysis

The inventories are stressors or pollutants causing environmental impacts under various categories. Their analysis is about inlet and outlet mass and energy flow analysis. The inventory analysis is to identify each block of a process life cycle, for example, Figures 4.1 to 4.3, and to quantify the material and energy inputs and outputs for each of these stages.

The inventory analysis includes the following steps, detailed definition of the system, data collection, allocation and quantification of the environmental burdens. Each of the steps in the flowchart in Figures 4.1 to 4.3 can be expanded to look into substeps and to establish the mass and energy flows in and out of the boxes from/to the environment. Further, the compositions of streams emitted to water, land and air must be estimated for the assessment of impacts under various categories. This step may involve simulation/data collection/modeling of each box (e.g., fertilization and control of the crop yield step in Figure 4.8). The environmental burdens (B_j) can be quantified for each step, shown as

$$B_j = \sum bc_{j,i}x_i \tag{4.1}$$

where $bc_{j,i}$ is the burden j from the process i, while x_i is the mass or energy flow associated with that activity. The calculation is further explained by using example problems from biorefinery systems.

Broadly, there are three categories of environmental impacts: resource use, human health and ecological consequences (Table 4.2). They include:

1. Global impacts (global warming, ozone depletion, eutrophication, aquatic ecotoxicity)
2. Regional impacts (acidification)
3. Local impacts (photochemical oxidant creation, biodiversity).

These impact categories are further discussed in the Impact Assessment section.

Various LCI databases exist: Ecoinvent, ILCD/ELCD (ILCD: International reference Life Cycle Data system and ELCD: European reference Life Cycle Database), US-LCI, national ones such as in Australia and older ones include Buwal, IDEMAT, etc. In order to make an LCA study report transparent, the year of data publication, data source and the geographical relevance should be included. The data sets are adaptable and to bridge a gap may exist for process blocks.

Exercise 1. Draw a flowchart schematic with an inventory analysis for a wheat bioethanol plant consisting of processes shown in Table 4.5. The feedstock and raw material consumption rates on a daily basis and production specifications of various processes are shown in Table 4.5[7].

Table 4.5 *Basis for wheat bioethanol process flowsheet mass balance for Exercise 1. (Reproduced with permission from Sadhukhan et al. (2008)[7]. Copyright © 2013, Elsevier.)*

Process Unit	Feedstock	Product	Other Raw Materials	Specification
Milling (hammer)	Wheat: 340 kt	Milled wheat	–	–
Liquefaction	Milled wheat	Liquified grain	Process water	625.6 kt
			Sodium hydroxide	1.70 kt
			Calcium chloride	0.41 kt
			α-Amylase	0.28 kt
Saccharification	Liquified grain	Fermenter feed	Sulfuric acid	0.73 kt
			Glucoamylase	0.37 kt
Fermenter	Fermenter feed	Fermenter product: 88.27% CO_2 rich stream	Yeast	0.07 kt
CO_2 recovery	CO_2 rich stream	CO_2: 90%	–	–
Centrifugation	fermenter product	Ethanol rich stream: 74.68% Waste stream	–	–
Ethanol production	Ethanol rich stream	Ethanol: 17.934%	–	–
Rotary dryer	Waste stream	DDGS: 38.59%	–	–

Solution to Exercise 1. Figure 4.10 shows the flowchart schematic with an operational inventory analysis of a wheat bioethanol plant consisting of processes shown in Table 4.5.

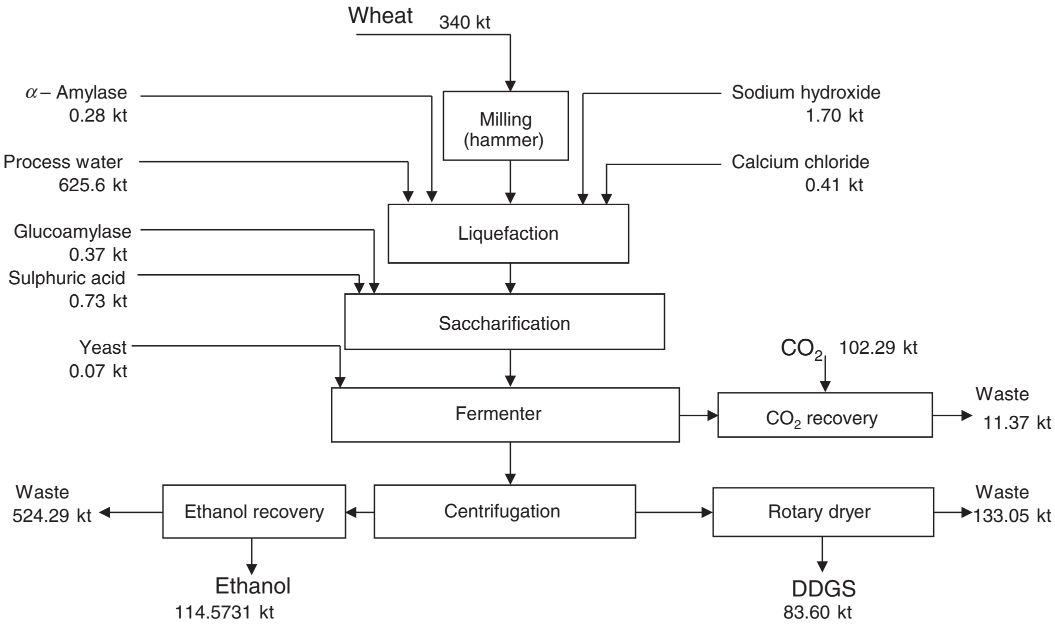


Figure 4.10 *Inventory analysis of wheat to bioethanol production plant operation. (Reproduced with permission from Sadhukhan et al. (2008)[7]. Copyright © 2013, Elsevier.)*

Exercise 2. The mass and energy distribution for a wheat bioethanol and straw combined heat and power (CHP) system in the UK is given in Table 4.6[8].

a. Complete the wheat bioethanol and straw CHP system mass and energy balance for a functional unit of 1 hectare of land use for the cultivation, shown in Figure 4.11(a). Sketch the system with completed operational inventory data.

Table 4.6 *Stream data for Exercise 2. (Reproduced with permission from Martinez-Hernandez et al. (2013)[8]. Copyright © 2013, Elsevier.)*

Subsystem	Product	Yield	LHV (GJ t^{-1})
Wheat cultivation	Wheat	6.96 t DM ha^{-1}	18.6
	Straw[a]	3.49 t ha^{-1}	14.6
Bioethanol plant	Ethanol	0.34 t t^{-1} (DM wheat basis)	26.7
	DDGS	0.25 t t^{-1} (DM wheat basis)	18.2
Straw CHP plant (processes 60% of the total straw cultivated)	Electricity	1060 kW h t^{-1} (straw basis)	
	Heat	567 kW h t^{-1} (straw basis)	

[a] Total amount of straw cultivated before soil retention; 40% of this amount is retained in the soil for enriching nutritional value.

DDGS: dried distillers grains and solubles.

DM: dry matter.

LHV: lower heating value (*c.f.* Section 10.2.2).

1 GJ = 304.2 kW h based on 8000 operating hours per year. This is based on the following calculation: 1 GJ = $\frac{10^6}{3600} \times \frac{365 \times 24}{8000}$ kW h.

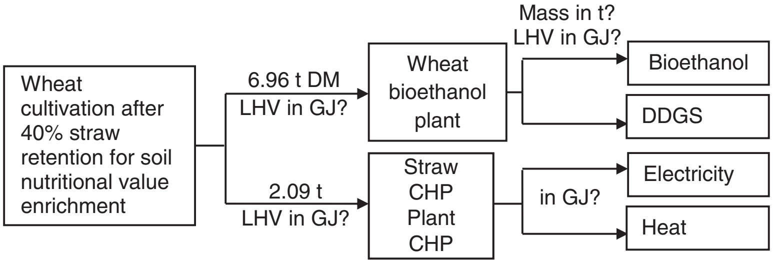


Figure 4.11(a) *Development of wheat bioethanol and straw CHP system mass and energy balance.*

b. Repeat the calculation for a functional unit of 100 t d^{-1} of bioethanol production. Sketch the mass and energy flow diagram. Calculate the land use for the production of 100 t d^{-1} of wheat bioethanol in the UK.
c. Calculate the energy efficiency of the straw based CHP plant.
d. Calculate the energy efficiency of the wheat bioethanol plant, if only bioethanol is used as an energy product.
e. In 2010 in the UK, there were 1.2 million hectares of land available for wheat cultivation. The CHP requirement from the biomass in the UK was 48.2 PJ y^{-1} (1 petajoule = 10^{15} joule). Estimate the percentage contribution potential of CHP from the available wheat straw.

Solution to Exercise 2

a. Figure 4.11(b) shows the completed mass and energy balance on the flowchart on the basis of 1 hectare.
b. Hint: the basis a functional unit of 100 t d^{-1} of ethanol production. Multiply all the mass and energy values in Figure 4.11(a) by 42.26 (obtained from 100/2.37). The UK land requirement for the production of 100 t d^{-1} of wheat bioethanol is 42.26 hectares.
c. The energy efficiency of the straw based CHP plant = 37% (obtained from the energy balance in Figure 4.11(b): $(7.3 + 3.9)/30.6 \times 100$).
d. The energy efficiency of the wheat bioethanol plant is 49%, if bioethanol is only used as an energy product (obtained from the energy balance in Figure 4.11(b): $63.2/129.5 \times 100$). All the energy inputs and outputs other than the wheat energy input and bioethanol energy output are neglected.
e. The UK straw CHP generation per unit land is 11.2 GJ per hectare (Figure 4.11(b)). Thus, the excess straw CHP energy yield is: $11.2 \times 1.2 = 13.44$ PJ y^{-1} from 1.2 million hectares of land available for wheat cultivation. The percentage contribution potential of CHP from the available wheat straw towards UK's total CHP requirement of 48.2 PJ y^{-1} is 28%.

Process simulation can also be used for data extraction for an inventory analysis. An example of the use of Aspen Plus, a process simulator, for the impact assessment of a bio-oil based methanol and a bio-oil based Fischer–Tropsch (FT) liquid synthesis plant[9,10] is shown as follows in Exercise 3.

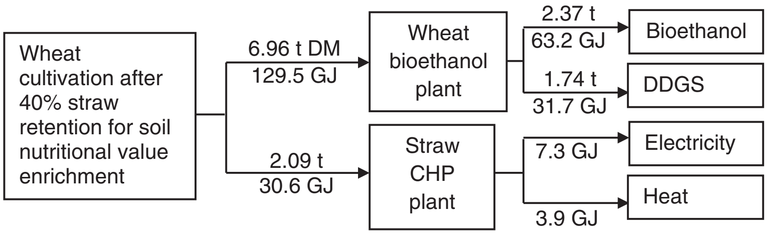


Figure 4.11(b) *A wheat bioethanol and straw CHP system mass and energy balance on the basis of 1 hectare land use.*

Exercise 3. The inventory analysis of a bio-oil based methanol and a bio-oil based Fischer–Tropsch (FT) liquid synthesis plant is shown in Figure 4.12. The details of these process simulations and technoeconomic analyses are available in Ng and Sadhukhan (2011)[9, 10] and Sadhukhan and Ng (2011)[11]. A portion of CO_2, 0.75 kg per kg of bio-oil separated by Sulfinol unit (from the "Heat recovery, Water gas shift and Gas cleaning block" in Figure 4.12) is capture-ready and, therefore, is not accounted for in the plant GWP impact. CO_2 along with water vapor and nitrogen (in air) in the exhaust gas is emitted to the atmosphere after combined heat and power (CHP) generation. Calculate the GHG impact from the exhaust gas for the given plant capacity.

Mass fraction of exhaust gas	Methanol synthesis	FT synthesis	GHG impact kg CO_2 eq.
CO_2	0.16	0.17	1
H_2O	0.15	0.13	0.08218
N_2	0.69	0.7	
Exhaust gas, kt d^{-1}	57	37	
GHG impact, kt CO_2 eq. d^{-1}	9.9	6.7	

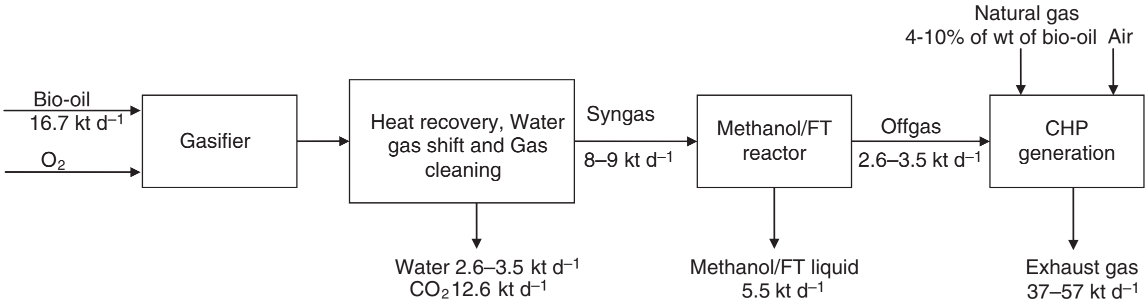


Figure 4.12 *Simulation results of kt CO_2 eq. d^{-1} bio-oil based methanol and a bio-oil based Fischer–Tropsch (FT) liquid synthesis plants for the impact assessment. The GHG impact (in kt CO_2 eq. d^{-1}) from the exhaust gas for the given plant capacity calculated is shown in the inset table.*

Solution to Exercise 3. Figure 4.12 shows the problem data and the inset table shows the solution in terms of the GHG impact from the exhaust gas.

The mass fractions and flow rates of the exhaust gases from the methanol and FT liquid synthesis centralized plants are shown in Figure 4.12. CO_2 and water vapor contribute to the GWP by a total of $(57 \times 0.16 + 57 \times 0.15 \times 0.08218) = 9.9$ kt CO_2 eq. d^{-1} or $(9.9/16.7) = 0.6$ kg CO_2 eq. kg^{-1} of bio-oil and 6.7 kt CO_2 eq. d^{-1} or 0.4 kg CO_2 eq. kg^{-1} of bio-oil from methanol and FT synthesis centralized plants, respectively.

Exercise 4. A biomass boiler can use straw/wood/RDF (refuse-derived fuel) fuels to produce 50 MW energy output. The ultimate analyses of the fuels are shown in Tables 4.7 to 4.9, respectively. If the fuels are fully combusted in the presence of a stoichiometric amount of oxygen, estimate the composition and the GWP of the exhaust gas resulting from the combustion of the fuels. Assume that nitrogen, sulfur and chlorine present in the fuels do not contribute to the GHG emissions. Assume that ash is removed completely in the solid phase from the biomass boiler.

Solution to Exercise 4. To calculate the emissions resulting from the process operation, mass balance and energy efficiency are used in the first place. The basis assumed in this case is 50 MW of energy output.

Table 4.7 *Proximate and ultimate analyses of straw. (Reproduced with permission from Sadhukhan et al. (2009)[12]. Copyright © 2009, American Chemical Society.)*

Proximate Analysis (wt%)		Ultimate Analysis (wt%)	
Moisture	8.5	C	36.57
Volatile matter	64.98	H	4.91
Fixed C	17.91	O	40.7
Ash	8.61	N	0.57
LHV, MJ kg^{-1}	14.6	S	0.14

Table 4.8 *Proximate and ultimate analyses of wood[12].*

Proximate Analysis (wt%)		Ultimate Analysis (wt%)	
Moisture (after long storage)	25	C	51.8
		H	5.7
Ash (dry basis)	1.1	O	40.9
LHV (dry basis), MJ kg^{-1}	19.3	N	0.1

Table 4.9 *Proximate and ultimate analyses of RDF.*

Proximate Analysis (wt%)		Ultimate Analysis (wt%)	
Moisture	50	C	45.5
Volatile matter	79.6	H	5.8
Fixed C	10	O	37.8
Ash	10.5	N	0.3
		S	0.2
LHV, MJ kg^{-1}	17.73	Cl	0.4

An energy efficiency value should be assumed to determine the biomass feed flow rate from its lower heating value (LHV). The energy efficiency that is calculated using the equation below is found to be 40–45% for combined heat and power (CHP) generation from a biomass[12]:

$$\text{Energy efficiency of CHP generation from biomass} = \frac{\text{Output energy generation}}{\text{Energy input in biomass}} \tag{4.2}$$

Based on a realistic assumption of an energy efficiency of 0.4 of the biomass CHP plant, the mass flow rates of straw (LHV = 14.6 MJ kg^{-1}), wood (19.3 MJ kg^{-1}) and RDF (17.73 MJ kg^{-1}) biomass feedstocks required are calculated as follows.

Assume 8000 operating hours per year. Then

$$\frac{50}{0.4 \times 14.6} \times 3600 \times \frac{8000}{365} \times \frac{1}{1000} = 675\ \text{t d}^{-1}\ \text{straw feedstock}$$

$$\frac{50}{0.4 \times 19.3} \times 3600 \times \frac{8000}{365} \times \frac{1}{1000} = 511\ \text{t d}^{-1}\ \text{wood feedstock}$$

$$\frac{50}{0.4 \times 17.73} \times 3600 \times \frac{8000}{365} \times \frac{1}{1000} = 556\ \text{t d}^{-1}\ \text{RDF feedstock}$$

However, the energy efficiency is not a flat number for any type of biomass feedstock. For more precise results, a rigorous process simulation must be undertaken to determine the energy efficiency for specific biomass processing plants for a range of given operating conditions.

Table 4.10 *Emissions to atmosphere, land and water from the operation of 50 MWe of electricity generation plant for the three types of biomass.*

Emissions to:	Pollutant[1] or Component[2]	Straw ($t\ d^{-1}$)	Wood ($t\ d^{-1}$)	RDF ($t\ d^{-1}$)
Atmosphere	[1]CO_2	906	728	923
	[2]N_2	1029	1110	2050
Land	[2]S	0.9	0	1.1
	[1]Ash	58	6	58
Water	[1]Effluent	35.6	32.4	28.9
	Total oxygen (air) requirement	649 (2786)	548 (2350)	719 (3085)

Hence, the following emissions result from the fuel combustion into 50 MW energy generation:
Straw: 906 t CO_2 d^{-1}
Wood: 728 t CO_2 d^{-1}
RDF: 923 t CO_2 d^{-1}

Table 4.10 shows the emissions to atmosphere, land and water from the operation of 50 MWe of an electricity generation plant using mass balance based on the three types of biomass selected. The exhaust gas has primarily carbon dioxide and steam generated from carbon and hydrogen combustion, respectively. Several other assumptions are required.

Nitrogen present in the biomass leaves along with the exhaust gas as gaseous nitrogen. Hence there is no atmospheric emission impact associated with the processing of nitrogen embedded in the biomass body. Though the impact of nitrogen and other GHGs will be significant, if inventories for fertilizer production for biomass growth are considered.

Sulfur present in the biomass is converted into hydrogen sulfide that is generally removed during gas clean-up. Hence, the exhaust gas is free of any sulfur compound. The hydrogen sulfide removed is finally recovered as metallic sulfur using the Claus process. Hence, there is no associated sulfur emission in the exhaust gas from the operation of a biomass boiler.

Land emission from a biomass CHP plant operation results from the ash present in the biomass. A small percentage of the land emissions can be leached into the aqueous body. Metallic components present in the biomass can also be emitted to land and water.

Component Balance

Carbon. The carbon content of the biomass (C in weight %, obtained from the ultimate analysis given in Tables 4.7 to 4.9) is converted into carbon dioxide. The molar mass of carbon dioxide is 44 and that of carbon is 12.

$$CO_2 \text{ mass flow rate in t d}^{-1} = \frac{(C)}{100} \times \frac{44}{12} \times \text{Biomass feedstock mass flow rate in t d}^{-1} \tag{4.3}$$

Sulfur. Sulfur (S in weight % in Tables 4.7 to 4.9) in a biomass feedstock is recovered as a solid product using the sulfur recovery unit via the production of hydrogen sulfide.

$$\text{S mass flow rate in t d}^{-1} = \frac{(S)}{100} \times \text{Biomass feedstock mass flow rate in t d}^{-1} \tag{4.4}$$

Ash. Ash (*Ash* in weight % in Tables 4.7 to 4.9) in a biomass feedstock is disposed to land.

$$\text{Ash mass flow rate in t d}^{-1} = \frac{(\text{Ash})}{100} \times \text{Biomass feedstock mass flow rate in t d}^{-1} \tag{4.5}$$

Water. Hydrogen present (H in weight % in Tables 4.7 to 4.9) in a biomass is combusted to generate steam. This steam and moisture present (H_2O in weight % in Tables 4.7 to 4.9) in the body of a biomass give rise to condensate after energy recovery.

$$\text{Effluent purge flow rate in t d}^{-1} = 0.1 \times \left(\frac{(H)}{100} \times \frac{18}{2} + \frac{(H_2O)}{100} \right) \times \text{Biomass feedstock mass flow rate in t d}^{-1} \tag{4.6}$$

Some negligible amount of hydrogen is used up by the sulfur and chlorine present in the biomass. After effluent purge (10% by mass of the condensate), the remaining condensate is recovered as boiler feed water (BFW). An equal amount of fresh BFW is required to make up for the lost amount. Moisture can also emit with the exhaust gas in some process configurations without heat recovery from the exhaust gas. Some industrial systems still adopt this to maintain a required chimney length for releasing exhaust gas to the atmosphere. The downside of such a process is the lost opportunity for heat recovery, resulting in lower energy efficiency. The molar mass of water is 18 and that of hydrogen is 2.

Oxygen. The oxygen required is calculated from the balance of stoichiometric oxygen required for the combustion of carbon and hydrogen present in the biomass and the oxygen available (O in weight % in Tables 4.7 to 4.9) in the biomass.

$$\text{Oxygen required in t d}^{-1} = \left(\frac{(\text{H})}{100} \times \frac{16}{2} + \frac{(\text{C})}{100} \times \frac{32}{12} - \frac{(\text{O})}{100}\right) \times \text{Biomass feedstock mass flow rate in t d}^{-1} \tag{4.7}$$

The source of oxygen is air.

$$\text{Air required in t d}^{-1} = \frac{\text{Oxygen required in t d}^{-1}}{32} \times \frac{(0.79 \times 28 + 0.21 \times 32)}{0.21} \tag{4.8}$$

The atomic mass of oxygen required to combust 1 mole of hydrogen (molar mass = 2) into 1 mole of water is 16. The molar mass of oxygen to combust 1 mole of carbon (molar mass = 12) into 1 mole of carbon dioxide is 32. Assume that air consists of 79 volume or molar % of nitrogen and rest of oxygen. Molar mass of nitrogen is 28 and that of oxygen is 32. A part of the oxygen is produced from the air separation unit (ASU).

For straw:

$$\text{Oxygen produced from the ASU in t d}^{-1} = 0.5 \times \text{Biomass feedstock mass flow rate in t d}^{-1} \tag{4.9}$$

For wood:

$$\text{Oxygen produced from the ASU in t d}^{-1} = 0.67 \times \text{Biomass feedstock mass flow rate in t d}^{-1} \tag{4.10}$$

For RDF:

$$\text{Oxygen produced from the ASU in t d}^{-1} = 0.61 \times \text{Biomass feedstock mass flow rate in t d}^{-1} \tag{4.11}$$

Nitrogen. The source of nitrogen outlet from a biomass based energy generation plant to the atmosphere is that supplied with the air and that present in the biomass feedstock (N in weight % in Tables 4.7 to 4.9), shown in the following equation:

$$\begin{aligned}&\text{Nitrogen outlet flow rate in t d}^{-1}\\ &\quad = \frac{\left(\text{Oxygen required in t d}^{-1} - \text{Oxygen produced from the ASU in t d}^{-1}\right)}{32} \times \frac{0.79 \times 28}{0.21}\\ &\quad + \frac{(\text{N})}{100} \times \text{Biomass feedstock mass flow rate in t d}^{-1}\end{aligned} \tag{4.12}$$

Chlorine in the case of RDF can be removed during process clean-up.

Exercise 5. Biomass gasification processes are commonly integrated to gas turbine for combined heat and power (CHP) generation. Figure 4.13 shows a biomass integrated gasification combined cycle (BIGCC) flowsheet configuration.

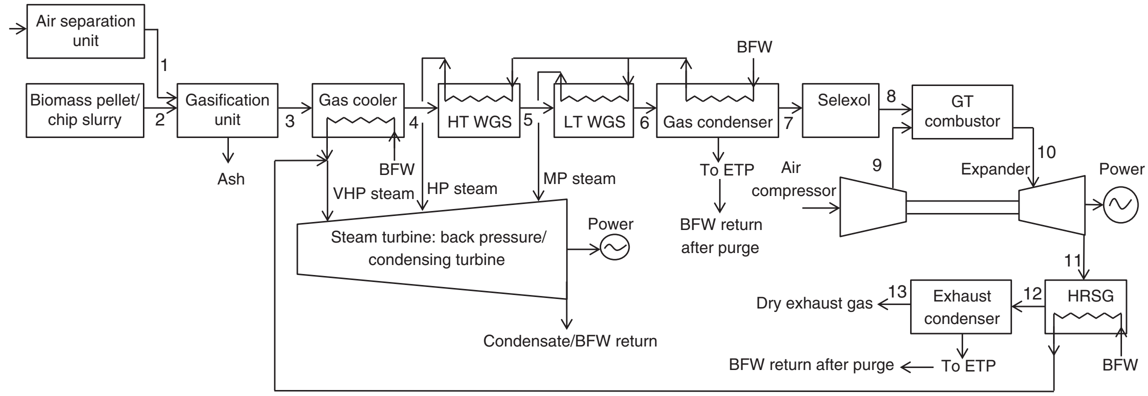


Figure 4.13 *Biomass integrated gasification combined cycle (BIGCC) flowsheet configuration. BFW, boiler feed water; ETP, effluent treatment plant; GT, gas turbine; HRSG, heat recovery steam generator; HP, high pressure; MP, medium pressure; VHP, very high pressure.*

Simulate the BIGCC process flowsheet based on the process models shown in Table 4.11[10]. Table 4.12 shows the correlations for the yields of products: gas, tar and char from biomass primary pyrolysis or devolatilization[12]. Primary pyrolysis or devolatilization is a common occurrence as soon as biomass comes in contact with the hot bed in the gasifier. Biomass breaks down into gas, tar and char products. Gas and tar are steam gasified into a product gas. Char could be combusted in a separate combustor to supply the reforming heat in the gasifier. Alternatively, char could be gasified in the same gasifier. The product gas from the steam gasifier after purification mainly consisting of carbon monoxide and hydrogen is called syngas.

Determine the mass and energy inventories of the BIGCC plant operations for straw, wood chip and refuse-derived fuel (RDF). The proximate and ultimate analyses of straw, wood and RDF are shown in Tables 4.7 to 4.9, respectively.

The solution of this exercise problem is given in the ***Online Resource Material in the Companion Website: Case Study 1.***

4.6 LCA: Impact Assessment

In this phase, the results from the inventory analysis are used to evaluate the potential of different environmental impacts. The inventory data are converted into environmental effects by multiplying a flux of an inventory with an impact characterization factor. The impact characterization factor of an environmental load (or substance or chemical or pollutant) indicates its intensity to an impact category with respect to a reference substance. For example, methane's GWP impact characterization factor of 25 g CO_2 equivalent means that methane has 25 times more GWP compared to carbon dioxide. Various methodologies for LCIA exist, detailed in Section 4.8. Different extents of effects, such as primary, mid- and end-points, normalization, weighting and valuation are used in different LCIA methodologies. Different impact categories are also included in different LCIA methodologies. The assessment is done on the basis of the scope and goal defined for the study. The impact assessment can be carried out using the following steps:

1. Classification
2. Characterization
3. Normalization
4. Valuation.

In classification, inventory data are assigned to different impact categories. Various pollutants resulting from an inventory analysis are classified under various impact categories.

Table 4.11 *BIGCC flowsheet modeling. (Reproduced with permission from Sadhukhan et al. (2009)*[12]*. Copyright © 2009, American Chemical Society.)*

Unit Names	Modeling Framework	Process Specification
Gasification	Estimate pyrolysis or devolatilization product yield using EXCEL spreadsheet based model shown in Table 4.12. Use RGibbs reactor in Aspen Plus for the gasification of pyrolysis product into product gas.	Temperature = 900–950 °C. Desired product decides the system and the gasification operating pressure. Pressure = near atmospheric when integrating to fuel cell or 25–30 bar for combined cycle integration and fuel and chemical production.
Air compressor	Compressor Isentropic model in Aspen Plus.	Desired product decides the system and compressors' operating pressure. Isentropic efficiency = 75%.
Gas cooler and heat recovery steam generator (HRSG)	Cooler in Aspen Plus.	Temperature is just above the dew point of the gas/flue gas at the system/gasification pressure, such that single-phase gas still leaves the cooler/HRSG without requiring special design of the gas cooler/HRSG.
Gas or exhaust condenser	Flash2, two-phase flash separator in Aspen Plus.	Keep at or lower than the dew point of the gas, so as to dry the gas from the water present in the gas. After purification in the effluent treatment plant (ETP) and 10% purge, the rest of the water is recovered as boiler feed water (BFW).
High temperature water gas shift reactor (HT WGS)	REquil: Rigorous Equilibrium reactor based on stoichiometric approach in Aspen Plus.	Temperature = 450 °C at the system pressure. The water gas shift reaction is as follows: $CO + H_2O \rightleftharpoons CO_2 + H_2$
LT (low temperature) WGS	REquil in Aspen Plus.	Temperature = 350 °C at the system pressure.
Gas clean-up and carbon capture and storage; air separation unit	Sep2: two-outlet component separator based on component purity, flow, etc., for the site flowsheet simulation in Aspen Plus. Individual processes (such as Selexol) can be simulated in detail.	Specify the mole fraction of the component to be separated as 1 in the outlet pure gas.
Gas turbine (GT) combustor	REquil in Aspen Plus.	1300 °C temperature at the system pressure. This temperature restricts the NO_x emission. The combustion reactions of syngas include the following: $CO + 0.5O_2 \rightleftharpoons CO_2$ $H_2 + 0.5O_2 \rightleftharpoons H_2O$ $CH_4 + 2O_2 \rightleftharpoons CO_2 + 2H_2O$
GT expander	Turbine Isentropic model in Aspen Plus.	Exit pressure = Near atmospheric but allowing pressure drop across HRSG. Isentropic efficiency = 75–90%.
Steam gasifier in allothermal gasification	RGibbs reactor in Aspen Plus. Gas and tar yields from the spreadsheet based pyrolysis or devolatilization product yield modeling (Table 4.12) are to be entered as feedstock to the steam gasifier model in Aspen Plus.	Temperature = 900–950 °C. Desired product decides the system and the gasification operating pressure. Pressure = near atmospheric (when integrating to fuel cell) or 25–30 bar (IGCC, fuel and chemical production).
Char combustor cooler	Cooler in Aspen Plus.	Temperature is above the dew point of the flue gas at atmospheric pressure, such that single-phase gas still leaves the cooler without requiring special design of the cooler.
Direct quench	Flash2, two-phase flash separator in Aspen Plus.	Kept at or lower than the dew point of the gas, so as to dry the gas from the water present in the gas. After effluent treatment and 10% purge, the rest of the water is recovered as BFW.
Char combustor in allothermal gasification	RGibbs reactor in Aspen Plus. Char yield from the spreadsheet based pyrolysis or devolatilization product yield model entered as feedstock to the char combustor model in Aspen Plus.	About 50 °C higher temperature than steam gasifier to maintain the temperature gradient and supply exothermic heat of the combustion reaction to the steam gasifier.

Table 4.12 *Correlations for the yields of products: gas, tar and char from biomass primary pyrolysis or devolatilization*[12].

Component	kg per kg biomass
Total devolatilization	0.96
Total gas	0.48
H_2	0.00
CH_4	0.02
C_2	0.12
CO	0.22
CO_2	0.03
H_2O	0.08
Tar	Total devolatilization – Total gas
Char	1 – Total devolatilization

The characterization factors are assigned to them according to their relative contributions to the environmental impacts. For example, for calculating the GWP, the contribution of methane or any other GHG is given in relation to the impact of CO_2. Some of the impact categories are the GWP over 20, 50 or 100 years, eutrophication potential (EP), acidification potential (AP), ozone depletion, human toxicity and aquatic toxicity. The environmental impact can be calculated using.

$$E_k = \sum\nolimits_{j=1}^{J} ec_{k,j} B_j \tag{4.13}$$

where $ec_{k,j}$ is the relative contribution of burden B_j (j is the index for pollutant; J is the total number of pollutants) to environmental impact E_k (k is the index for impact category.

In normalizing, impacts are represented with respect to the total emissions in certain areas or over a period of time. This can be useful to assess the potential effects of the activity on a regional or global environment. However the normalization results are not always reliable due to lack of reliable data for many impacts.

Valuation is the final step of impact assessment wherein relative importance of each impact is determined on the basis of a value or weight assigned to it. The environmental impacts (EI) can be aggregated into a single environmental impact function, shown as

$$EI = \sum\nolimits_{k=1}^{K} w_k E_k \tag{4.14}$$

where w_k is the relative importance of E_k and K is the total number of environmental impact strategies.

The commonly occurring pollutants from power plants are carbon dioxide, methane, chlorofluorocarbons (CFCs), VOCs, nitrous oxide, nitrogen oxides (NO_x) and sulfur dioxide. Figure 4.14 shows commonly occurring atmospheric pollutants and their characterization factors, resulting in various environmental impacts. The characterization factors depend on physicochemical properties of pollutants and are provided in relative terms compared to a base pollutant (assumed a value of 1 in an impact category). For example, CO_2 is a base pollutant for the GWP impact category, that is, its GWP characterization factor is 1.

One of the most effective sets of primary impact characterizations and their units, developed by CML, are shown in the following list from the Institute of Environmental Sciences, Leiden University, Netherlands. A spreadsheet with the primary impact characterization factors of all tested chemicals is freely available from their website. Various other

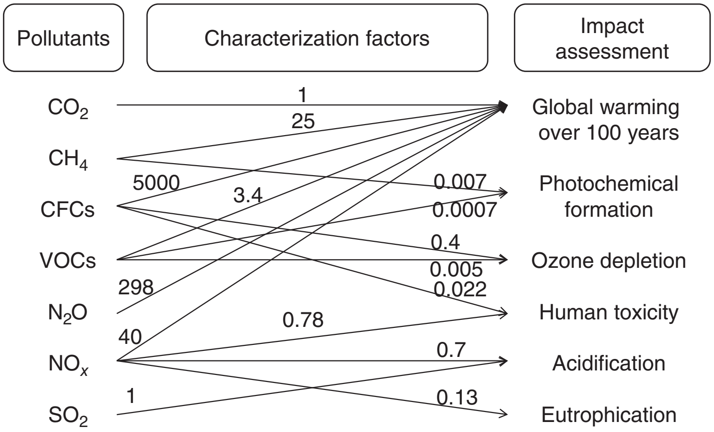


Figure 4.14 *Pollutants with characterization factors resulting in various environmental impacts.*

sources of characterization factors are available[13–20]. 1,4-Dichlorobenzene (DCB) is used as the base chemical for the toxicity categories. The various impact categories for assessment are discussed thereafter.

Resources
1. Abiotic depletion element (kg Sb equivalent)
2. Abiotic depletion fossil (MJ)

Emissions
1. Global warming potential (kg CO_2 equivalent)
2. Acidification potential (kg SO_2 equivalent)
3. Eutrophication potential (kg phosphate equivalent)
4. Ozone layer depletion potential (kg R-11 equivalent; chlorofluorocarbon-11 or CFC-11 or refrigerant-11)
5. Photochemical oxidant creation potential (kg ethylene equivalent)
6. Freshwater aquatic ecotoxicity potential (kg DCB equivalent)
7. Human toxicity potential (kg DCB equivalent)
8. Marine aquatic ecotoxicity potential (kg DCB equivalent)
9. Terrestric ecotoxicity potential (kg DCB equivalent)

4.6.1 Global Warming Potential

The global warming potential (GWP) of all pollutants is presented relative to CO_2. The GWP of a pollutant is the ratio between the infrared absorption by the pollutant and the infrared absorption by an equal amount of CO_2. The GWP of CFCs is 5000 over a 100 year lifespan. Their units are also represented in terms of CO_2 equivalent, for example, kg CO_2 equivalent. The GHGs have different lifespans and therefore a basis of 20, 100 and 500 years is generally assumed over which the total GWP is predicted. In evaluating the environmental impact characterization factors, there is no geographical segregation considered. Henceforth, these environmental impact characterization factors, generally restricted up to the primary level of impacts, can be applied to analyze life cycle impacts of any products or process systems, irrespective of geographic locations. The following section provides an assessment of environmental impact characterization factors using example problems. The other important impact categories of global importance for biorefinery systems are explained as follows.

4.6.2 Land Use

Land is an important resource used for renewable energy supply. Biomass uses land for energy and value-added productions. Even though the second generation residues use much less land than the first generation crops, there are land implications during their growth phase. Imagine an agricultural residue, for example, straw, husk, corn stover, sugarcane, etc., is used for energy generation. Without land, these residues cannot be grown. These residues should be used for value-added productions: bulk, fine and specialty chemicals, for which there is no alternative sustainable carbon source. For energy generation, however, land use could be reduced by tidal, hydro, wind, solar, geothermal, etc., alternative to biomass. Municipal wastes have least implication of land use amongst all lignocellulose or waste biomasses.

The type of land differs widely within a geographical boundary. High to low grass lands are used for animal grazing and high fertile lands are used for arable feed crops. Poultry and pigs live on arable crops and therefore rely on fertility of arable lands graded as 3a, while grass lands belong to grade 2. Land use for organically grown systems is more due to building of fertility of the land. From an energy efficiency and environmental impact point of view, the objective is to maximize energy yield, for example, in joules per unit land used, for example, per hectare. Exercise 2 shows the energy yield calculation per unit land use. Sustainable energy crops must use lesser land compared to lignocellulose.

However, fertilizers are needed for growing any kind of crops, arable or energy crops. Fertilizer production and emissions are the hot spots of biomass production systems. The key to successful biorefineries is to mitigate these hot spots and minimize land use for biomass growth and land transformation from it. Both the type of land used and the fertilization application decide the energy or crop yield per unit land used. Thus, within the subject of land use, the steps involved in the agriculture of crops are highlighted from input–output with respect to system boundaries and environmental footprint perspectives. An illustration of the steps involved in the agriculture of arable crops is shown in Figure 4.8. A measure of land use refers to the crop or energy yield per unit land use during a steady-state period of an agricultural system shown within the boundary in Figure 4.8.

Outside this boundary, to prepare a land for agriculture for the first time, the subsoil nutritional value is enriched by nitrogen (N), phosphorus (P) and potassium (K) fertilizer applications. During this time, the input and output of N, P, K around the land are not in balance. Once the land reaches the required maximum nutritional stage for seed bed establishment, a steady state or equilibrium is reached, when N, P, K inputs to the land (fertilizer applications) and outputs from the land (fixation within a plant body and emission to the atmosphere in the case of nitrogen) are in balance. During this time, crops stabilize to steady yields. This is the time for crop rotation. Amongst N, P, K fertilizers, P and K fertilizers remain in solid forms. Hence, these solids form the basis of constitution of higher plants and animals and eventually at the end of their life cycles through various chemicals and species they return to mining extraction, sea bed, etc., via sludge.

However, nitrogen may be emitted as the atmospheric nitrogen gas as well as in eight various forms of NO_x, of which nitrous oxide (N_2O), nitric oxide (NO) and nitrogen dioxide (NO_2) are the more commonly occurring ones. Because of denitrification of the soil, nitrogen fertilizer is applied periodically during a crop rotation period to keep up with the soil nitrogen balance. Once a crop is harvested, dehulled to recover grain, the grain is stored, dried, cooled and transported to various application points. A similar process applies to agricultural residues after dehulling from harvested grains. A part of the residues dehulled from the grain is bedded into the soil to particularly retain the soil carbon balance and other nutritional balances for the next phase of seed bed establishment. Additional fertilizer may be needed at this point to keep the steady balance of N, P, K. Also herbicide is used for crop protection over a rotation.

Figure 4.15 shows the cumulative primary energy and the GWP impacts from a *Jatropha* agricultural system. The inventory refers to the production of 4.21 t of *Jatropha* fruit per hectare of land.

Impacts from fertilizers are the most notoriously known for any agricultural system. The biggest hot spot identified from an agricultural system impact assessment is the application of fertilizer, still primarily sourced from fossil resources.

The field emissions due to NO_x, mainly N_2O, followed by NO and NO_2, and seed conditioning are the second worst impact hot spots. Because of the prominent effect of nitrogen oxides on the environment, many scientists look at the nitrogen footprint, especially for agricultural systems (due to the application of fertilizers), separately from other GHG emissions, but analogous to the carbon footprint to get an idea of the magnitude of the problem.

The GWP, carbon footprint and nitrogen footprint can be estimated from an inventory analysis, shown in the following exercise problem, for two types of fertilizers.

Exercise 6. Calculate the GWP impact and the carbon and nitrogen footprint for two types of fertilizers, ammonium nitrate and urea, for the data shown in Table 4.13.

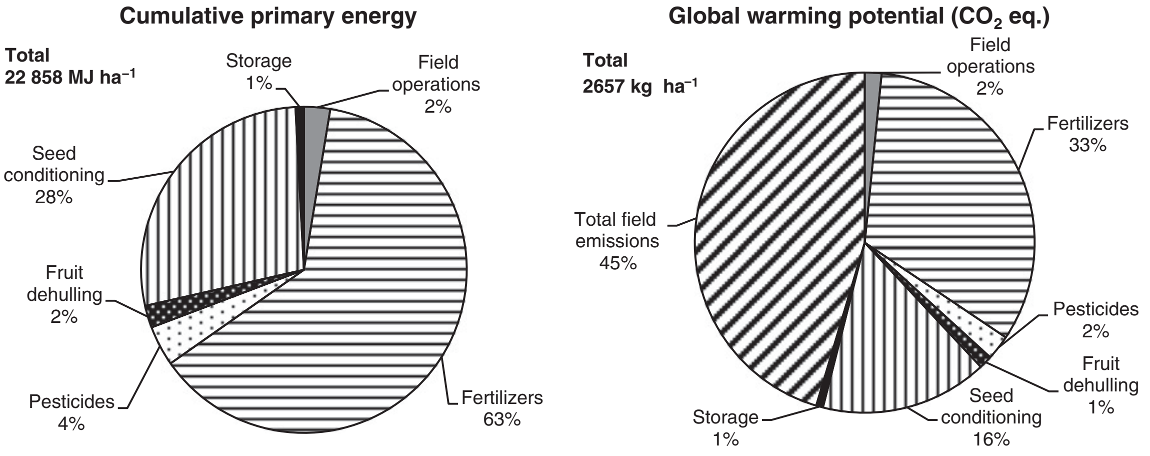


Figure 4.15 *Impact assessment of* Jatropha *fruit agricultural system for hot spot analysis on the basis of 1 hectare of land use.*

Table 4.13 *Pollutant emission data for ammonium nitrate and urea fertilizers and the characterization factors of the pollutants.*

	Pollutants					
Impact characterization factor	N_2O (kg)	CO_2 (kg)	VOC (kg)	CH_4 (kg)	NO_2 (kg)	CO (kg)
Global warming potential 100 years kg CO_2 eq.	298	1	3.4	25		1.9
Pollutant emissions	N_2O as nitrogen (kg)	CO_2 (kg)	VOC (kg)	CH_4 (kg)	NO_2 (kg)	CO (kg)
Ammonium nitrate as per kg nitrogen	0.005592	2.241140	0.000132	0.007007	0.002030	0.000690
Urea as per kg nitrogen	0.000008	2.713971	0.000123	0.008618	0.002310	0.000810

Solution to Exercise 6

GWP of ammonium nitrate

$$= \left(298 \times 0.005592 \times \frac{28+16}{28}\right) + (1 \times 2.241140) + (3.4 \times 0.000132) + (25 \times 0.007007) + (1.9 \times 0.000690)$$

$$= 5.0\ CO_2\text{ eq. per nitrogen, kg kg}^{-1}$$

GWP of urea

$$= \left(298 \times 0.000008 \times \frac{28+16}{28}\right) + (1 \times 2.713971) + (3.4 \times 0.000123) + (25 \times 0.008618) + (1.9 \times 0.000810)$$

$$= 2.9\ CO_2\text{ eq. per nitrogen, kg kg}^{-1}$$

Carbon footprint of ammonium nitrate

$$= [(1 \times 2.241140) + (3.4 \times 0.000132) + (25 \times 0.007007) + (1.9 \times 0.000690)] \times \frac{12}{44}$$

$$= 0.66\text{ carbon per nitrogen, kg kg}^{-1}$$

Carbon footprint of urea

$$= [(1 \times 2.713971) + (3.4 \times 0.000123) + (25 \times 0.008618) + (1.9 \times 0.000810)] \times \frac{12}{44}$$
$$= 0.8 \text{ carbon per nitrogen, kg kg}^{-1}$$

Nitrogen footprint of ammonium nitrate

$$= 0.005592 + \left(0.00203 \times \frac{14}{14+32}\right)$$
$$= 0.0062 \text{ nitrogen per nitrogen, kg kg}^{-1}$$

Nitrogen footprint of urea

$$= 0.000008 + \left(0.002310 \times \frac{14}{14+32}\right)$$
$$= 0.0007 \text{ nitrogen per nitrogen, kg kg}^{-1}$$

Regarding land use impacts, there are three terms frequently used,

1. *Land use.* This is a measure of the actual use of land per unit yield of biomass, sometimes referred to the dry matter (DM) of the biomass. Its unit is m^2 per kg yield of biomass or m^2 per kg yield of DM of biomass.
2. *Land transformation.* It is a value lower than the value of land use. A fraction of the total land used for a given service (bioenergy production) can be transformed from one type to another, for example, cutting forest into a forest road for transporting timber. The land transformation constantly happens due to production of food, fiber and energy.

   The land transformation can be contributed by a range of activities on arable land, forest, construction, dump sites, industrial, mineral extraction, pasture and meadow, sea and ocean, permanent crop, shrub land, tropical rain forest, rail, road, urban and artificial water bodies and courses. Figure 4.16 shows an overview of the types of land transformation.

   A decision must be made in terms of selecting the feedstock with minimum land use for a required service, for example, heat and power production. The unit of land use or land transformation can be:

   m^2 per m^3 of biomass produced,
   m^2 per kg of biomass produced,
   m^2 per MJ of biomass calorific value,
   m^2 per MJ of net energy production.

3. *Land occupation.* Land transformation data can be converted into land occupational data, by multiplying the land transformation with the number of years for which the land is used after transformation. Hence, the unit for land occupational data is:

   m^2 year per m^3 of biomass produced,
   m^2 year per kg of biomass produced,
   m^2 year per MJ of biomass calorific value,
   m^2 per MJ of net energy production.

On the basis of inventory data of 1 kg of wheat grain production and corresponding straw production, the land occupation is 0.159 m^2 year per kg of wheat grain production; 99% of this land occupation is in the arable nonirrigated land and the remaining 1% is in forest, intensive, normal. Taking account of the yearly rotation of the crop, the land transformation for 1 kg of wheat grain and corresponding straw production is 0.159 m^2 per kg of wheat grain.

Table 4.14 shows % contributions of various categories in Figure 4.16 in land occupation for wood production. The value of land transformation varies between 0.89 m^2 m^{-3} for soft wood to 1.89 m^2 m^{-3} for hard wood, respectively. If the lifetime of the infrastructure used is assumed as 100 years, the land occupation is 89 m^2 year per m^3 of soft wood and 189 m^2 year per m^3 of hard wood, respectively.

The land use of soft and hard wood is 7.5–13.5 m^2 m^{-3}.

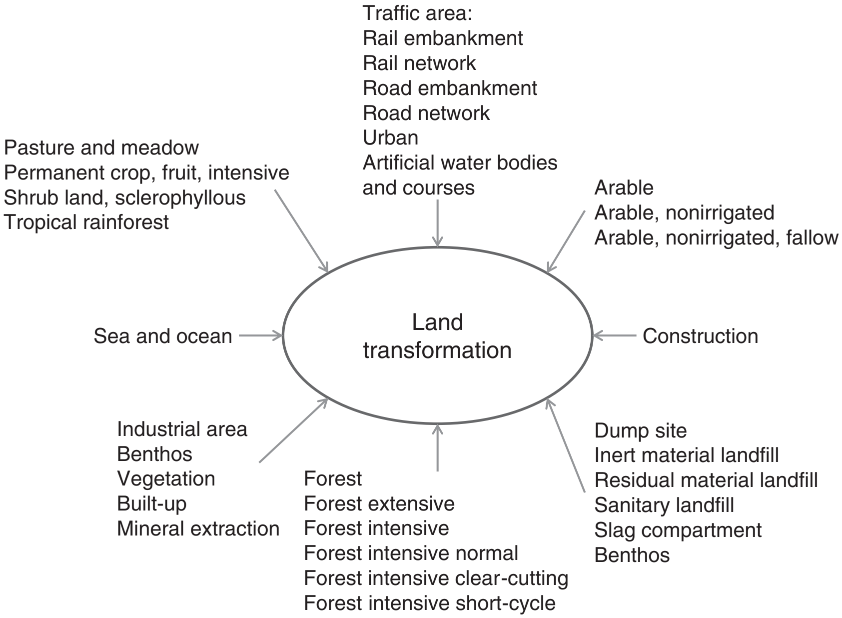


Figure 4.16 *Overview of land transformation types.*

Table 4.14 *The % contributions of various categories in Figure 4.16 in land occupation for wood production.*

Arable	0.00
Arable, nonirrigated	0.06
Arable, nonirrigated, fallow	0.00
Construction site	0.04
Dump site	0.50
Dump site, benthos	0.01
Forest, intensive	3.28
Forest, normal	87.52
Forest, short-cycle	0.00
Industrial area	0.18
Industrial area, benthos	0.00
Industrial area, built-up	0.84
Industrial area, vegetation	0.15
Mineral extraction site	1.49
Permanent crop, fruit, intensive	0.00
Shrub land, sclerophyllous	0.13
Traffic area, rail embankment	0.02
Traffic area, rail network	0.02
Traffic area, road embankment	0.95
Traffic area, road network	0.49
Urban, discontinuously built	0.00
Water bodies, artificial	0.39
Water courses, artificial	0.18

4.6.3 Resource Use

The implication of resource depletion must be understood, mainly that nonrenewables are compared to global reserves when using them for energy commodity productions. Nonrenewable resources including fossil resources, minerals and clays can only be regenerated within human lifetimes. The heaviest to lightest fossil resources are coal (also tar and heavy oils) > medium to light crude oils > natural gas. Unlike renewable resources, solar, wind and tidal, the nonrenewable resources are not continuously regenerated and are depleted over time. Therefore, the depletion of their reserves must be within control all the time and included in environmental impact characterization. The evaluation of the environmental impact characterization factors of nonrenewable resources is dependent on the energy efficiency of their conversion processes. The lower heating value (LHV: an indication of the transferable calorific value) of a nonrenewable resource and the efficiency of conversion processes into useful energy commodities can be multiplied to evaluate the output energy generation. Therefore, if the desired output energy and efficiency of conversion process are known, the nonrenewable resource depletion can be calculated.

Energy resource input (in MJ) × Efficiency of conversion process systems (in fraction) = Output energy generation (in MJ)

Like all other impacts, engineers need to understand the implication of resource depletion, mainly of nonrenewables, compared to global reserves when using them for energy commodity productions.

Exercise 7. Twenty-five million households with an annual average total heating and electricity demands (in the ratio of 2:1) of 172 15 kW h y^{-1} per household are to be supplied by coal and natural gas based energy systems, given in Table 4.15. It is proposed to build city level centralized and household–community level decentralized energy conversion systems. This high level analysis is aimed at assessing whether the resources available are adequate for meeting the household energy demand for two scenarios, the lowest cost scenario and the lowest GHG emission scenario. The LHV of coal and natural gas, the conversion system efficiency into electricity or heat generations, maximum resource supplies, cost ratio of systems compared to the lowest cost technology option and the GHG emission reduction potential are given in Table 4.15. The conversion systems under consideration are electricity generation without carbon capture and storage (CCS) using coal, heat generation using natural gas, electricity generation using natural gas and electricity generation with CCS using coal, from the lowest to the highest cost technology options, respectively. Determine the lowest cost scenario and the lowest GHG emission scenario in terms of the use of resource mix to meet the total household electricity and heat demands (1 PJ = 10^{15} J; 1 MT = 10^6 tonne).

Table 4.15 *Coal and natural gas data to supply household energy.*

	LHV (MJ kg^{-1})	Conversion into	Efficiency (%)	Resource Supply, (MT y^{-1})	Cost Ratio	GHG Emission Reduction (%)
Coal	28	Electricity without CCS	70	<40	1	0
		Electricity with CCS	36	<15	5	90
Natural gas	50	Heat	90	<14	2	40
		Electricity	70	<14	3	30
Electricity		Heat	90			

Solution to Exercise 7. The household electricity and heat demands on a yearly basis are calculated as follows:

Total household electricity and heat demands = $\left(25 \times 10^6\right) \times 17215 \times \frac{1000 \times 3600}{10^{15}} = 1549$ PJ y^{-1}
Total household electricity demand = $1549 \times \frac{1}{3} = 516$ PJ y^{-1}
Total household heat demand = $1549 \times \frac{2}{3} = 1033$ PJ y^{-1}

The maximum energy resource supply constraints from the lowest to the highest cost technology options are as follows:

Coal energy used for electricity generation without CCS = 40 × 28 = 1120 PJ y^{-1}
Natural gas energy used for heat generation = 14 × 50 = 700 PJ y^{-1}
Natural gas energy used for electricity generation = 14 × 50 = 700 PJ y^{-1}
Coal energy used for electricity generation with CCS = 15 × 28 = 420 PJ y^{-1}

Lowest Cost Scenario. For the lowest cost energy resource use scenario, electricity generation from coal without CCS is selected first, as the lowest cost option, to meet the entire electricity demand of households of 516 PJ y^{-1}.

The total potential for electricity generation from coal at 70% efficiency is 1120 × 0.7 = 784 PJ y^{-1}. After meeting the household electricity demand of 516 PJ y^{-1}, the balance of electricity available from coal without CCS, 268 PJ y^{-1}, is converted into 241 PJ y^{-1} of heat at an efficiency of 90%, assuming that the cost of heat generation from electricity is not considerable.

This consumes all 1120 PJ y^{-1} of coal available.

The balance of heat (1033 − 241 = 792 PJ y^{-1}) is supplied by a natural gas based heat generation system at first, followed by heat from a natural gas electrification system. The maximum amount of natural gas energy available for direct heat generation is 700 PJ y^{-1} and can generate 630 PJ y^{-1} of heat, at 90% energy efficiency. Thus, the remaining household heat demand of 162 PJ y^{-1} is to be supplied from the natural gas based electricity system.

Natural gas consumed for meeting the rest of the heat requirements (162 PJ y^{-1}) via electrification is $162/(0.7 \times 0.9) = 257$ PJ y^{-1}.

Natural gas remaining after meeting the heat requirement via electrification is 700 – 257 = 443 PJ y^{-1}.

The total amount of natural gas resources used is then 700 + 257 = 957 PJ y^{-1}. The coal to natural gas resource mix used to meet the total household heat and electricity demands is 1.2:1.

Table 4.16 shows the resource supply in terms of energy contents, output heat and electricity generations for households, energy efficiencies and the GHG emission reduction potential compared to the case of the coal energy system without CCS, where all GHGs are emitted to the atmosphere.

The evaluation shows that due to the mix of natural gas by 46% with the rest as coal, as the resources used, the overall GHG emission is reduced by 19% based on the output energy distribution. Overall 75% of energy efficiency is obtained. Note that the actual efficiency would be lower and GHG emission would be higher due to transmission losses, not taken into account in this high level analysis. The cost ratio shown is calculated on the basis of energy resource use as follows:

$$\frac{738 + 382 + 700 \times 2 + 257 \times 3}{2077} = 1.58$$

Lowest GHG Emission Scenario. For electricity generation, the order of preference of technologies for the lowest GHG emission scenario is the electricity generation from coal with CCS and electricity generation from natural gas, respectively.

For the heat supply, the order of preference for the lowest GHG emission scenario is as follows: heat generation from natural gas, heat generation from natural gas based electricity and electricity from coal with CCS systems, respectively.

Table 4.16 *Resource supply, output heat and electricity generations for households, energy efficiency and cost ratio, for the lowest cost resource use scenario.*

	Resource (PJ y^{-1})	Generation (PJ y^{-1})	Efficiency (%)	GHG Emission Reduction (%)	Cost Ratio
Coal without CCS electricity	738	516	70	0	1
Coal without CCS electricity – heat	382	241	63	0	1
Natural gas – heat	700	630	90	40	2
Natural gas electricity – heat	257	162	63	30	3
Total	2077	1549	75	19	1.58

Table 4.17 *Resource supply, output heat and electricity generations for households, energy efficiency and cost ratio, for the lowest cost resource use scenario.*

	Resource ($PJ\ y^{-1}$)	Generation ($PJ\ y^{-1}$)	Efficiency (%)	GHG Emission Reduction (%)	Cost Ratio
Coal with CCS electricity	420	151	36	90	5
Natural gas electricity	522	365	70	30	3
Natural gas – heat	700	630	90	40	2
Natural gas electricity – heat	178	112	63	30	3
Coal without CCS electricity – heat	461	291	63	0	1
Total	2281	1549	68	32	2.66

The resource use, output heat and electricity production for the household supply, efficiency, GHG emission reduction potential and cost implications for the lowest GHG emission scenario are shown in Table 4.17. The natural gas use as a resource compared to coal is higher by 1.6 times, for achieving the lowest emission energy scenario. Following the approach for the lowest cost scenario, try working out the solution for the lowest GHG emission scenario.

The GHG emission reduction potential is improved by 32% based on the output energy generation, with a cost implication (ratio) of 2.66 (based on the resource energy used). Only 10% of the output energy can be supplied from a 90% decarbonization technology, coal electricity generation with CCS.

4.6.4 Ozone Layer Depletion

The upper atmosphere called the stratosphere contains ozone that absorbs ultraviolet (UV) rays of the sun, which otherwise would have reached the lower atmosphere and surface of the earth. The ozone layer depletion implies thinning of the stratospheric ozone. UV rays cause skin cancer and endanger polar species. Destruction of ozone creates ozone holes (thinnest ozone layers) at the North and South Poles. The ozone layer depletion is a global problem and hence a global solution is required. NO_x emission is partly responsible for decomposing stratosphere ozone into oxygen:

$$\begin{aligned} O_3 + NO &\rightarrow NO_2 + O_2 \\ 2NO_2 &\rightarrow N_2O_4 \\ 2NO_2 &\rightarrow 2NO + O_2 \end{aligned} \tag{4.15}$$

The stratospheric ozone layer is also destroyed by halocarbons, for example, CCl_4, $CHCl_3$, CFCs that occur naturally by volcanic eruption, marine species and wood fire. This reaction occurs through chlorine, chlorine oxide or halogen radical formations. Catalyzed by these radicals, ozone breaks down into the oxygen molecule, which is not good for the upper atmosphere:

$$\begin{aligned} Cl\cdot + O_3 &\rightarrow ClO\cdot + O_2 \\ ClO\cdot + O &\rightarrow Cl\cdot + O_2 \end{aligned} \tag{4.16}$$

Trichlorofluoromethane, commonly presented as CFC-11, is known to display the highest stratospheric ozone depletion potential. CFC-11 used to be widely applied as a refrigerant due to its phase changing behavior at relatively low pressures compared to other refrigerants. However, due to the presence of chlorine and its associated damaging effect on the environment, its use was banned.

The stratospheric ozone depletion potential is well established for chlorinated and brominated compounds. However, this potential for other halocarbons is yet to be established. The convention is to present the stratospheric ozone depletion potential for any chemical relative to that of the CFC-11 assumed stratospheric ozone depletion potential of 1. If all other CFCs are grouped together, their stratospheric ozone depletion potential is ~0.4 in 100 years, relative to CFC-11. It is seen that CFC-11 has the highest stratospheric ozone depletion potential. Hence, all other chemicals have fractional

Table 4.18 *Inventory analysis in kg of chemicals, for ozone layer depletion on the basis of 1 kg of wheat grain production and corresponding straw production. (Reproduced with permission from GaBi and Ecoinvent database[21].)*

Benzene	4.4311×10^{-14}
Butadiene	4.1979×10^{-14}
Cadmium	2.2211×10^{-17}
Carbon dioxide, fossil	6.9965×10^{-9}
Carbon monoxide, fossil	8.2181×10^{-12}
Chromium	1.1106×10^{-16}
Copper	3.7758×10^{-15}
Dinitrogen monoxide	6.6634×10^{-14}
Ethylene oxide	4.0579×10^{-13}
Formaldehyde	3.4984×10^{-13}
Hydrogen chloride	1.9102×10^{-15}
Lead	4.4423×10^{-17}
Mercury	1.5548×10^{-19}
Methane, fossil	1.1106×10^{-13}
Nickel	1.5548×10^{-16}
Nitrogen oxides	3.1095×10^{-11}
Non-methane volatile organic compounds	1.4903×10^{-12}
Particulates, <2.5 μm	8.4403×10^{-14}
Selenium	2.2211×10^{-17}
Sulfur dioxide	2.2211×10^{-12}
Water	2.7541×10^{-9}
Zinc	2.2211×10^{-15}

stratospheric ozone depletion potentials relative to that of CFC-11 eq. The ozone depletion rate of these substances is considerable over the short term; hence their remediation must also mean controlling the emission of these substances.

Exercise 8. The inventory analysis of wheat cultivation includes the processes of soil cultivation, sowing, weed control, fertilization, pest and pathogen control, harvest and grain drying. Machine infrastructure and a shed for machine sheltering are included. Inputs of fertilizers, pesticides and seed as well as grain transports in the EU regional processing centre (10 km) are considered. The direct emissions on the field are also included.

Table 4.18 shows the cultivation inventory data of various chemicals that have impacts on ozone layer depletion[21]. The basis of inventory data is 1 kg of wheat grain production and a corresponding straw production. The same basis used in Exercise 2, 6.96 t of wheat grains per hectare and corresponding 3.49 t of straw per hectare production, can be assumed.

Figure 4.17 shows the group impact characterization factor of the chemicals in terms of kg CFC-11 eq. over a 5 to 40 year span. For the equation shown, y is the ozone depletion potential impact characterization factor of the chemicals in terms of kg CFC-11 and x is the number of years. The coefficient of determination (defined as $R^2 = 1 - \text{SSQ}/\text{summation}$ of square (SSQ) of variance) close to 1 shows a very good fit of the empirical equation given.

a. Calculate the total impact potential of the chemicals in kg CFC-11 eq. over a 100 year span generated from 1 kg of wheat grain production and corresponding straw production by extrapolation of the group impact characterization factor.
b. Calculate the impact potential of the chemicals in kg CFC-11 eq. over a 100 year span based on the characterization factor calculated in (a) from 1 kg of straw production. An economic allocation to impact potentials with an allocation factor of 92.5% to wheat grains can be assumed[21].

Solution to Exercise 8

a. Adding all the inventory analysis data of the chemicals, for ozone layer depletion on the basis of 1 kg of wheat grain production and corresponding straw production, shown in Table 4.18, the total inventory obtained is

$$9.79 \times 10^{-9} \text{ kg}$$

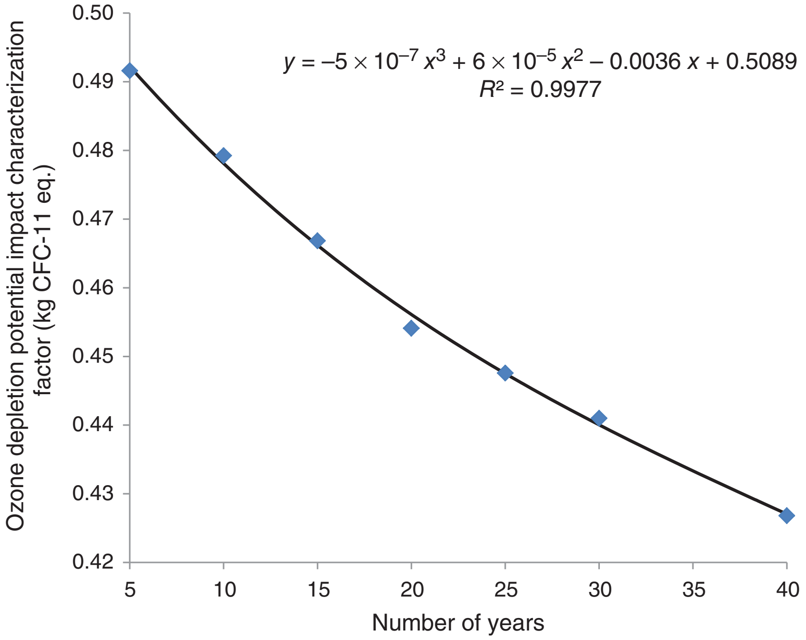


Figure 4.17 *Group impact characterization factor of the chemicals in terms of kg CFC-11 eq. over a 5 to 40 year span.*

By substituting 100 years in the place of x in the equation shown in Figure 4.17, the ozone depletion potential impact characterization factor (y) is calculated as

$$0.25 \text{ kg CFC-11 eq.}$$

The total impact of the chemicals in kg CFC-11 eq. over a 100 year span from 1 kg of wheat grain production and corresponding straw production is

$$9.79 \times 10^{-9} \times 0.25 = 2.44 \times 10^{-9} \text{ kg CFC-11 eq.}$$

Though extrapolation is perfectly feasible for the set of data provided, the reliability of the characterization factor obtained by extrapolation must be examined from physicochemical data and atmospheric science.

b. A kg of straw produced per kg of wheat = 3.49/6.96 = 0.5 kg.

Hence, 1.5 kg of wheat grain and straw produce 2.44×10^{-9} kg CFC-11 eq.

Hence, 1 kg of wheat grain and straw produce 1.63×10^{-9} kg CFC-11 eq.

Out of 1.63×10^{-9} kg CFC-11 eq. a $(1 - 0.925) = 0.075$ fraction can be allocated to the straw.

The ozone depletion potential impact of chemicals in kg CFC-11 eq. over a 100 year span, generated from 1 kg straw production is $1.63 \times 10^{-9} \times 0.075 = 1.22 \times 10^{-10}$ kg CFC-11 eq.

4.6.5 Acidification Potential

Sulfur and nitrogen oxides, SO_x and NO_x (except N_2O, which contributes to GWP), are generated from chemical processes and inefficient combustion processes. In addition, carbon oxides emit from the processes. These gaseous emissions dissolve in atmospheric moisture to form sulfurous, sulfuric, nitrous, nitric and carbonic acids, reducing the natural pH from 5–6 to 2–4 (acidic).

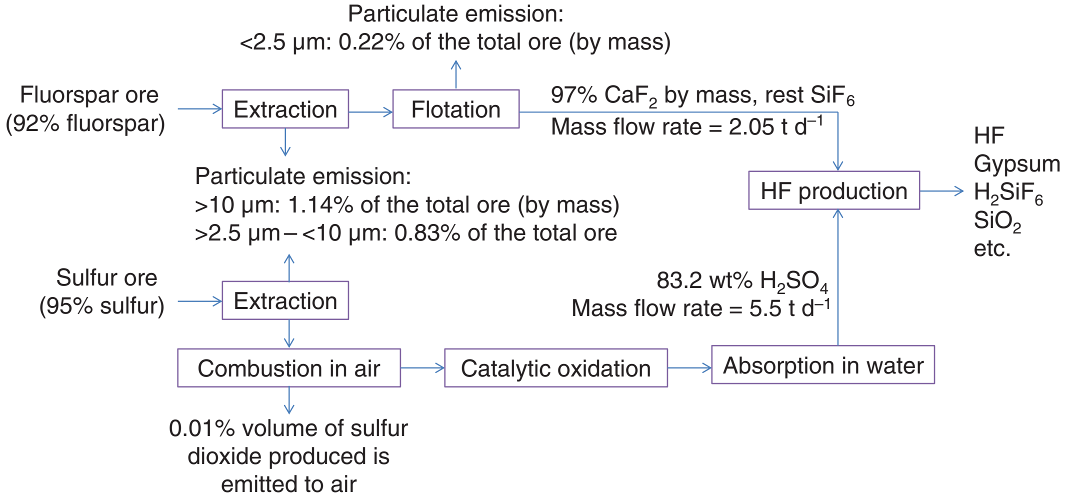


Figure 4.18 *Flow chart from sulfur and fluorspar ore extraction to the production of hydrogen fluoride and other products at the plant gate. The total ore includes both the fluorspar and sulfur ores.*

Acid rain or acidification is a regional problem as acidic clouds can travel. Scandinavia's acid rain is caused by emissions from the UK, Germany and France. The effect is acidification of water that damages water life, water quality, plant life and forests and causes dead lakes and streams. Buildings, particularly of marble and sandstone materials, can also corrode.

The acidifying chemicals commonly generate H^+ ions, responsible for lowering of atmospheric pH. The acid rain potential of a chemical is presented by the maximum number of H^+ ions that can be produced per unit mole of the chemical. In environmental impact potential terms, this potential of a chemical is presented relative to that of sulfur dioxide (SO_2). Sulfur takes part in a number of reactions. It is an important element for a number of chemicals, such as sulfuric acid, sulfites, gypsum, etc. The smelting process that recovers copper from ores can also emit sulfur compounds. When fuels or even desulfurized fuels are processed, sulfur present in the body is emitted mainly in oxidized form, SO_2. Sulfur compounds in gaseous forms, especially sulfur oxides, cause acid rain. Though there is a maximum acid rain potential for every chemical, the actual acid rain effect depends on many factors, such as the buffering capacity of soil and water, sunlight, temperature and moisture content of the atmosphere and air entrapment.

Exercise 9. Hydrogen fluoride is the main component for Teflon (polytetrafluoroethylene) production; 80% of the world's hydrogen fluoride is produced by reaction between extracted fluorspar containing 97% CaF_2 and the rest of SiF_4 by mass and sulfuric acid with a mass concentration of 83%, shown below in Equation (4.17). Gypsum ($CaSO_4.2H_2O$) can be produced as a by-product from the reaction. The SiF_4 present reacts with excess water to produce hexafluoride silica acid and silica, shown below in Equation (4.18). Figure 4.18 shows the flow chart from the extraction of sulfur and fluorspar

Table 4.19 *Molar mass of chemicals.*

Chemical	CaF_2	H_2SO_4	$CaSO_4$	HF	SiF_4	H_2SiF_6	SiO_2	H_2O
Full name	Calcium fluoride	Anhydrous sulfuric acid	Calcium sulfate	Hydrogen fluoride	Silicon tetrafluoride	Hexafluorosilicic acid	Silica	Water
Molar mass	78.07	98	136	20.01	104.08	144.09	60.08	18

Table 4.20 *Molar and mass flow rates of the reactants consumed and products produced by the two reactions in Equations (4.17) and (4.18).*

Reaction	Reactant Consumed				Product Produced			
	kmol d^{-1}	t d^{-1}	kmol d^{-1}	t d^{-1}	kmol d^{-1}	t d^{-1}	kmol d^{-1}	t d^{-1}
Reaction 1 in Equation (4.17)	CaF_2		H_2SO_4. $2H_2O$		Gypsum		HF	
	25.5	1.9885	25.5	3.413	25.5	4.381	51	1.0205
Reaction 2 in Equation (4.18)	SiF_4		H_2O		H_2SiF_6		SiO_2	
	0.591	0.0615	0.394	0.0071	0.394	0.0568	0.197	0.0118

ores to the production of hydrogen fluoride and other products at the plant gate. The required reaction conversion and yield data are also shown. Table 4.19 shows the molar masses of the chemicals involved in the process.

$$CaF_2 + H_2SO_4.2H_2O \rightarrow CaSO_4.2H_2O + 2HF \tag{4.17}$$

$$3SiF_4 + 2H_2O \rightarrow 2H_2SiF_6 + SiO_2 \tag{4.18}$$

a. Calculate the inlet and outlet mass flow rates of the flowchart in Figure 4.18.
b. Determine the relevant environmental impact characterizations from the resulting emissions.

Solution to Exercise 9. Calculate the mass of the fluorspar ore assuming 92% of it is the fluorspar:

$$= 2.05/0.92 = 2.23\ \mathrm{t\,d^{-1}}$$

The ore extraction processes are assumed to give an ideal split of 100%. This assumption will not affect the impact on land as after extraction the residual ore goes back to the land. Hence, the net effect is the depletion of the fluorspar and sulfur from the land. They are amongst the most abundant elements on the earth.

Calculate the mass of sulfur ore using the mass balance, starting from the reactant consumptions in the reactions in Equations (4.17) and (4.18).

Assume complete conversion of CaF_2 and SiF_4 in the two respective reactions. Table 4.20 shows the amounts of reactants consumed and the amounts of products produced by the two reactions.

Assume complete conversion of sulfur dioxide into sulfur trioxide in the catalytic oxidation in the reaction

$$SO_2 + 0.5O_2 \rightarrow SO_3 \tag{4.19}$$

Assume complete sulfur trioxide absorption into water to form sulfuric acid, shown as

$$SO_3 + 3H_2O \rightarrow H_2SO_4.2H_2O \tag{4.20}$$

Doing a backward calculation from the amount of H_2SO_4 solution (at 83.2% in weight basis), the molar flow rate of SO_2 produced from sulfur ore is (1 kmol of H_2SO_4 weighs 98 kg and requires 1 kmol of SO_3, which requires 1 kmol of SO_2, according to Equations (4.19) and (4.20)):

$$\frac{5.5 \times 0.832 \times 1000}{98} = 46.7\ \mathrm{kmol\,d^{-1}}$$

The mass flow rate of sulfur ore required (assuming that 0.01% by volume of sulfur dioxide is emitted to air, the ore contains 95% sulfur by mass and a 100% split in the extraction process) is

$$\frac{46.7}{0.9999 \times 1000} \times \frac{32}{0.95} = 1.573\ \mathrm{t\,d^{-1}}$$

(The atomic mass of sulfur is 32.)

Table 4.21 *Product distribution corresponding to unit mass production of HF.*

HF	Gypsum	H_2SiF_6	SiO_2	Anhydrous H_2SO_4
1	4.3	0.056	0.012	2.04

HF is the precursor to many important compounds including pharmaceuticals and polymers such as Teflon. However, upon contact with moisture it forms corrosive hydrofluoric acid. The gas can also cause blindness. Hence, an important aspect of further research will be to find a replacement safer precursor. The results in Table 4.21 will allow comparison with a substitute product and process.

Calculate the total amount of ore:

$$(2.23 + 1.573) = 3.8\ \mathrm{t\,d^{-1}}$$

Particulate emissions (calculated based on the total ore including both the fluorspar and sulfur ores):

$$\begin{aligned}&<2.5\ \mu\mathrm{m}:\ 8.4\ \mathrm{kg\ d^{-1}}\\&>2.5\ \mu\mathrm{m} - <10\ \mu\mathrm{m}:\ 31.6\ \mathrm{kg\ d^{-1}}\\&>10\ \mu\mathrm{m}:\ 43.3\ \mathrm{kg\ d^{-1}}\end{aligned}$$

Sulfur dioxide emission to air:

$$\frac{46.7 \times 0.0001}{0.9999 \times 1000} \times 64 = 0.3\ \mathrm{kg\ d^{-1}}$$

(The molar mass of sulfur dioxide is 64.)
The acidification potential of the flowchart is:

$$0.3\ \mathrm{kg\ SO_2\ equivalent}$$

In addition to the products shown in Table 4.20, there will be unreacted anhydrous sulfuric acid:

$$2.08\ \mathrm{t\ d^{-1}}$$

Residual ore (including the particulates present) from fluorspar ore from the extraction process:

$$0.18\ \mathrm{t\,d^{-1}}$$

Residual ore (including the particulates present) from sulfur ore from the extraction process:

$$0.08\ \mathrm{t\,d^{-1}}$$

On the basis of the unit mass flow rate of HF produced, the product distribution is as shown in Table 4.21.

4.6.6 Photochemical Oxidant Creation Potential

This impact is also known as urban smog, brownish colored air, commonly found in modern cities, especially where air is trapped in a basin, for example, Los Angeles, Mexico City, etc. Photochemical pollutants have harmful effects on living tissue and on buildings. Together, the formation of ozone in the lower atmosphere, the troposphere, adds to detrimental impacts on ecological and human health.

The volatile organic compounds react with NO_x in the presence of sunlight to produce ozone and photochemical pollutants in the lower atmosphere. Photochemical pollutants include peroxyacetyl nitrate (PAN), formaldehyde, acetic acid, etc. These pollutants are named as photochemical pollutants, because their formations are catalyzed by sunlight. These pollutants and ozone, known as photochemical oxidant, in the lower atmosphere are extremely detrimental to health and the environment. The photochemical oxidant creation potential is expressed in terms of the ethylene equivalent.

VOCs are carbon containing compounds that take part in photochemical reactions. VOCs do not include carbon dioxide, carbon monoxide, carbonic acid, metallic carbide, carbonates and ammonium carbonates. VOCs are responsible for urban smog and ground level ozone formation. When there is a mixture of VOCs, the concentration-average photochemical oxidant creation potential of the mixture is estimated.

The various photochemical reaction products they contribute to are also very harmful to health and the environment. High levels of these pollutants cause breathing difficulties and bring on asthma attacks, which can be fatal. Warm weather and still air can exacerbate the problem. Therefore, VOC emissions must be controlled and regulated. The photochemical oxidants are formed when NO_x, VOC and sunlight are present. Therefore, regional effects must be considered in estimating the photochemical oxidant creation potential. See Web Chapter 1 for VOC measurements and mitigation pathways.

4.6.7 Aquatic Ecotoxicity

The effect of manufactured chemicals on aquatic organisms at subcellular, organism, population, community and ecosystem levels is commonly known as aquatic ecotoxicity. There are two main ways of measuring concentration levels of toxic chemicals, at the mark of mortality by 50% of test organisms within a specified time and a specific effect grown by 50% in test organisms within a specified time. Wastewater and sewage treatment discharges are the core causes of aquatic ecotoxicity. PCBs (polychlorinated biphenyls), DDT (dichlorodiphenyltrichloroethane) and dioxins are the main chemical constituents causing aquatic ecotoxicity. As can be noted, some of the toxicities are more human health related than others, with profound impacts on the environment. Thus, human toxicity is differentiated from ecotoxicity, which includes aquatic as well as terrestrial toxicities.

Within aquatic toxicity, both freshwater and marine water toxicities are included. This differentiation is to structure primary impacts of chemicals relevant to different impact characterizations as precisely as possible. The more exhaustive the division the more targeted are the estimations of the environmental impact characterizations of the chemicals. To express toxicity, a critical volume approach is sometimes adopted. The critical volume is the volume of water needed (in the case of aquatic toxicity) to dilute a pollutant to an acceptable or safe limit. At some other times, a toxicity can be measured in terms of the kg of DCB equivalent.

It can be interpreted that a global consensus needed to be agreed to decide on environmentally safe limits for various pollutants to mitigate the toxicity impact potential. The physicochemical properties are also counted to evaluate the primary impacts to aquatic, terrestrial and human bodies. Similar to other characterizations, there is a base chemical, DCB, against which the primary level of toxicity for other chemicals is defined.

4.6.8 Eutrophication Potential

Eutrophication is a result of leaching of soil nutrients into a water body, particularly applicable for biorefinery systems, because of the application of nutrients to agricultural land. It is caused by nutrients, mainly nitrates and phosphates, leaching into a water body. The sources are agricultural, animal and sewage activities. The fertilizers applied in agriculture can be transmitted with rain through soil into the water body. As a result of eutrophication, there is an increase in biomass, for example, algal bloom, on the surface of water bodies, preventing light reaching inside the water bodies. As living creatures, fish lives are endangered. When algae start dying, aerobic bacteria use up dissolved oxygen to decompose algae. Increasing biological oxygen demand (BOD) indicates decreasing dissolved oxygen in water bodies. Nitrates (in fertilizers) are able to enter water bodies easily, because of their high water solubility. Phosphates (also in fertilizers), though water insoluble, can adhere to soil particles eroding into water bodies. All pollutants leaching into a water body have one common characteristic, dissolved oxygen reduction in the water. Thus, the eutrophication potential of a substance can be interpreted in terms of its ability to reduce the dissolved oxygen content in fresh water, with respect to a base chemical, phosphate in this case.

As seen in an agricultural system, nitrogen fertilization is crucial to plant growth, which proportionally increases with increasing nitrogen fertilizer intake. This implies that nitrate leaching into a water body is due to agricultural activity. The main source of phosphate, however, is the sewage discharge. After the treatment of black water (e.g., sewage discharge) and grey water (e.g., water returned from other household activities) the resulting sludge is generally embedded within the sea bed. Given that phosphate is water insoluble, the sea bed discharge of sludge was seen to be a reasonable thing to do. However, soil eroded into water and phosphate content in fresh water increased over the years. One of the ways for reducing phosphate leaching into fresh water is to deposit sludge in deep rocks for mineral formation. It is thus implied that the eutrophication potential is directly linked with human activity, for example, agricultural practices and effluent treatment strategies, etc.

4.6.9 Biodiversity

Amongst all impact categories, biodiversity is the end-point in the cause and effect chain of environmental impacts and directly affects nature. Biodiversity was introduced at the United Nations Conference on Environment and Development in Rio de Janeiro in 1992 (Rio Earth Summit). The International Convention on Biological Diversity was agreed amongst 150 countries and moved to halve the loss of biodiversity, wildlife and habitats. Responsibility at national level includes an action plan and programmes to reduce biodiversity loss of species under their jurisdiction. The UK Biodiversity Action Plan implemented in 1994 focused on the delivery of actions for conservation and protection of priority/targeted species and habitats (1150 species and 65 habitats in 2007–2011). Biodiversity assessment relies on analysis and understanding the whole cause and effect chain of environmental impacts. For example, the aquatic ecotoxicity and marine ecotoxicity can be measured. Their effect can be death to marine life or even species extinction. The latter is the end effect of a cause, ecotoxicity, and a direct effect on nature. An end effect analysis is not straightforward, requiring longer term qualitative as well as quantitative dimensions and multidisciplinary interventions. Often LCA studies are done up to the primary impact characterizations and biodiversity but other end-point impacts are not included because of the evaluation uncertainty.

4.7 LCA: Interpretation

This is the final phase of LCA, where the results of inventory analysis and impact assessment are gathered together with an aim to improve system performance and suggest possible changes. Interpretation of an LCA study includes identification of major burdens, impacts, hot spots; identification of areas with a scope for improvement; sensitivity analysis; robustness of results; evaluation and recommendations. Reliability and applicability of the data are a major issue, for which sensitivity must be analyzed for variability and uncertainty in the data used. Furthermore, there are various issues around the LCA methodology.

Even for primary effect assessments, different characterization factors have been suggested by different research groups, though with little variation. Some works undertake normalization to understand the relative importance and magnitude of the environmental benefits/damages of the technology or product and thereby compare the reliability of such studies, which must be carefully assessed. Characterization and normalization must be drawn on common references and may be related to a given community, country or region over a period of time. After normalization, results are given in the same unit and all the normalized indicator results corresponding to each impact category can be added. A single score for each technology or product is then obtained. It is an effective tool for comparisons of environmental benefits and business generation, if undertaken reliably and responsibly. LCA studies can be of a stand-alone, accounting (consequential) and change oriented (attributional) type. The sets of questions that can be answered using the three different types of LCA follow.

The following chapter discusses the data uncertainty analysis and LCA interpretation.

4.7.1 Stand-Alone LCA

- Product/process/systems/network focused.
- What is the environmental impact of a product/process/system/ …?
- What are the relevant impact characterizations of a product/ … ? What are the key pollutants?
- What are the input parameters that have the maximum impact on the key pollutant emissions and on the relevant impact characterizations?
- Analyze the sensitivity of the significant input parameters on the key pollutant emissions and on the relevant impact characterizations and decide the bounds of their acceptable values.
- What are the limits of the pollutants and what are the optimal design and operating conditions to keep the pollutants within their limits?
- What are the key observations that can be communicated to the policy makers, design and decision makers?
- The approach is stand-alone; hence no comparison is made with an existing product/ … . This implies that the product / … can be functionally different.
- It is a useful attribute of the LCA study that the hot spots and the causes for hot spots are identified and remedial actions are made to mitigate impacts.

4.7.2 Accounting LCA

- This type is about replacement of an existing product/process/systems/network. Hence LCA is to provide a comparison of a decision today with existing ones, retrospectively. This implies that the new product/ … is intended to replace a similar functionality product/ … . A comparison can be made between a number of different products with similar functionality or providing similar services.
- If a product/ … is replaced by another type of product/ …, how can the impact under a given characterization be improved?
- Identify the areas of major improvements with the least cost achievable.
- What would be an appropriate policy measure if a particular product or production route is held responsible for a major impact under a characterization?
- A typical example is the recycling of extracted material in the place of virgin material. What are the additional environmental impacts of using recycled material in place of virgin material? Compare the consequential impacts between landfill disposal and the material being recycled. Take account of the additional material use from construction to decommissioning to process the recycled material in the place of virgin material. Produce the entire flowchart and indicate the impact hot spots.
- The standard set of sensitivity analysis questions can be answered.

4.7.3 Change Oriented LCA

- The change oriented LCA is useful in making comparisons between products/activities prospectively. This is therefore used in making choices of products and processes, while considering growing environmental concerns and policies.
- This LCA is effective in the minimization of resource use, waste management and ways of reusing the materials after the end of product life.
- Thus it allows a comparison amongst a number of options to govern a whole system decision from resource selection through the conversion process decision making to the product end of life, prospectively.
- While the stand-alone LCA is just the beginning of an exercise, the accounting and change oriented LCAs are more appropriate to answer a number of relevant sustainable business development questions.

4.7.4 Allocation Method

The allocation of impact to different products utilizing the same processes and pathways is a difficult decision for an LCA study. The allocation can be done using the by economic value (if market prices are known). If products are functionally the same, allocation by unit functional value or allocation by substitutions/contributions to the service concerned can be useful. In the case of energy production, allocation of impacts by energy values of products is a rational way. Table 4.22 shows the environmental impact allocation to two main products from wheat cultivation, grain and straw. The allocation

Table 4.22 Allocation of environmental impacts from wheat cultivation. ARU, abiotic resource use.

Functional Unit	CPE (MJ)	GWP (kg CO_2 eq.)	EP (kg PO_4^{3-} eq.)	AP (kg SO_2 eq.)	ARU (kg Sb eq.)
ha^{-1} grain	18335	3426	16.1	15.8	10.8
ha^{-1} straw	632	77	0.2	0.2	0.30
Total (ha^{-1})	18967	3503	16.3	16.0	11.1
t^{-1} grain	2634	492	2.3	2.3	1.5
t^{-1} straw	181	22	0.1	0.1	0.1
y^{-1} grain	3.16×10^9	5.91×10^8	2.77×10^6	2.72×10^6	1.85×10^6
y^{-1} straw	1.09×10^8	1.33×10^7	4.17×10^4	4.25×10^4	5.26×10^4
Total (y^{-1})	3.27×10^9	6.04×10^8	2.81×10^6	2.76×10^6	1.91×10^6
Land use	Grade 2	Grade 3a	Grade 3b	Grade 4	
ha y^{-1}	151685	172370	186159	193054	
ha t^{-1} grain	0.13	0.14	0.16	0.16	

was done by their relative economic values. Hence, wheat had a bigger burden than straw. Also, note the choices of functional units for comparison with other cultivation systems.

Refer to the ***Online Resource Material in the Companion Website: Case Studies 1 to 4*** for LCA based problem solving approaches for industrial systems.

4.8 LCIA Methods

A number of LCIA methods exist to predict impact under various categories. A method can focus on the primary impact characterizations, such as, by CML. However, the LCIA methods can also include combinations of primary as well as mid- or end-point impacts. A cause–effect chain is created using characterization factors to predict the mid-point and end-point impacts. Needless to say, the latter approaches introduce more uncertainties in LCIA modeling results.

In this book, the CML 2010 method has primarily been used (http://www.cml.leiden.edu/research/industrialecology/researchprojects/finished/new-dutch-lca-guide.html) for comparisons, for example, between biorefinery configurations, feedstock selections, product selections by avoided emissions and focusing on the primary impact characterizations.

The EC-ILCD International Reference Life Cycle Data System and ELCD European Reference Life Cycle Database are available on http://lca.jrc.ec.europa.eu/lcainfohub/index.vm.

ILCD recommendations (http://lct.jrc.ec.europa.eu/pdf-directory/ILCD-Handbook-General-guide-for-LCA-DETAIL-online-12March2010.pdf) include primary as well as mid-point estimations as follows. For some primary impacts, such as the eutrophication potential, the method provides individual impact values in kg N or S equivalent (terrestrial) and in kg P equivalent (for water). For some others, such as the abiotic depletion potential, the combined resource depletion in terms of fossil and mineral reserves is shown.

The USA-TRACI "Tool for the Reduction and Assessment of Chemical and Other Environmental Impacts" method is available on http://www.epa.gov/nrmrl/std/traci/traci.htm and http://www.gabi-software.com/support/gabi/gabi-lcia-documentation/life-cycle-impact-assessment-lcia-methods/traci/. The method provides primary as well as mid-point characterizations. In addition to some of the CML primary categories, but often in different units except GWP, mid-point impacts to human health are estimated.

The various methodologies are in-built and offered by commercially available LCA software, recommended to use. The units used for various impact characterizations included under ILCD recommendations, CML 2001 – November 2010, TRACI and ReCiPe in GaBi, are shown in four parts in Table 4.23[21].

Table 4.23(a) *Units for various impact characterizations under ILCD recommendations.*

Impact Characterization	Accepted Unit
Climate change	kg CO_2 equivalent
Ozone depletion	kg CFC-11 equivalent
Human toxicity, cancer effects	CTUh (comparative toxic unit for human)
Human toxicity, non-cancer effects	CTUh
Particulate matter, respiratory inorganics	kg PM2.5 equivalent
Ionising radiation, human health	Human exposure efficiency relative to U^{235}
Photochemical ozone formation	kg NMVOC (non-methane volatile organic compounds) equivalent
Acidification	kg N or S equivalent
Eutrophication, terrestrial	kg N or S equivalent
Eutrophication, aquatic	Fraction of nutrients reaching end compartment
Ecotoxicity	CTUe (comparative toxic unit for ecosystem)
Resource depletion, water	Water stress index (WSI)
Resource depletion, mineral, fossil and renewable	kg Sb equivalent

Table 4.23(b) *Units for various impact characterizations under CML 2001 – November 2010.*

Impact Characterization	Accepted Unit
Global warming potential	kg CO_2 equivalent
Acidification depletion potential	kg SO_2 equivalent
Eutrophication potential	kg phosphate equivalent
Ozone layer depletion potential	kg CFC-11 equivalent
Abiotic depletion potential, elements	kg Sb equivalent
Abiotic depletion potential, fossil	MJ
Freshwater aquatic ecotoxicity potential	kg DCB equivalent
Human toxicity potential	kg DCB equivalent
Marine aquatic ecotoxicity potential	kg DCB equivalent
Photochemical ozone creation potential	kg ethylene equivalent
Terrestric ecotoxicity potential	kg DCB equivalent

Table 4.23(c) *Units for various impact characterizations under TRACI.*

Impact Characterization	Accepted Unit
Global warming potential	kg CO_2 equivalent
Acidification depletion potential	kg H^+ equivalent
Eutrophication potential	kg N equivalent
Ozone layer depletion potential	kg CFC-11 equivalent
Ecotoxicity air	PAF (potentially affected fraction) m^3 day kg^{-1}
Ecotoxicity soil	PAF m^3 day kg^{-1}
Ecotoxicity water	PAF m^3 day kg^{-1}
Human health cancer air	Cases
Human health cancer soil	Cases
Human health cancer water	Cases
Human health non-cancer air	Cases
Human health non-cancer soil	Cases
Human health non-cancer water	Cases
Human health criteria air	kg PM10 equivalent
Smog air	kg O_3 equivalent

Table 4.23(d) *Units for various impact characterizations under ReCiPe.*

Impact Characterization	Accepted Unit
Climate change	kg CO_2 equivalent
Terrestrial acidification	kg SO_2 equivalent
Freshwater eutrophication potential	kg P equivalent
Ozone depletion potential	kg CFC-11 equivalent
Fossil depletion	kg oil equivalent
Freshwater ecotoxicity	kg DCB equivalent
Ionizing radiation	kg U235 equivalent
Marine ecotoxicity	kg DCB equivalent
Marine eutrophication	kg N equivalent
Metal depletion	kg Fe equivalent
Natural land transformation	m^2
Particulate matter formation	kg PM10 equivalent
Photochemical oxidant formation	kg NMVOC equivalent
Terrestrial ecotoxicity	kg DCB equivalent
Water depletion	m^3

CML2001 - Dec. 07, Experts IKP (Central Europe)
CML2001 - Dec. 07, Experts IKP (Northern Europe)
CML2001 - Dec. 07, Experts IKP (Southern Europe)
CML2001, Experts IKP (Central Europe)
CML2001, Experts IKP (Northern Europe)
CML2001, Experts IKP (Southern Europe)
CML96, Expert judgement, IKP
CML96, Experts, IKP
CML96, Policy long term, IKP
CML96, Policy short term, IKP
CML96, Policy, IKP
CML96, Population, IKP
CML96, Survey Europe, IKP
CML96, Survey Germany, IKP
CML96, Sustainable development, IKP
EDIP 1997, Env. imp. eval. (PET W, EU 2004)
EDIP 1997, Ress. eval. (PR W 2004)
EDIP 1997, Toxicity eval. (PET EU 2004)
EDIP 1997, Waste eval. (PET DK 2000)
EDIP 2003, Env. imp. eval. (PET W, EU 2004)
EI95
EI95 (incl. ionizing radiation, RF)
EI99, EE (Egalitarian approach)
EI99, HA (Hierarchist approach)
EI99, II (Individualist approach)
PE LCIA Survey 2012 (Europe; CML and ReCiPe)
PE LCIA Survey 2012 (Global; CML, ReCiPe and Traci)
PE LCIA Survey 2012 (North-America; Traci)

Figure 4.19 *A comprehensive list of LCIA methodologies.*

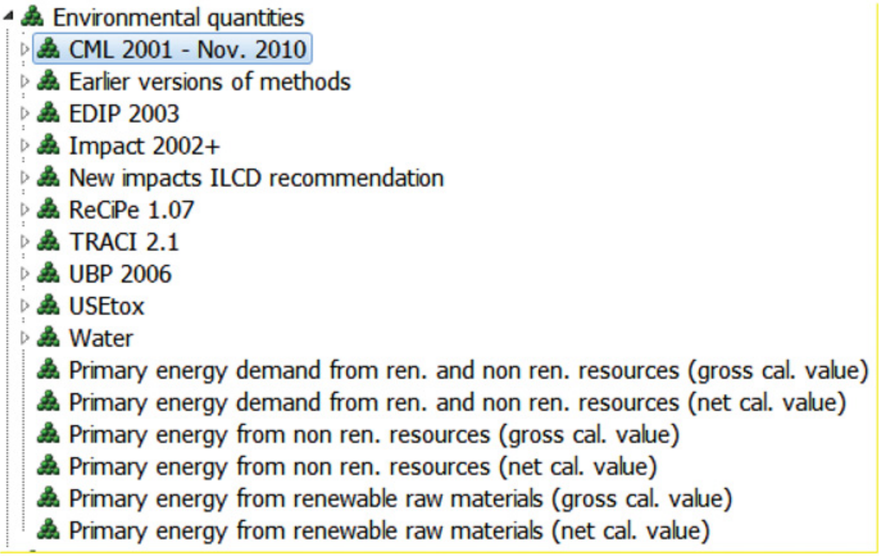
Figure 4.19 shows a comprehensive list of LCIA methodologies and regions applied for, which include CML, EDIP, EI and the PE LCIA survey, offered in GaBi 6, from PE International. The most recent LCIA methodologies are shown in Figure 4.20 (a) to (h). Each of the LCIA methodologies is then elaborated to show the impact characterizations, under the methodology shown in Figure 4.20.

Foundation Concepts Quiz (20 marks in total)

Problem 1. Carries 5 Marks

Consider the emissions from the conversion of two feedstocks, shown on the basis of the weight percentage in Table 4.24.

1. Calculate the global warming potential of the emissions from the two feedstocks. (2.5 marks)
2. Calculate the CO_2 credit gain by environmentally better performing feedstock compared to inferior feedstock. (2.5 marks)

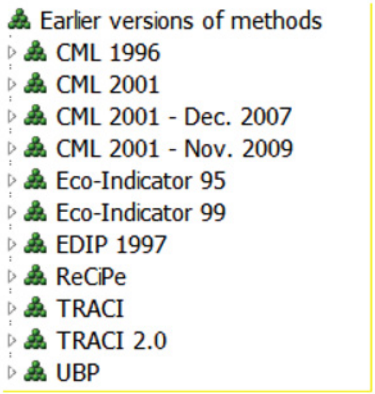


- Environmental quantities
  - CML 2001 - Nov. 2010
  - Earlier versions of methods
  - EDIP 2003
  - Impact 2002+
  - New impacts ILCD recommendation
  - ReCiPe 1.07
  - TRACI 2.1
  - UBP 2006
  - USEtox
  - Water
  - Primary energy demand from ren. and non ren. resources (gross cal. value)
  - Primary energy demand from ren. and non ren. resources (net cal. value)
  - Primary energy from non ren. resources (gross cal. value)
  - Primary energy from non ren. resources (net cal. value)
  - Primary energy from renewable raw materials (gross cal. value)
  - Primary energy from renewable raw materials (net cal. value)

Figure 4.20 *LCIA methodologies and their impact characterizations available in LCA software (a to h).* ***(a)*** *LCIA methodologies available in LCA software.*

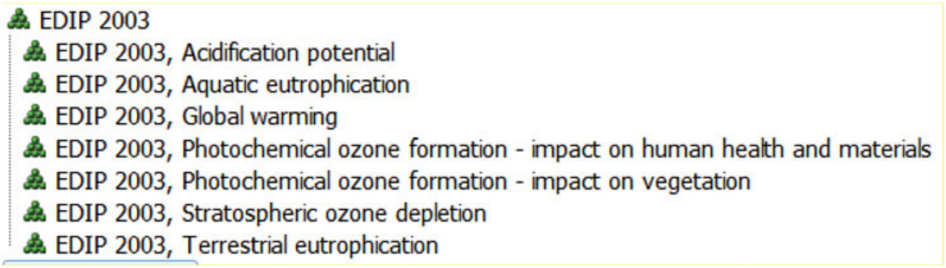
- CML 2001 - Nov. 2010
  - CML2001 - Nov. 2010, Abiotic Depletion (ADP elements)
  - CML2001 - Nov. 2010, Abiotic Depletion (ADP fossil)
  - CML2001 - Nov. 2010, Acidification Potential (AP)
  - CML2001 - Nov. 2010, Eutrophication Potential (EP)
  - CML2001 - Nov. 2010, Freshwater Aquatic Ecotoxicity Pot. (FAETP inf.)
  - CML2001 - Nov. 2010, Global Warming Potential (GWP 100 years)
  - CML2001 - Nov. 2010, Global Warming Potential, excl biogenic carbon (GWP 100 years)
  - CML2001 - Nov. 2010, Human Toxicity Potential (HTP inf.)
  - CML2001 - Nov. 2010, Marine Aquatic Ecotoxicity Pot. (MAETP inf.)
  - CML2001 - Nov. 2010, Ozone Layer Depletion Potential (ODP, steady state)
  - CML2001 - Nov. 2010, Photochem. Ozone Creation Potential (POCP)
  - CML2001 - Nov. 2010, Terrestric Ecotoxicity Potential (TETP inf.)

Figure 4.20(b) *Primary impact characterizations included in CML 2001 – November 2010.*



Earlier versions of methods
- CML 1996
- CML 2001
- CML 2001 - Dec. 2007
- CML 2001 - Nov. 2009
- Eco-Indicator 95
- Eco-Indicator 99
- EDIP 1997
- ReCiPe
- TRACI
- TRACI 2.0
- UBP

Figure 4.20(c) *Earlier versions of LCIA methods.*

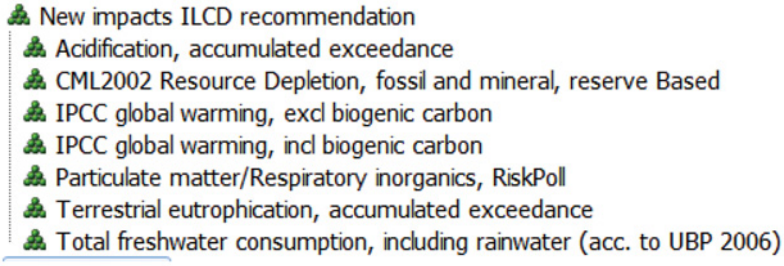


EDIP 2003
- EDIP 2003, Acidification potential
- EDIP 2003, Aquatic eutrophication
- EDIP 2003, Global warming
- EDIP 2003, Photochemical ozone formation - impact on human health and materials
- EDIP 2003, Photochemical ozone formation - impact on vegetation
- EDIP 2003, Stratospheric ozone depletion
- EDIP 2003, Terrestrial eutrophication

Figure 4.20(d) *Primary impact characterizations included in EDIP 2003.*

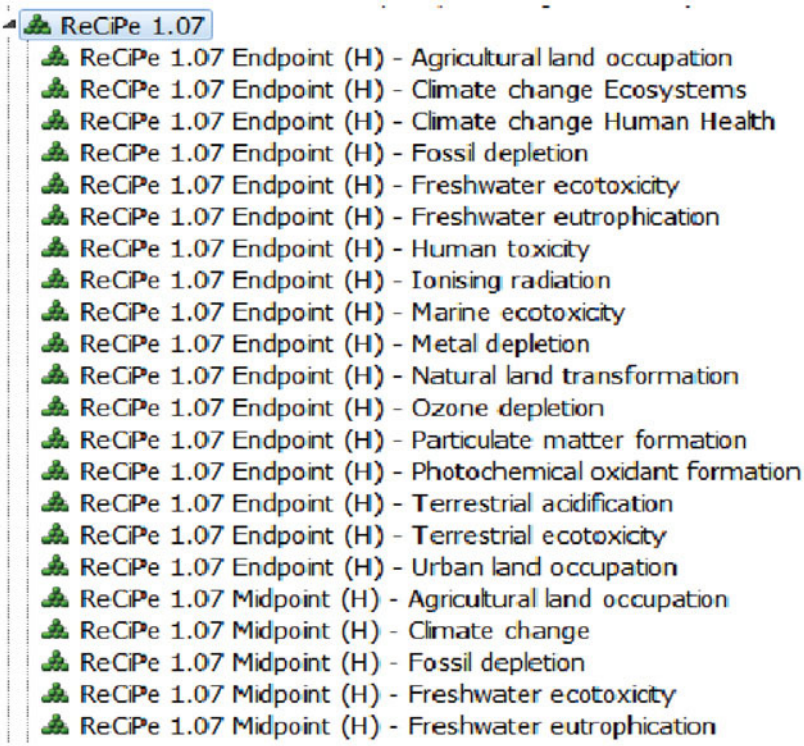
Impact 2002+
- I02+ v2.1 - Aquatic acidification - Midpoint
- I02+ v2.1 - Aquatic ecotoxicity - Midpoint
- I02+ v2.1 - Aquatic eutrophication - Midpoint
- I02+ v2.1 - Carcinogens - Midpoint
- I02+ v2.1 - Global warming 500yr - Midpoint
- I02+ v2.1 - Ionizing radiation - Midpoint
- I02+ v2.1 - Land occupation - Midpoint
- I02+ v2.1 - Mineral extraction - Midpoint
- I02+ v2.1 - Non-carcinogens - Midpoint
- I02+ v2.1 - Non-renewable energy - Midpoint
- I02+ v2.1 - Ozone layer depletion - Midpoint
- I02+ v2.1 - Photochemical oxidation - Midpoint
- I02+ v2.1 - Respiratory effects - Midpoint
- I02+ v2.1 - Terrestrial acidification/nutrification - Midpoint
- I02+ v2.1 - Terrestrial ecotoxicity - Midpoint

Figure 4.20(e) *Mid-point impact characterizations included in Impact 2002+.*



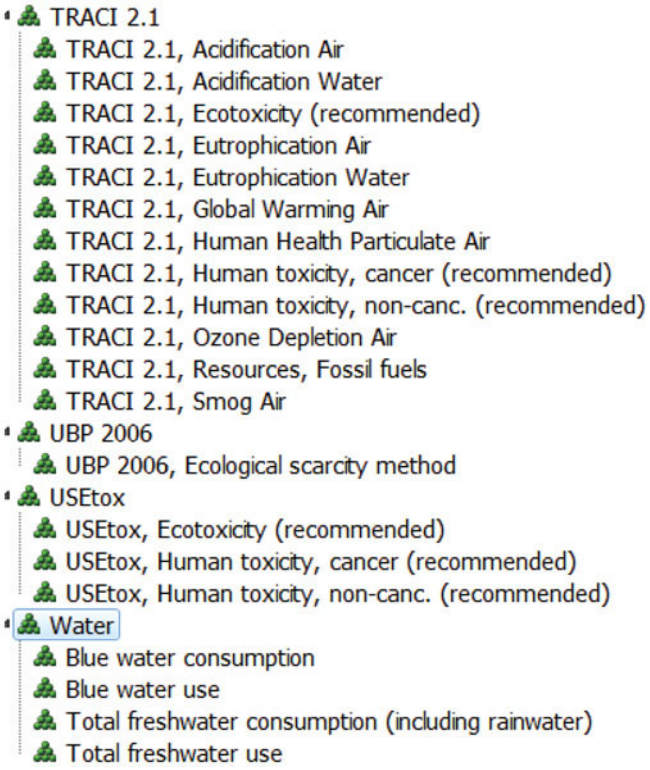
- New impacts ILCD recommendation
  - Acidification, accumulated exceedance
  - CML2002 Resource Depletion, fossil and mineral, reserve Based
  - IPCC global warming, excl biogenic carbon
  - IPCC global warming, incl biogenic carbon
  - Particulate matter/Respiratory inorganics, RiskPoll
  - Terrestrial eutrophication, accumulated exceedance
  - Total freshwater consumption, including rainwater (acc. to UBP 2006)

Figure 4.20(f) *New impacts recommended in ILCD.*



- ReCiPe 1.07
  - ReCiPe 1.07 Endpoint (H) - Agricultural land occupation
  - ReCiPe 1.07 Endpoint (H) - Climate change Ecosystems
  - ReCiPe 1.07 Endpoint (H) - Climate change Human Health
  - ReCiPe 1.07 Endpoint (H) - Fossil depletion
  - ReCiPe 1.07 Endpoint (H) - Freshwater ecotoxicity
  - ReCiPe 1.07 Endpoint (H) - Freshwater eutrophication
  - ReCiPe 1.07 Endpoint (H) - Human toxicity
  - ReCiPe 1.07 Endpoint (H) - Ionising radiation
  - ReCiPe 1.07 Endpoint (H) - Marine ecotoxicity
  - ReCiPe 1.07 Endpoint (H) - Metal depletion
  - ReCiPe 1.07 Endpoint (H) - Natural land transformation
  - ReCiPe 1.07 Endpoint (H) - Ozone depletion
  - ReCiPe 1.07 Endpoint (H) - Particulate matter formation
  - ReCiPe 1.07 Endpoint (H) - Photochemical oxidant formation
  - ReCiPe 1.07 Endpoint (H) - Terrestrial acidification
  - ReCiPe 1.07 Endpoint (H) - Terrestrial ecotoxicity
  - ReCiPe 1.07 Endpoint (H) - Urban land occupation
  - ReCiPe 1.07 Midpoint (H) - Agricultural land occupation
  - ReCiPe 1.07 Midpoint (H) - Climate change
  - ReCiPe 1.07 Midpoint (H) - Fossil depletion
  - ReCiPe 1.07 Midpoint (H) - Freshwater ecotoxicity
  - ReCiPe 1.07 Midpoint (H) - Freshwater eutrophication

Figure 4.20(g) *End- and mid-point impact characterizations included in ReCiPe.*



- TRACI 2.1
  - TRACI 2.1, Acidification Air
  - TRACI 2.1, Acidification Water
  - TRACI 2.1, Ecotoxicity (recommended)
  - TRACI 2.1, Eutrophication Air
  - TRACI 2.1, Eutrophication Water
  - TRACI 2.1, Global Warming Air
  - TRACI 2.1, Human Health Particulate Air
  - TRACI 2.1, Human toxicity, cancer (recommended)
  - TRACI 2.1, Human toxicity, non-canc. (recommended)
  - TRACI 2.1, Ozone Depletion Air
  - TRACI 2.1, Resources, Fossil fuels
  - TRACI 2.1, Smog Air
- UBP 2006
  - UBP 2006, Ecological scarcity method
- USEtox
  - USEtox, Ecotoxicity (recommended)
  - USEtox, Human toxicity, cancer (recommended)
  - USEtox, Human toxicity, non-canc. (recommended)
- Water
  - Blue water consumption
  - Blue water use
  - Total freshwater consumption (including rainwater)
  - Total freshwater use

Figure 4.20(h) *Primary impact characterizations included in TRACI, UBP, USEtox and Water.*

Problem 2. Carries 10 Marks

A comparison of the environmental impact assessment results between anaerobic digestion and natural gas based production systems is shown in Figures 4.21 to 4.28. Neglect the differences due to geographic locations (CH in the figures refers to Switzerland and RNA refers to North America, according to the geographical codes used in GaBi software, http://www.gabi-software.com/support/gabi/geographical-codes/ and <u-so> or <p-agg> indicates the impact potential from that process block only).

1. Calculate the credit gain by environmentally better performing feedstock compared to inferior feedstock in each impact category shown. (2 marks)

Table 4.24 *Emissions from the conversion of two feedstocks on the basis of weight percentage.*

Chemical	Feedstock 1 (weight%)	Feedstock 2 (weight%)	GWP Characterization Factor
CO_2	80	65	1
CH_4	10	30	25
CFC	0.05	0	5000
N_2O	4	5	298
NO	5.95	0	40

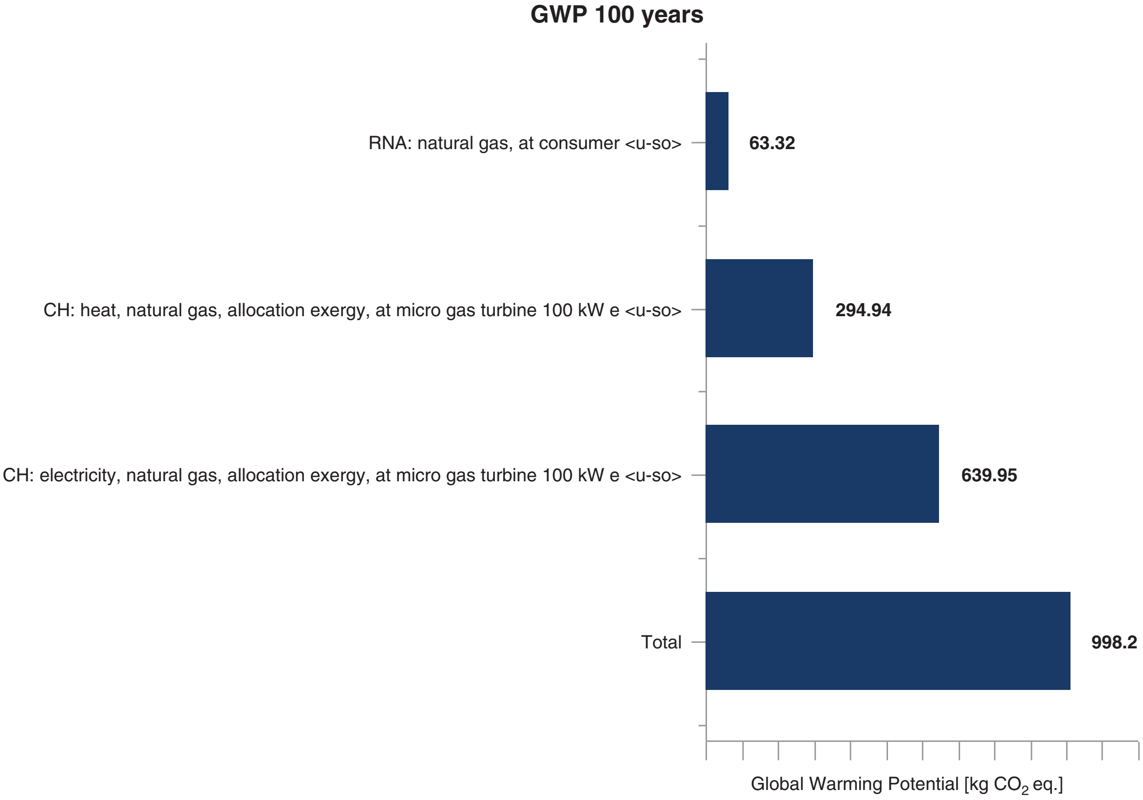


Figure 4.21 *GWP from natural gas based CHP generation system (basis 11 340 MJ energy content in natural gas).*

2. Give the reason for the credit gained by biogas compared to natural gas or otherwise, for each of the categories shown. (3 marks)
3. State the hot spot for each feedstock under each category. (2 marks)
4. Explain how these hot spots may be mitigated. (3 marks)

Problem 3. Carries 5 Marks

A biomass integration gasification combined cycle plant is required to produce 50 MW e output. The biomass feedstock can be wheat straw, waste wood and refuse-derived fuel (RDF), which is produced by shredding and dehydrating municipal solid waste. Their ultimate analyses are shown in Table 4.25.

1. Name the impact categories that can be evaluated to create a hierarchy of biomass feedstocks from most to least beneficial ones. Assume that the toxicity potentials in all categories are comparable between feedstocks. Given that the data generation is a huge constraint in the LCA study, your list must not consist of more than three most important impact categories. (1.5 marks)
2. Give the reasoning for your above selection. (3.5 marks)

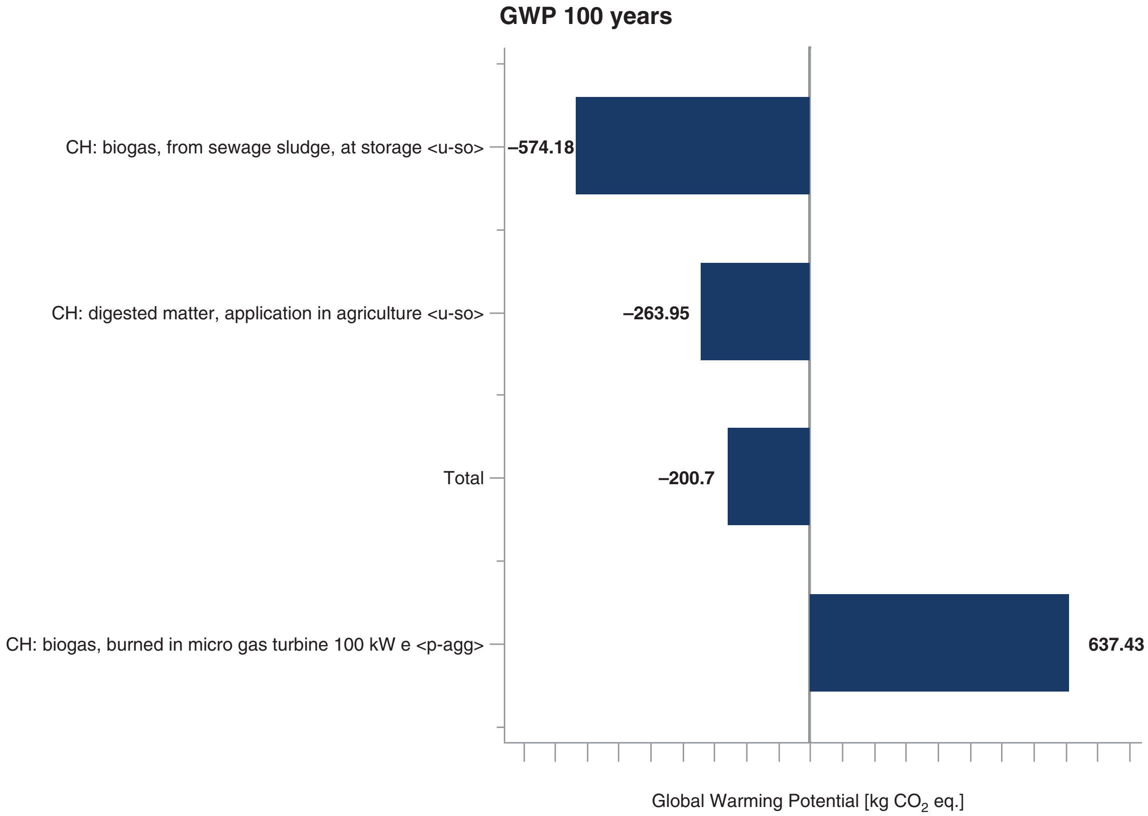


Figure 4.22 *GWP from anaerobic digestion based production system (basis 11 340 MJ energy content in biogas).*

Test of Peer Review Skill

The LCA study is proving to be effective for LCA studies. Amongst the various environmental impact categories, the most important issues considered are the global warming potential impact saving, land use and water footprint. Various journals provide numerous LCA studies of biorefinery systems. Though not exhaustive, the following list of journals can be searched for biorefinery LCA papers. Select studies under topic areas, such as Bioethanol, Biorefinery, Polygeneration, CHP, Sustainability and LCA and test your review skills.

- Nature journals: http://www.nature.com/siteindex/index.html
- Science: http://www.sciencemag.org/magazine
- Environmental Science and Technology
- Energy and Environmental Science
- Water Research
- Journal of Power Sources
- Applied Energy
- Biomass and Bioenergy
- Atmospheric Environment

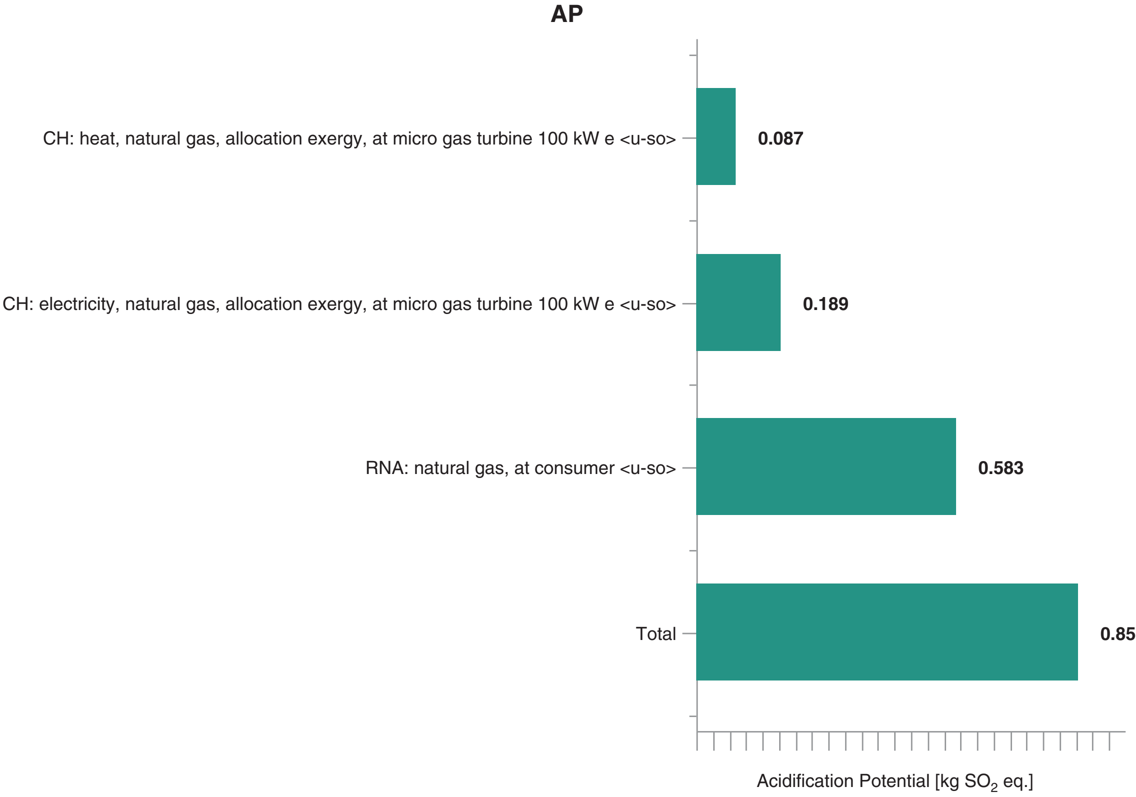


Figure 4.23 *Acidification potential (AP) from natural gas based CHP generation system (basis 11 340 MJ energy content in natural gas).*

- Ecological Economics
- International Journal of Life Cycle Assessment
- Journal of Industrial Ecology
- Energy
- Energy Policy
- Environmental Science and Pollution Research
- Journal of Environmental Management
- Water Resources Management
- Renewable and Sustainable Energy Review
- Solar Energy
- Resources, Conservation and Recycling
- International Journal of Energy Research
- Journal of Cleaner Production
- Technological Forecasting and Social Change
- Energy and Buildings
- Sustainable Development
- Chemical Engineering Research and Design
- Industrial and Engineering Chemistry Research

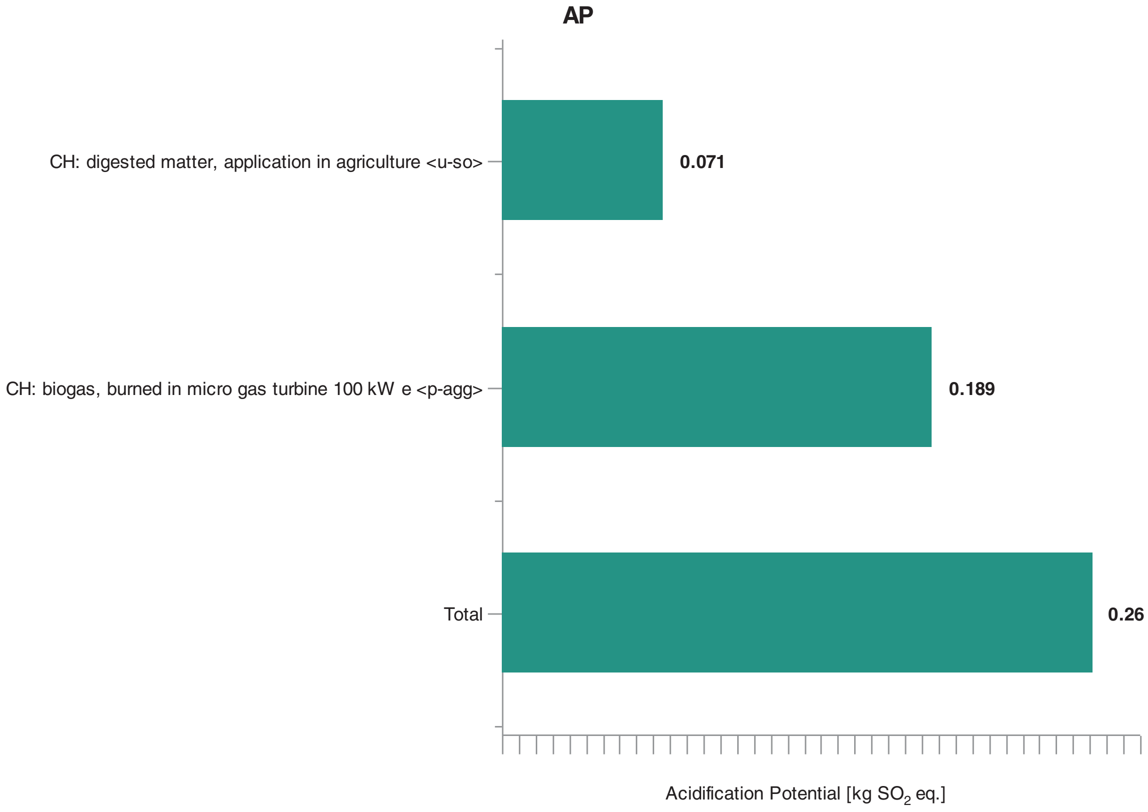


Figure 4.24 *Acidification potential (AP) from anaerobic digestion based production system (basis 11 340 MJ energy content in biogas).*

- Sustainability
- Journal of Applied Microbiology
- Critical Reviews in Environmental Science and Technology

Answer to the Following Questions

Goal and Scope Definition

Are the boundaries defined for the systems appropriate? What other blocks/subsystems could have been added (or otherwise) within the boundaries to make differences in impact assessment values and interpretation?

A biorefinery LCA publication may show the use of various units to present results, such as, per land use, per mass, per energy and per annual bases. Explain the reason for using each unit.

Which other impact categories might have been relevant for the study? Remember “less” is “more” when a study is complete, transparent and coherent. LCA study results should also be in transferable form such that these can be used/adapted and cited in another study (an example is shown in Table 4.4).

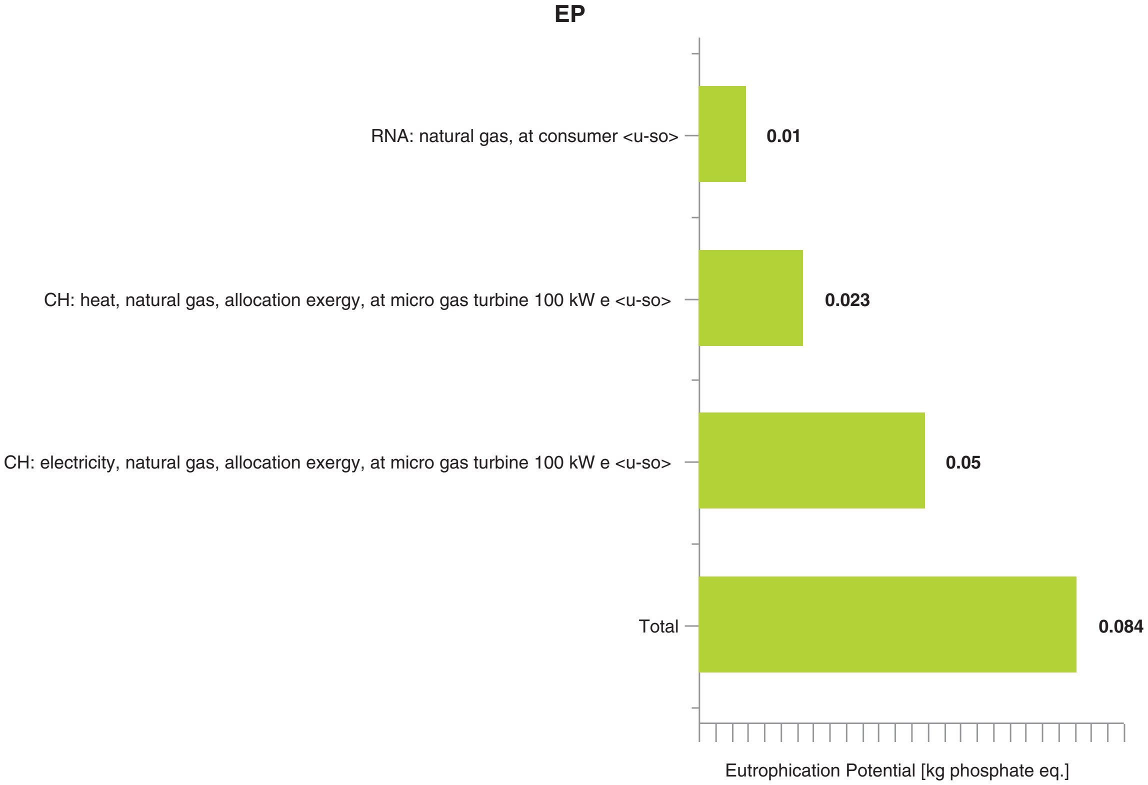


Figure 4.25 *Eutrophication potential (EP) from natural gas based CHP generation system (basis 11 340 MJ energy content in natural gas).*

Inventory Analysis

What are the advantages in showing inventories around various internal boundaries in the system (i.e., cultivation, processing and then for each unit operation)?

What are the advantages and disadvantages of using simulation results, databases from software such as GaBi and primary social science research data?

Interpretation

Are the results clearly shown? Are the expected results clearly stated in the goal and scope definition?

Is this a stand-alone, accounting (consequential) or change oriented (attributional) type of study?

How would you like to improve the presentation of the sensitivity analysis results?

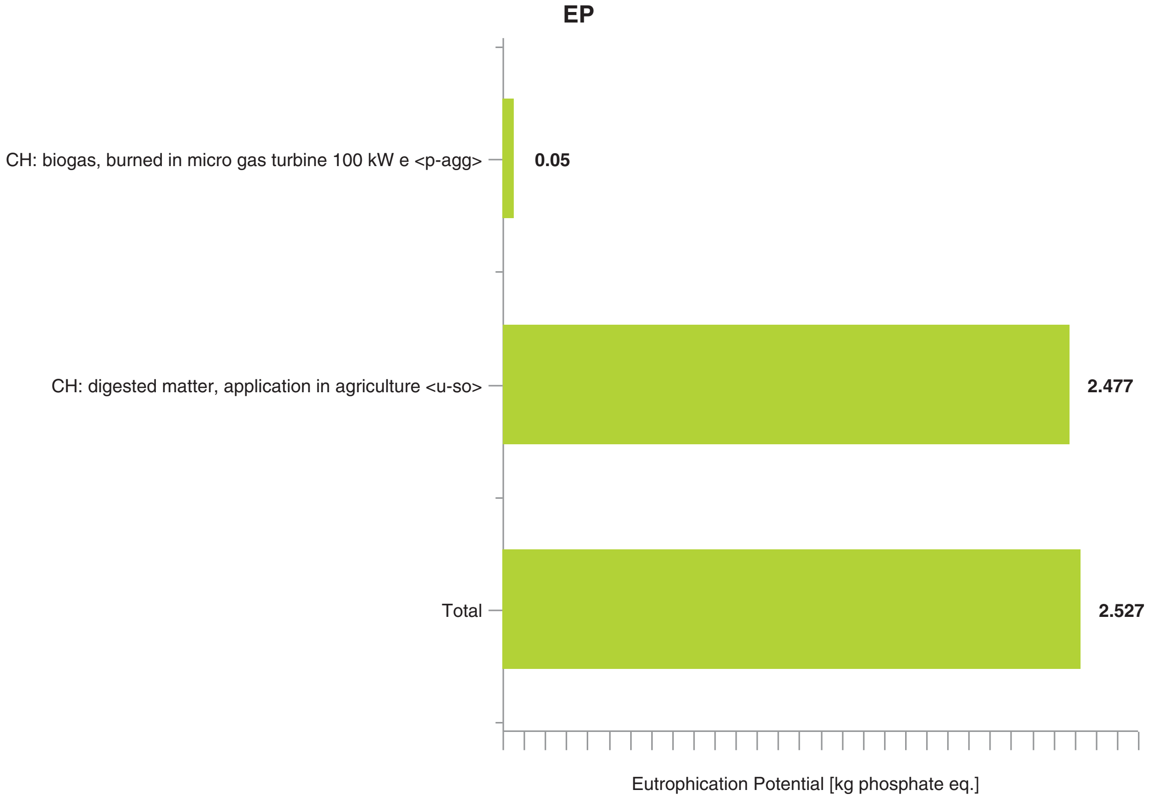


Figure 4.26 *Eutrophication potential (EP) from anaerobic digestion based production system (basis 11 340 MJ energy content in biogas).*

Essay writing (100 marks)

Task

Write a research paper on LCA studies of **your chosen case study or one of the following topics**. It is important that your research refers to a variety of sources, of which a significant proportion should be peer-reviewed journal papers. Answers must be fully referenced using the author–date (Harvard) system. The report may contain solutions for the following issues as appropriate. The list is not exhaustive and only meant to provide a guidance. Please include any other issues as you consider appropriate.

- Identify alternative technology options.
- Select one or two technologies to do LCA in detail.
- Identify system boundary and functional units (suitable for making comparisons with other systems).
- State assumptions and limitations.
- Identify hot spots in alternative technology options.
- Identify key pollutants.
- Identify geographic locations and any associated transport.
- Identify utility requirements (e.g., electricity and heat, etc.) and sources of them.
- Discuss hot spots, types of pollutants and ways to remedy in detail (see the next chapter).
- Make comparison with other equivalent systems for environmental sustainability.

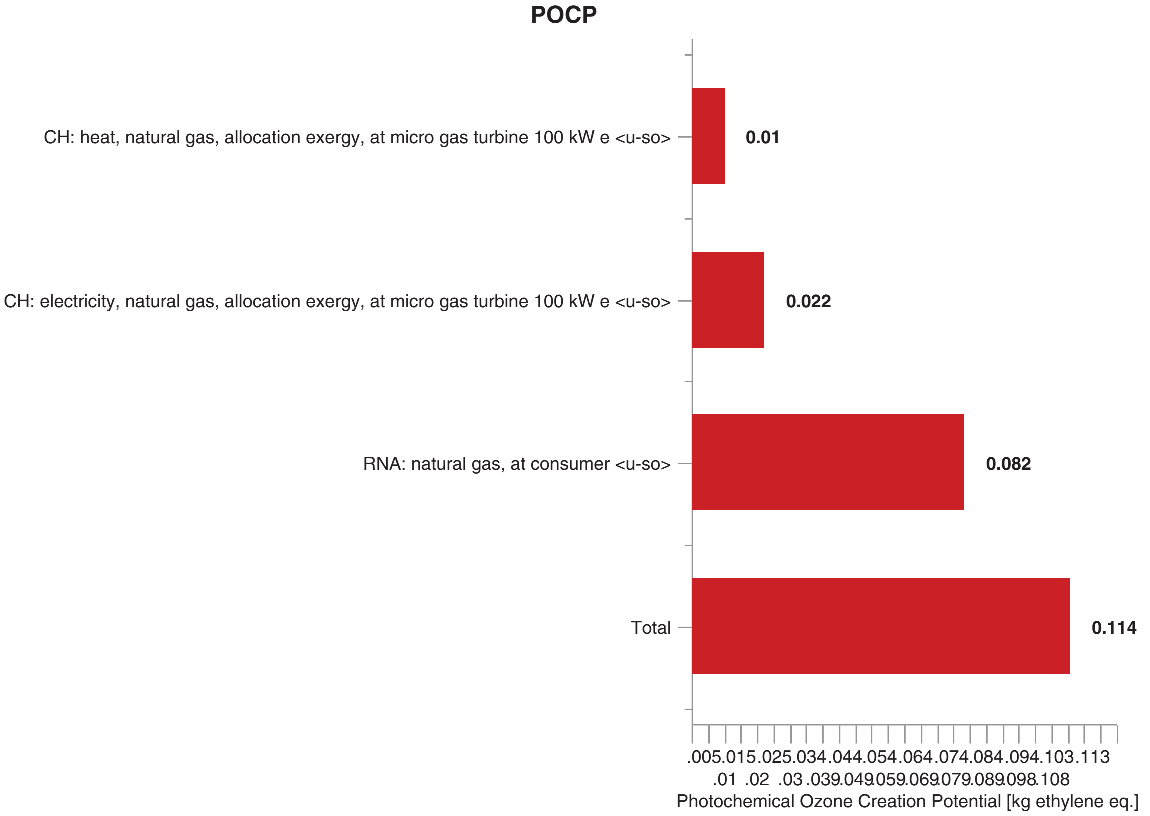


Figure 4.27 *Photochemical oxidant creation potential (POCP) from natural gas based CHP generation system (basis 11 340 MJ energy content in natural gas).*

- Report critical input parameters and sensitivity analysis results.
- Include critical analysis of the quality of results and LCA done by you and others in the field.
- Report results ***in transferable form.***
- Include techno-economic and socio-economic analyses as appropriate.
- Discuss policy drivers and barriers; learning points from the case study; action and policy recommendations.
- Discuss key benefits and challenges of the application of LCA.

Option 1. LCA of solar photovoltaic for electricity generation.
Option 2. LCA of energy generation from wastewater sludge.
Option 3. LCA of energy generation from municipal solid wastes.
Option 4. LCA of biofuel production from waste wood.
Option 5. LCA of composite/polymer production from biomass, with applications in aeronautics, automotive industry, construction, etc.

For your own case study:

Describe how LCA can be applied to a specific case. This can be, for example, a specific substance, or a specific product or service or technology.

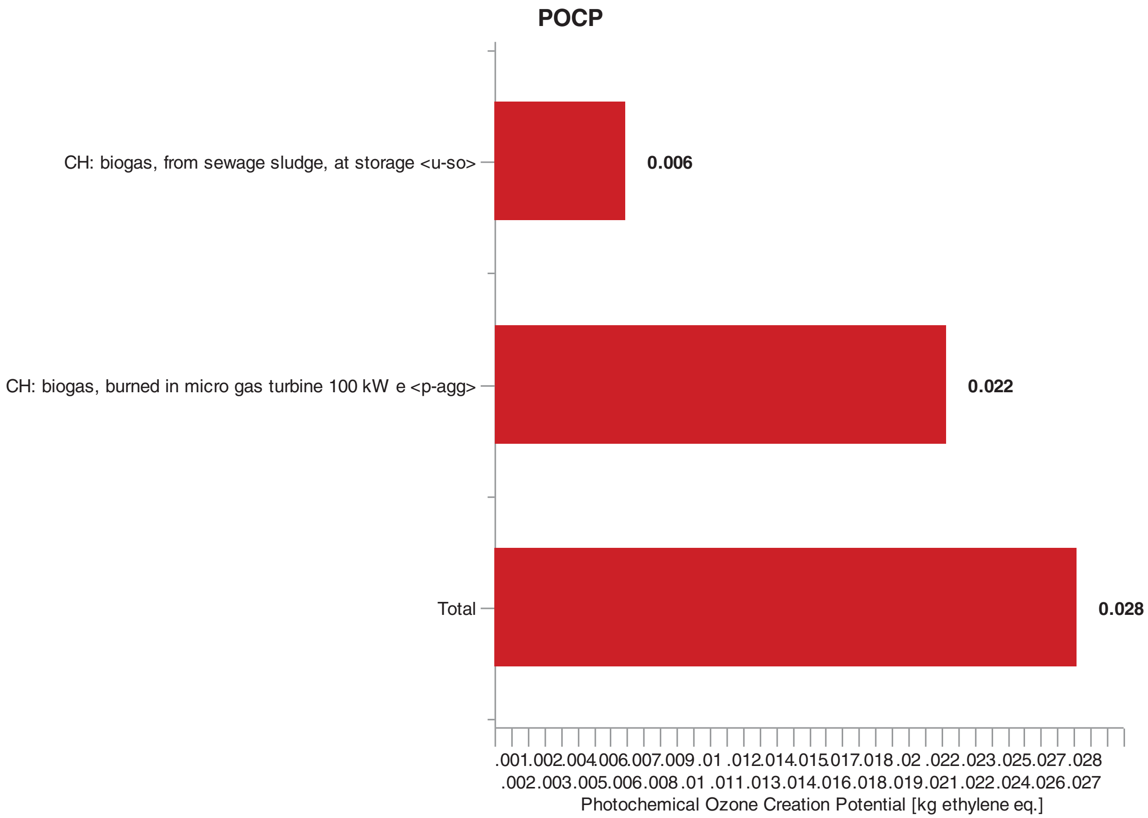


Figure 4.28 *Photochemical oxidant creation potential (POCP) from anaerobic digestion based production system (basis 11 340 MJ energy content in biogas).*

Format

- The content of paper should not exceed 5000 words (this excludes title, abstract, table of contents, reference list and appendix mainly used to show calculations).
- Use standard report format (including abstract, table of contents, headings, subheadings, reference list).

Table 4.25 *Biomass composition in weight %.*

Component in weight %	Straw	Wood	RDF
C	18.66	29.94	35.25
H	4.91	4.28	5.77
O	40.7	30.69	37.59
N	0.57	0.075	0.298
S	0.14	0	0.199
Cl	0	0	0.398
Moisture	8.5	25	0
Fixed C	17.91	8.92	10
Ash	8.61	1.1	10.5
Lower heating value (MJ kg^{-1})	14.6	19.3	17.73

Criteria for Assessment

- Demonstrated understating of LCA and LCT (25%).
- Appreciation of the application of theory to practice in the selected case (25%).
- Evidence of research to develop arguments, and the clarity and comprehensiveness of the arguments (35%).
- Overall structure, quality of the writing and presentation as well as the appropriate use and citing of reference materials (15%).

4.9 Future R&D Needs

Investment for biorefineries should be justified by a more holistic evaluation of social consequences (the agricultural focus may be shifted to energy crops rather than food crops due to subsidies and business cases that would fuel further to the energy demand), economic impacts (food price is likely to increase and affordability is likely to decrease) and long-term environmental implications on land, water and biosphere. It is imperative to compare land to energy yields, life cycle costs and environmental, economic and social sustainability between various energy systems with similar functional products. It is imperative to have an understanding of the value implications across supply chains that are global in some connections, complemented by bottom-up LCA approaches. Crop cultivation mapping on temporal and spatial scales using LCA is also a useful exercise. Research effort in the overall process and energy integration and enhancement of efficiency of integrated biorefinery systems is not apparent. Thus current deployment of process integration and life cycle approaches for the maximization of energy efficiency and minimization of life cycle inventories will be highly relevant for sustainable application of biorefineries.

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