Sustainability within the Polyester Value Chain

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Preface

The work described in this dissertation was carried out in the Department of Chemical Engineering and Biotechnology, University of Cambridge, between October 2011 and February 2015. It is the original and independent work of the author, except where specifically acknowledged in the text. Neither the present dissertation, nor any part thereof, has been submitted to any other university.

This dissertation contains 44426 words and 48 figures.

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Abstract

Polyethylene terephthalate (PET) is used to make textile fibres, bottles and packaging films. The global production in 2013 was 65 Mt, growing at 5-7% per year over the last decade. PET is manufactured by the continuous polymerisation of ethylene glycol and terephthalic acid, both of which are produced from fossil fuels.

This Dissertation examines the environmental impact of manufacturing PET using process modelling and life cycle assessment. The work focused on ways of reducing the environmental impact of the polymer manufacture by using biomass instead of conventional fossil fuels, either as a raw material for producing ethylene glycol or terephthalic acid, or as a fuel to supply process heating or electricity.

The environmental impacts of producing a PET bottle using ethylene glycol derived from two types of biomass, sugarcane and willow, were investigated and compared with conventional production. For sugarcane, the sugars were fermented to bioethanol, then dehydrated to ethylene. By using sugarcane, it was found that the global warming potential (GWP) and non-renewable resource use could be reduced by 28% and 16% respectively. Ethanol, and hence ethylene, can also be produced from willow, a lignocellulosic biomass, which could also potentially reduce non-renewable resource use by 16%. However, for sugarcane there was a significant increase in other environmental impacts, *e.g.* acidification and eutrophication potential; these increases were smaller when using willow. From supply chain analysis, the transport of finished and intermediate products only made a minor contribution to the environmental impacts.

The principal raw material for terephthalic acid is *p*-xylene, conventionally made from naphtha. It is feasible, however, to manufacture *p*-xylene by the catalytic conversion of sugars extracted from biomass sources. A PET bottle made using *p*-xylene derived from willow could reduce the GWP and non-renewable energy use by 32% and 2%, respectively, or 87% and 26% using sugarcane. Again, the disadvantage of using biomass was that all other environmental impact categories were increased over materials derived from petrochemicals.

Biomass can also be used for generating process heat or electricity. It was found that the best possible use of biomass within the PET value chain would be combustion to supply process heat, followed closely by burning to generate electricity. In fact, only where ethylene is produced *via* the fermentation of sugars from hydrolysed willow, and for one measure, GWP, was producing a chemical from biomass more sustainable than combustion for process heating. This conclusion is sensitive to the energy sources from which heat and grid electricity are otherwise produced and might therefore alter as future conventional energy sources change.

Finally, the possible savings in GWP and energy use by recycling PET bottles were evaluated for both closed-loop and open-loop systems. Open-loop recycling gave better savings for GWP and energy use when compared with closed-loop recycling. The transport associated with the international trade of baled bottles, largely imported by China, has a minimal effect on the possible savings by recycling.

This work has established that there is scope for improving the sustainability of the polyester industry; however trade-offs need to be carefully considered on a case by case basis.

Publications

The following papers have been published or are in progress for publication:

Published:

Impact of Biomass on Industry: Using Ethylene Derived from Bioethanol with the Polyester Value Chain.

Van Uytvanck, P.P., Hallmark, B., Haire, G., Marshall, P.J., Dennis, J.S., 2014. ACS Sustainable Chemistry & Engineering. 2, 1098-1105. doi:10.1021/sc5000804

Commercial report (in progress):

“The Outlook for Polyester Sustainability Improvements 2015-2025”

PCI Xylenes & Polyesters

In progress (delayed for commercial reasons):

Impact on the Polyester Value Chain of Using *p*-Xylene Derived from Biomass

Van Uytvanck, P.P., Dennis, J.S.

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Chapter 1 Introduction

The motivations for this research are that existing literature on the life cycle assessment of polyester products varies significantly and the impacts of using biomass as a raw material in the production of polyester have not been investigated in detail. The key objective for this research is to perform a rigorous and detailed life cycle assessment to quantify the environmental impacts associated with the production of polyester from both fossil fuel and biomass sources. This Chapter discusses the principal route, and alternative routes, to produce polyethylene terephthalate (PET) polyester. It also sets out the background to sustainability and its assessment using life cycle assessment. Finally, the objectives of the research are discussed in detail.

1.1 The Polyester Value Chain

Polyethylene terephthalate (PET) is principally used to make textile fibres, bottles and packaging films (McIntyre, 2003). In terms of annual production, it is ranked third, behind polyethylene and polypropylene: 65 Mt was manufactured in 2013, an output which has grown 5-7% per annum over the last decade (PCI Xylenes & Polyesters, 2013). Of the total PET production, around 30% is used to make bottles, 67% is used for fibres and the remaining 3% for films and other uses (PCI Xylenes & Polyesters, 2013). The PET packaging resin sector has shown demand growth at 5% in 2013 (PCI Xylenes & Polyesters, 2013). Of the total global demand for all fibres of 82 Mt in 2013, approximately half was contributed by polyester staple and filament fibres (PCI Xylenes & Polyesters, 2013). Currently, PET is most commonly manufactured by the continuous polymerisation of ethylene glycol and terephthalic acid (Rieckmann and Völker, 2003). Conventionally, both raw materials are derived from naphtha from crude oil; however, ethylene glycol is also manufactured from natural gas (PCI Xylenes & Polyesters, 2013).

A ‘value chain’ is defined as the set of processes involved in producing the final functional unit from the defined starting materials, where each process raises the value of the output over that of the input. The value chain for virgin PET produced from conventional crude oil and gas feedstocks is represented diagrammatically in Figure 1.1. Virgin PET refers to the polymer being produced from its raw materials rather than from recycled PET. From Figure 1.1, terephthalic acid is manufactured solely by the oxidation of *p*-xylene, which, in turn, is separated from reformed naphtha. Ethylene glycol is manufactured by the hydrolysis of ethylene oxide, which is produced from the oxidation of ethylene. Ethylene is derived by steam cracking naphtha or natural gas, depending on the regional production mix.

Downstream processing operations after the continuous polymerisation stage depend on the desired end product. The degree of polymerisation needed for bottle-grade PET is generally higher than that for fibre products and hence, typically, requires a further, solid-state polymerisation stage, not needed for fibres (Culbert and Christel, 2003). The bottle-grade PET resin is injection-moulded into preforms and then stretch blow-moulded to make bottles, which are filled and distributed. Fibre production typically involves spinning, weaving, dyeing, finishing, cutting and make-up in order to produce an item of clothing as the end product.

The end products also feature a use phase. For packaging, the environmental impacts during use are generally small compared with those incurred during production; however, for fibres, the use phase can account for a considerable proportion of the total environmental impacts. This will be discussed in more detail later. Considering the whole life, both end products will require a final disposal stage.

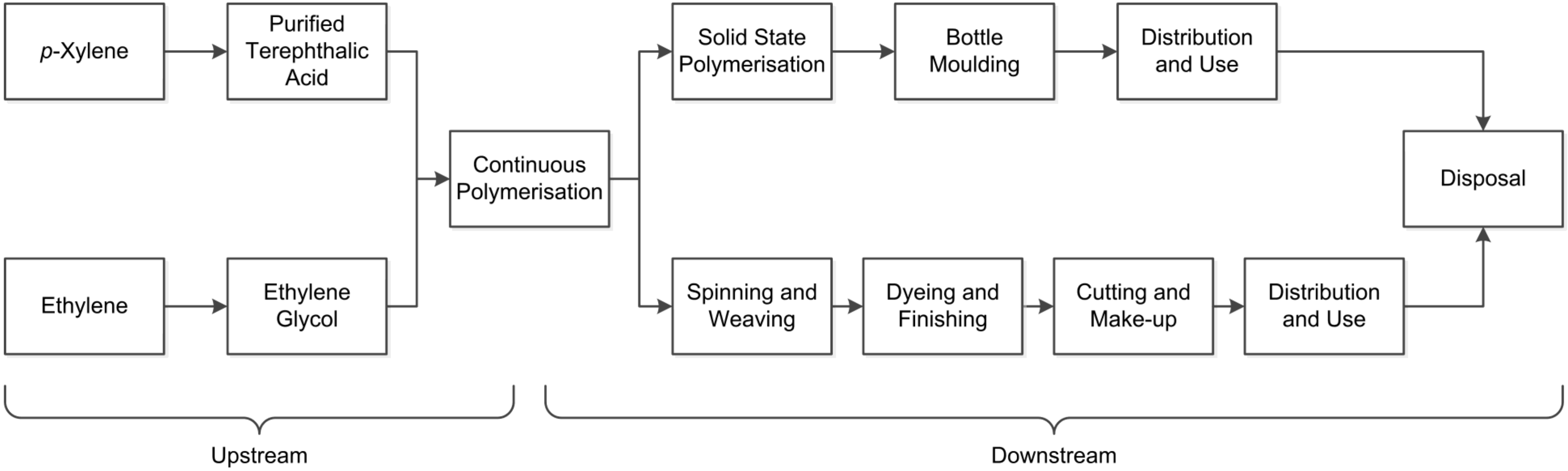

Figure 1.1. Value chain for the production of virgin polyester, used for either bottles or fibres.

1.2 Sustainability

The total human population reached seven billion in October 2011, increasing at a rate of 80 million/year (Worldometers, 2014). This large and rapidly-growing population places significant demands on the environment, both at a local and a global level, because of the increasing consumption of resources and quantity of waste generated. The environmental demands placed on the Earth by anthropogenic activities have been the subject of many studies, from land use (Meyer and Turner II, 1994) to industrial ecology (Socolow *et al.*, 1994). One measure of the demand on the environment is the 'global ecological footprint', defined as the area of land and water a human population requires to provide the resources it consumes and to absorb the wastes generated (Wackernagel and Rees, 1998). Wackernagel *et al.* (2002) have demonstrated a growing deficit between the global ecological footprint and the available 'carrying capacity' of the earth. The carrying capacity is the available capacity of ecosystems to produce useful materials, and to absorb waste materials generated, without undergoing irreversible change. On this basis, in 1991, the sum of human activities had exceeded the carrying capacity of the Earth by 20%, a deficit which had increased to 50% by 2007 and is projected to exceed 100% by 2030 (Global Footprint Network, 2014), which means that resources equivalent to two earths would be required to sustain human activity. The carbon footprint, *i.e.* the net carbon dioxide emissions from the burning of fossil fuels, is the dominant driver of the ecological overshoot (WWF *et al.*, 2014). In essence, the total of anthropogenic activities exceeds the ability of the Earth's biosphere to absorb them.

It is becoming increasingly clear that the Earth's natural capital can no longer be considered a 'free good' in economic analysis. Natural capital, defined as the stock of environmental assets, is so heavily used, that it has become the limiting factor for some industries (Daly, 2005). A typical illustration of this concept is the fishing industry, which is restricted by the decreasing numbers of fish, not by the number of fishing boats (Daly, 2005). The lack of concern for natural capital and environmental protection is often referred to as the 'tragedy of the commons' (Hardin, 1968). This occurs when self-interested groups or individuals seek to maximise economic gain from a common resource without regard for the collective interest; the results can be extreme in the absence of prohibitive legislation (Hardin, 1968).

The free-market economy has its limitations with respect to sustainable resource and environmental management. The principal causes are the conflicting economic and environmental interests and the associated time-scales on which they operate. One method to counter these limitations is through legislation to make the economic activity accountable for the externalities caused. In the case of climate change, there have been significant changes in public policy over the past decade, both on a national and international level. For example, in the UK, the Climate Change Act (2008) legally binds the UK to reduce total greenhouse gas emissions from 1990 levels by 26% before 2020 and by 80% before 2050 (UK Parliament, 2008). The European Union (EU) has committed itself to reduce net greenhouse gas emissions from 1990 levels by 20%, 40% and 80% by 2020, 2030 and 2050, respectively (European Commission, 2014). The EU has also established the EU Emission Trading System in an attempt to reduce greenhouse gas emissions from industry in a cost-effective manner (European Commission, 2014). Global commitment is encapsulated in the Kyoto Protocol, which initially required participating countries to reduce greenhouse gas emissions by 5% against 1990 levels in the five year period 2008-2012 (UNFCCC, 2014). This has since been amended to an 18% reduction in the eight year period 2013-2020; however, only 19 nations have ratified the amendment (UNFCCC, 2014).

Despite these measures, annual, global anthropogenic emissions of CO_2 from fossil fuel use and cement production have continued to increase and were estimated to be 34.5 billion tonnes CO_2 in 2013 (Olivier *et al.*, 2013). Whilst anthropogenic greenhouse gas emissions, measured on a CO_2-equivalents basis, from the UK fell 22.5% between 1990 and 2012 (DECC, 2014), it is important to note that, allowing for the emissions associated with imported goods and services, UK emissions have actually increased (Barrett *et al.*, 2013). In essence, as manufacturing has moved offshore, the associated pollution has been exported (Barrett *et al.*, 2013), thus shifting the burden rather than achieving a true overall reduction in emissions.

The above emphasises the need for clarity and definition in considering sustainability. A popular definition of sustainability was articulated by the Brundtland Commission as “meeting the needs of the present without compromising the ability of future generations to meet their own needs” (WCED, 1987). Since then, various other definitions have emerged; however, the concept and common principles often remain unchanged. The principles include: commitment to equity and fairness, prevention of environmental damage and degradation, and recognising the interdependent nature of the environment, economy, and society (Drexhage and Murphy, 2012). The latter principle is often called the triple bottom line, essentially sustainability is a balance between environmental, social and economic goals (Elkington, 1998). It is also appropriate here to note that the environmental impact of a nation in its consumption of a product is roughly proportional to (i) the size of the population, (ii) affluence *per capita*, (*i.e.* the ability to purchase the product), and (iii) the environmental impact of the technology associated with manufacture and use of the product (York *et al.*, 2003). Much research focuses on (iii); however, irrespective of how efficient the technological aspects are, the effects of technical improvements can be readily nullified by population growth and increase in affluence. Worse still, there are often limits to the degree to which technology can be refined to increase efficiency, imposed by, for example, thermodynamic constraints.

Having defined sustainability, the main problem is making the transition from the qualitative statements to pragmatic implementation. Sensible and quantifiable indicators are required to measure progress and improvements towards sustainable development. Such an indicator might be level of carbon dioxide emissions, as is used in many of today's policies. However, this single indicator does not encompass many other types of impact, such as the toxicity of waste streams. Furthermore, a product with low impact on the environment when produced, can have a large impact during use; *e.g.* a car. Essentially, sustainability cannot solely be measured based on one indicator and it needs to account for the entire life cycle of a product. One tool which achieves this is life cycle assessment (LCA).

1.3 Life Cycle Assessment

This section reviews life cycle assessment (LCA); further details on LCA methods are provided in Chapter 3. LCA is a technique used to quantify the environmental impacts associated with the whole life of a product or service, from the extraction of raw materials to the disposal of waste at the end of the product's life. LCA is a useful tool in making decisions because different scenarios can be compared systematically to determine which is the most environmentally sound. There are four stages in constructing an LCA (ISO, 2006a, 2006b):

1. Goal and scope, definition of the system boundaries and the functional unit.
2. Inventory analysis, that is to say, the compilation and quantification of inputs and outputs for the selected system throughout its life cycle.
3. Impact assessment, namely understanding and evaluating the magnitude and significance of the potential environmental impacts for the product system.
4. Interpretation, the findings are evaluated in relation to the defined goal and scope in order to reach conclusions and recommendations.

The functional unit is defined as a fixed quantity of a product or service and forms the basis for comparisons with other systems. The system boundary defines the processes or stages included within the LCA study. A complete LCA will include all processes involved in the life of the functional unit, including use and disposal; this is known as a cradle-to-grave LCA. However, some studies only consider the first few stages of the product's life, *e.g.* raw material extraction and manufacture; these studies are classified as cradle-to-gate, *i.e.* the system boundary has been drawn at the factory gate before the use and disposal. Finally, a gate-to-gate LCA covers intermediate processes, but not the initial raw material extraction. These boundary definitions have been summarised in Figure 1.2.

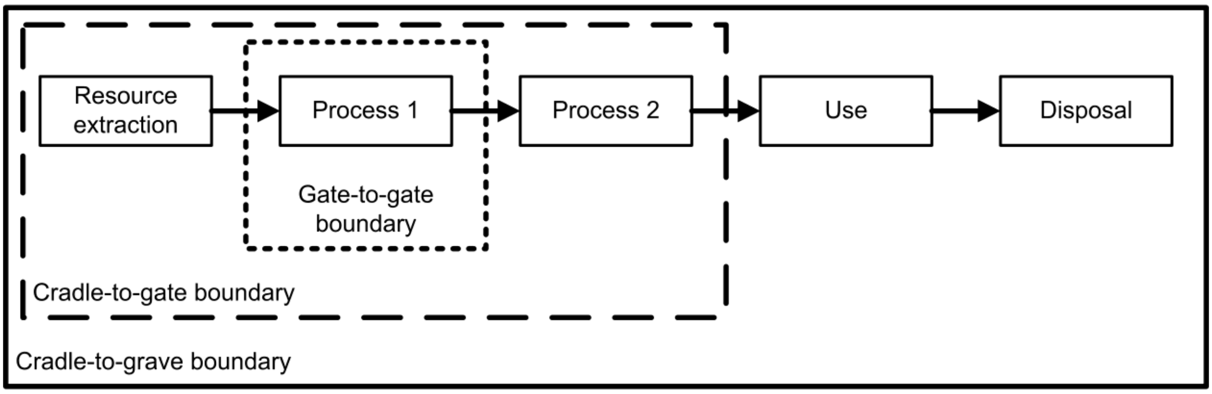

Figure 1.2. Cradle-to-grave, cradle-to-gate and gate-to-gate boundary definitions

The main outcomes from LCA are a set of quantified environmental impact categories, the impacts shown here are from the CML method (Guinée *et al.*, 2002):

- Energy requirements
- Global warming potential
- Abiotic depletion potential
- Acidification potential
- Eutrophication potential
- Ozone depletion potential
- Toxicity (human, freshwater, terrestrial, marine)
- Photochemical ozone creation potential.

These environmental impact categories can be used to accurately compare equivalent product systems.

Most studies publish the results for energy requirements and global warming potential. Briefly, global warming potential is defined as the impact of human emissions on the atmospheric absorption of radiation leading to an increase in global temperature, a more detailed definition is provided in Chapter 3. The definitions of the other environmental impacts used in this research are in Table 3.1 in Chapter 3.

Environmental impacts are quantified using a reference chemical. For example, global warming potential is quantified in terms of the equivalent mass of carbon dioxide. Emissions with the potential to cause global warming are converted to carbon dioxide equivalents using their potency. The potency is dependent on how effective the emission is at contributing to the environmental impact and how long the effects of a particular emission remain after first release.

1.4 Reducing the Environmental Impact of Using Polyester

The environmental impacts of anthropogenic activities, such as global warming and resource scarcity, are a growing concern. Increased legislation and incentives are persuading many industries to develop greater efficiency, reduce waste, and minimise the production and use of harmful raw materials or products. There is an increased awareness within the polyester industry of the need to make production routes as sustainable as possible. There are several routes already in use and new routes in development, summarised in Figure 1.3.

One proposed scheme, shown in Figure 1.3, is to use biomass, rather than naphtha and natural gas, as the principal raw material for producing ethylene, and hence ethylene glycol, which accounts for 28 wt% of PET. This substitution has the potential to reduce the greenhouse gas emissions by replacing part of the fossil fuel requirement. An advantage of using biomass in this way is that only minimal changes are needed to existing process plants. Two routes from biomass exist. The first is *via* the dehydration of bioethanol to ethylene (Morschbacker, 2009), which can then be converted to ethylene glycol using conventional processing. The second route is *via* the direct catalytic conversion of sugars to polyols, from which ethylene glycol can be separated (Ji *et al.*, 2008; Liu *et al.*, 2014; Wang and Zhang, 2013). Three companies, Braskem, India Glycols, and Solvay, are reportedly dehydrating ethanol to ethylene, with the largest projected capacity being 200 kt/y of ethylene (Braskem, 2014; Cooper, 2013; Fan *et al.*, 2012). The catalytic conversion of sugars is still under development and is not as close to commercialisation (Liu *et al.*, 2014; Wang and Zhang, 2013). The dehydration of bioethanol, as a means of producing ethylene glycol, is investigated in Chapter 4.

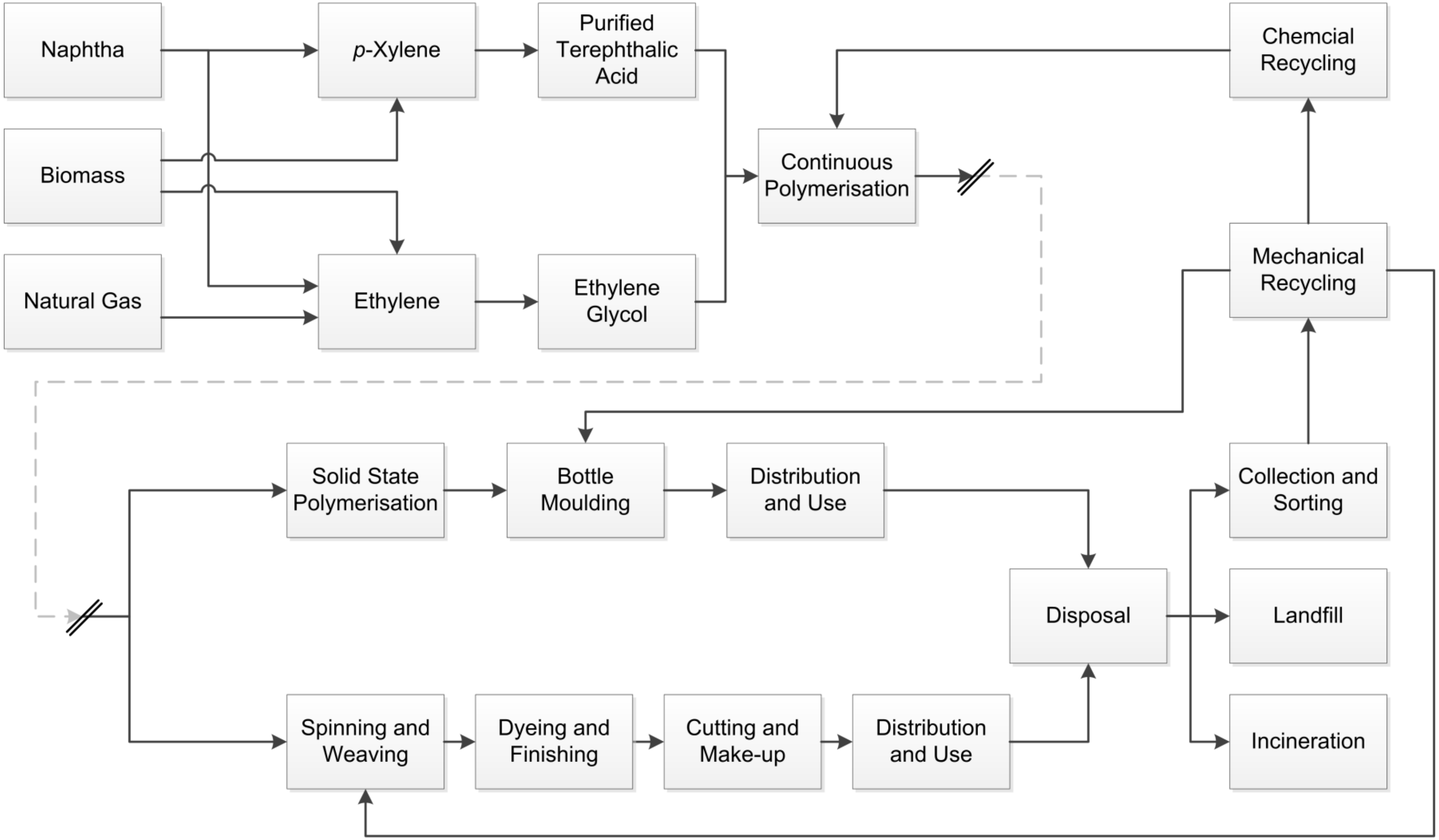

Figure 1.3. Detailed value chain including the range of feedstock sources and recycling routes.

As shown in Figure 1.3, biomass could also serve as the feedstock for terephthalic acid, which accounts for the larger proportion, *i.e.* ~72% by mass, of the final PET polymer. Therefore, biomass substitution for terephthalic acid has, in principle, substantial potential for reducing greenhouse gas emissions and fossil fuel use. There are several routes to produce terephthalic acid from biomass. One, currently at demonstration plant scale, uses the direct catalytic conversion of biomass sugars to produce reformate, from which *p*-xylene can be separated and then oxidised to terephthalic acid using conventional processing (Blommel and Cortright, 2008; Virent, 2014). This route is studied in detail in Chapter 5. Another scheme, also at demonstration plant scale, involves the catalytic conversion of isobutanol, derived from the fermentation of biomass sugars, to, *inter alia*, *p*-xylene (Gevo, 2014; Tuck *et al.*, 2012). While other methods of converting biomass to *p*-xylene exist, *e.g. via* 5-hydroxymethlyfurfural or catalytic fast pyrolysis, these routes are a long way from scale up and commercialisation (Anellotech, 2014; Gevo, 2014; Lin *et al.*, 2013; Virent, 2014). Finally, to avoid the production of *p*-xylene as an intermediate, it has been shown that terephthalic acid can be produced from sugars *via* muconate esters (Cooper, 2013). Another route being considered is the replacement of terephthalic acid with furandicarboxylic acid, derived from biomass. In this case, a different polymer, polyethylene furanoate (PEF), is produced. This technology is also currently at pilot scale (Avantium, 2014), but it is unclear if downstream PET processing operations, such as continuous polymerisation, can be used for PEF.

It is important to note that all the above routes require sugars as key intermediates, produced either (i) directly from sugarcane and sugar beet, or (ii) *via* the hydrolysis of either starchy crops, *e.g.* corn or wheat, or of woody biomass or agricultural residues, *e.g.* coppiced willow, corn stover or sugarcane bagasse. In most cases, lignin residues are burnt for energy recovery (Davis *et al.*, 2013). However, mechanisms are under development for the breakdown of lignin (Davis *et al.*, 2013). Of course, waste biomass can also be used directly for process heating or for generating electricity. These indirect uses of biomass are important, particularly where they displace fossils fuels for the same duty; this is discussed in Chapter 6.

One of the most direct methods of reducing environmental impacts would be to simply use less material. There are several mechanisms to reduce material demand, such as, creating products with a longer life, reuse, reducing scrap material and better utilisation. The process of ‘light-weighting’ PET bottles is briefly discussed in Chapter 4 of this Dissertation.

PET packaging can be recycled, exemplified commercially by the mechanical recycling of PET bottles, which are collected, baled and shredded into flake. PET flake can then be used to produce new bottles, thereby avoiding the use of virgin PET. Alternatively, mechanically-recycled PET flake can be used in melt-phase spinning to make fibres. It is also possible to recycle PET chemically. This involves the breakdown of the scrap polymer to chemical precursor by methanolysis, glycolysis, or hydrolysis. Chemical recycling allows stricter control of the quality, grade and degree of polymerisation. Considering the disposal, PET can be either sent to landfill or incinerated with energy recovery. Recycling and disposal are investigated in Chapter 7.

1.5 Aims and Objectives

The objective of the research presented in this Dissertation is to quantify and compare the environmental impacts associated with the individual operations in the polyethylene terephthalate (PET) value chain. Whilst the main focus is on fossil fuel use and global warming potential, other environmental impacts are also considered in order to provide a comprehensive picture of the systems analysed. To do this, life cycle assessment (LCA) has been undertaken to compare the conventional process route (with raw materials made from fossil fuels) to alternative process routes (using biomass and recycling). As discussed in the literature survey in Chapter 2, there is substantial scope to undertake rigorous life cycle assessment on PET production.

The environmental impacts of using biomass as a raw material, for the production of ethylene and *p*-xylene, on the polyester value chain have not hitherto been investigated thoroughly. This has been rectified in the present Dissertation. The land area required for global polyester production from biomass at various degrees of substitution has been quantified. The economic feasibility of using biomass as a raw material feedstock for polyester production *via* the dehydration of bioethanol to ethylene has also been considered.

Considering the triple bottom line of sustainability (Elkington, 1998), the focus of this Dissertation is on the environmental sustainability of the polyester value chain; social and economic issues are only briefly discussed.

1.6 Organisation of the Dissertation

In Chapter 2, the relevant literature on polyester is reviewed.

A detailed description of the technique of life cycle assessment used is provided in Chapter 3.

In Chapter 4, the environmental impacts of using biomass-derived ethylene feedstock in polyester production are investigated. The impact on land use of global scale PET production from biomass and the economic viability of a dehydration process are also assessed.

The sourcing of *p*-xylene from biomass is considered in Chapter 5. The sensitivity of the results to different methods of allocating the environmental burdens has been investigated in detail. The land requirements of cultivating biomass for the global PET demand and economic potential of biomass derived *p*-xylene are discussed.

Biomass can be used as a feedstock for ethylene glycol and *p*-xylene production, but it could also be burnt to provide heat or electricity to processes within the value chain. In Chapter 6, the optimal use for biomass within the value chain is considered in order to maximise the reduction of non-renewable energy use and global warming potential.

The various recycling and disposal methods for polyester are investigated in Chapter 7, allowing for the impact of global materials transport, *e.g.* the shipping of baled bottles from the EU and USA to China for recycling.

Finally, overall conclusions are drawn in Chapter 8.

An overview of the polyester value chain showing each analysis from Chapters 4-7 has been shown diagrammatically in Figure 1.4.

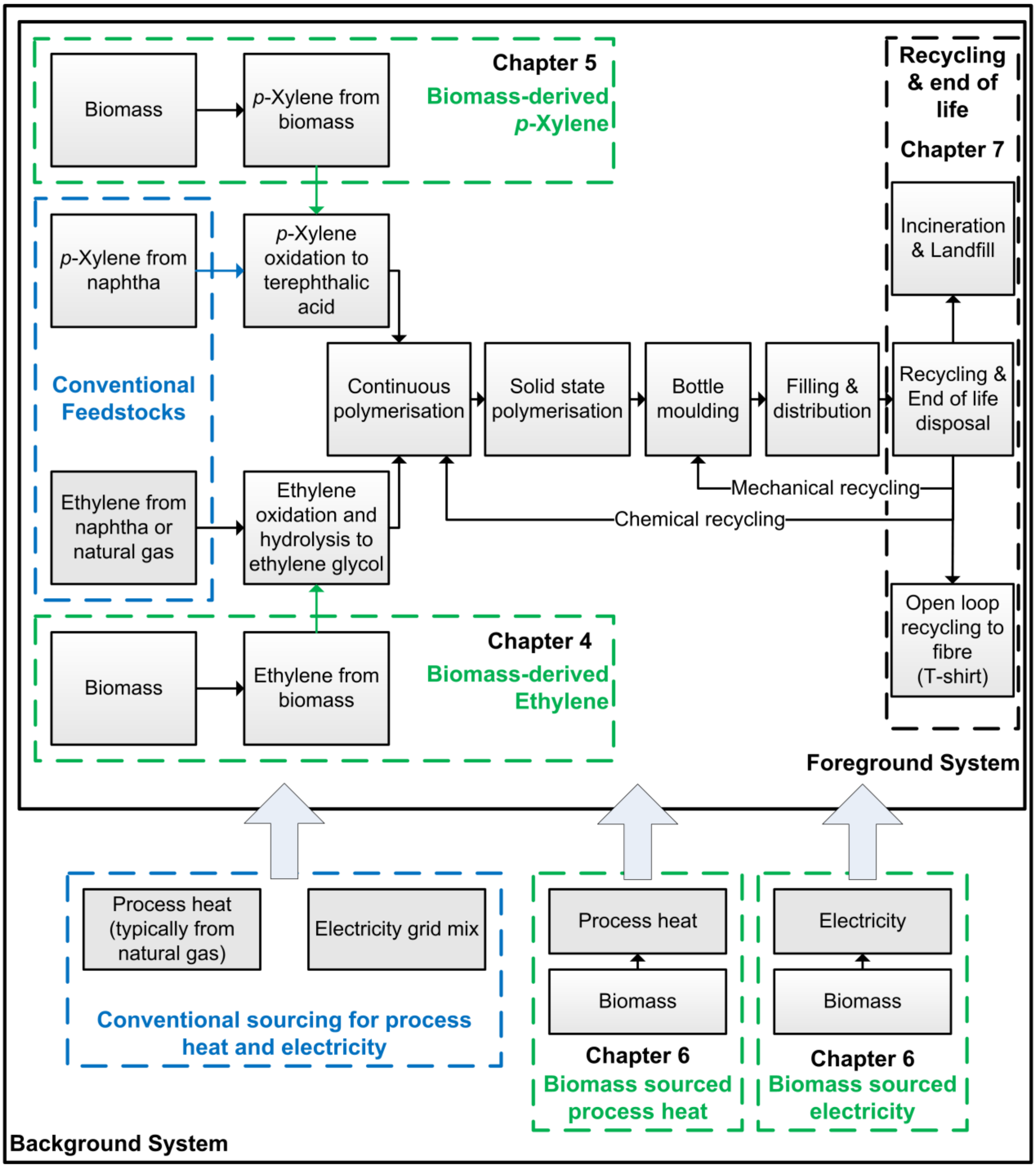

Figure 1.4. Overview of the processes analysed in each research chapter

Chapter 2 Polyester Literature Overview

In this Chapter the relevant literature on polyester and biomass is reviewed.

There have been several studies of the sustainability of various parts of the polyester value chain; however, much of this research has been conducted by commercial organisations, rather than academic researchers, resulting in a lack of peer-reviewed literature. Other studies consider polyester as a constituent material, quantifying its contribution to the environmental impact using pre-existing datasets. While the use of pre-existing datasets serves its purpose for studies considering the manufacture of polyester as a background process, much more detail is required when polyester is the actual focus of the study, *i.e.* when it is the foreground process.

As noted in Chapter 1, most studies commonly present two measures of environmental impact, namely non-renewable energy use and global warming potential. In Table 2.1, these two measures have been used to compare studies and indicate the variability in the literature. According to the international standards for LCA, ISO 14040 and ISO 14044, there is no strict requirement for LCA studies to consider a defined set of environmental impacts (ISO, 2006a, 2006b). Therefore, many studies do not include additional environmental impacts, *e.g.* acidification or eutrophication, beyond energy and global warming potential, and when they do, there is little consistency among studies. Worse still, a range of different impact assessment methods have been used in the literature, so that the results for other environmental impacts are not easily comparable. The results from studies summarised in Table 2.1 are normalised on the basis of 1 kg of PET for ease of comparison. Most of the variation among studies can be accounted for by differences in the system boundaries (*i.e.* the processes included in the study), the age of the study and the assumed geographical location.

Table 2.1. Summary of PET sustainability studies on the basis of 1 kg of PET

Study	Details	Global warming potential kg CO_2-eq	Non Ren. Energy MJ	Other impacts
PlasticsEurope study from 2005 (PlasticsEurope, 2011)	Virgin PET resin in Europe	3.49	82.3	Wide range of environmental impacts
PlasticsEurope (2011)	Virgin PET resin in Europe	2.15	68.6	Wide range of environmental impacts
Franklin Associates (2007)	PET *cf.* PLA bottle for water in USA.			Solid waste and inventory of air and water emissions
	No recycling, 20% incineration	3.73	81.8	
	23.5% recycling, 15.3% incineration	3.50	74.9	
Franklin Associates (2009) (12 fluid ounce, 340 mL addendum)	PET, Glass and Aluminium carbonated soft drink containers in USA. 23.5% recycling and 20% incineration with energy recovery	4.47	82.3	Solid waste and inventory of air and water emissions
Franklin Associates (2011a)	Virgin PET resin in USA. Incineration with energy recovery	2.73	69.7	Solid waste and inventory of air and water emissions
Gabi database	PET *via* dimethyl terephthalate	2.96	85.2	N/A – database
(PE International, 2013)	PET resin from PlasticsEurope	2.14	68.6	
	PET bottle from PlasticsEurope	4.68	104	
Ecoinvent v2.2 database	PET granules amorphous	2.70	77.2	N/A – database
(Ecoinvent Centre, 2010)	PET granules bottle grade	2.89	80.7	
Kalliala & Nousiainen (1999)	Polyester fibre	N/A	97.0	Inventory list
Range	N/A	2.14 – 4.68	68.6 – 104	N/A

2.1 PET Resin and Packaging

A commonly-quoted LCA study of PET production was that conducted by the Association of Plastics Manufacturers in Europe (PlasticsEurope, 2011), which considered the impact of producing 1 kg of bottle-grade PET resin. The LCA encompassed all the operations from the extraction of resources to produce the initial raw materials to the production of bottle-grade PET; however, bottle moulding, use and disposal were not included in the results. The study's results were based on averaging information from polyester producers in Europe in 2008. It was found that 1 kg of bottle-grade PET required 69.4 MJ of energy (99% from non-renewable sources) and emitted 2.15 kg CO_2-eq (PlasticsEurope, 2011). However, the research did not consider some potentially-important operations, *e.g*. the effect of imported PET, distribution of products, use, recycling and disposal. Compared with an earlier version of the study, conducted in 2005 with process information from 1999, there had been a 16% reduction in energy use, and 38% reduction in global warming potential (PlasticsEurope, 2011). The reductions largely arose from improved process efficiency in the production of purified terephthalic acid. While the efficiency of the polymerisation stage had also improved, the efficiency gains from terephthalic acid production were dominant (PlasticsEurope, 2011). Small savings in global warming potential also arose from changes in external energy supply, such as the energy mix used to generate grid electricity being less carbon-intensive at the later date (PlasticsEurope, 2011).

Franklin Associates, a LCA consultancy based in the USA, has published several studies, listed in Table 2.1, including a comparison of bottles made from PET with polylactide (PLA) (Franklin Associates, 2007) and with glass bottles and aluminium cans (Franklin Associates, 2009). PET resin was also compared with a range of other resins (Franklin Associates, 2011a). The research focused on three environmental categories: energy use, emissions of greenhouse gases and solid waste. Emissions to water and those to the atmosphere outside of global warming were also quantified but were not categorised into environmental impacts. The studies are, in essence, life cycle inventories, *i.e.* completing the first two stages of life cycle assessment (summarised in Section 1.3, with greater detail in Chapter 3, below); however, the results give useful insight into the energy requirements and greenhouse gas emissions even though drawing conclusions based on trade-offs allowing for a wider range of environmental impacts is not possible. Overall, while the cradle-to-gate analysis of the studies is detailed, the end of life analysis was simplistic; for example, although the research considered energy recovery from incineration, the full incinerator emissions were not considered (Franklin Associates, 2009). Whilst only non-renewable energy requirements have been summarised in Table 2.1, the contribution from renewable sources was approximately 1%. A comparison of the results for Franklin Associates (2009, 2007) and Franklin Associates (2011a) in Table 2.1 suggests that the system boundary in the earlier studies included the bottle-moulding process, whilst the later study did not, because the energy requirements and carbon emissions were larger in the earlier reports.

In the latest study, Franklin Associates (2011a) collected process information from producers and proceeded with averaging at different stages in the processes, using a similar technique as PlasticsEurope (2011). Comparing research on the production of virgin PET resin, *i.e.* Franklin Associates' (2011a) study with PlasticsEurope (2011), non-renewable energy requirements are within 2%. However, there is a substantial difference in global warming potential of 27%, probably reflecting differences in background energy sources and processing between the USA and Europe. For example, the electricity grid mix used in the USA study is more carbon intensive, having a larger fraction of natural gas (42% *cf.* 24%) and coal (9% *cf.* 6%) use, but a lower fraction of nuclear (3% *cf.* 5%) than the European study. Another difference between the studies is the system definition, Franklin Associates (2011a) allocated 15% of PET production *via* the dimethyl terephthalate route, an older technology, and 85% from the continuous polymerisation using purified terephthalic acid. The system diagram from PlasticsEurope (2011) reflected PET production from purified terephthalic acid only.

Finally, instead of creating new models, research such as the studies by Madival *et al*. (2009) and Gironi & Piemonte (2011), use databases of processes, in particular, those from Ecoinvent (Ecoinvent Centre, 2010) and Gabi (PE International, 2013). These values have also been summarised in Table 2.1. These databases contain the inventory analysis, the inputs and outputs, for individual processes or sets of aggregated processes. The organisations responsible for the databases, *e.g.* Ecoinvent and Gabi, either develop their own models of processes, collect averages from industry, or use studies such as those from PlasticsEurope (2011). Given the proprietary nature of these databases, it is impossible to ascertain the details of calculations involved for each dataset.

2.2 PET Packaging Substitutes

In comparing polylactide (PLA) bottles with PET bottles, it was found that PLA bottles required 15% more energy in their manufacture than PET bottles, for the same function (Franklin Associates, 2007). However, the amount of fossil fuel required to make PET bottles was greater because PET is made from crude oil, as opposed to corn for PLA bottles. Franklin Associates (2007) concluded that, for the two plastics, the greenhouse gas emissions were comparable within 5%, as were the waste and other emissions. Other research (Gironi and Piemonte, 2011; Madival *et al.*, 2009) has shown various savings on global warming potential and non-renewable energy use when using PLA instead of PET. Madival *et al*. (2009) and Gironi & Piemonte (2011) considered environmental impacts other than global warming potential and use of non-renewable energy, but there were considerable disparities between the two studies in this respect.

Franklin Associates (2009), compared a glass bottle, an aluminium can and a PET bottle of the same volume (12 fluid ounce, 340 mL). In terms of mass of packaging, a 340 mL container required 13.2 g aluminium, 211 g glass or 23.5 g PET. The relative weights of the material are an important factor for transportation to distribution facilities; however, the study did not include the transporting the final packaging in the system boundary. On the basis of energy required for producing 10000 drinks containers, there was little difference among packaging materials; aluminium required 20.3 GJ, glass 24.2 GJ, and PET 21.2 GJ. Of the 21.2 GJ energy required to make the PET bottles, ~42% is embodied in the plastic. On the basis of greenhouse gases, PET performed the most favourably with the aluminium and glass bottles producing 46% and 98% more greenhouse gases, respectively (on a CO_2-equivalent basis). Of course, this does not consider the end of life of the product. If the PET were to be incinerated, greenhouse gas emissions would increase; however, with energy recovery, heat or electricity could be generated from the energy embodied in the plastic. This is not the case for glass or aluminium. Again, whilst the study listed emissions to air and water, the lack of a more complete set of environmental impacts for comparison amongst the materials, means that a definitive comparison of their relative sustainability is not possible.

Amienyo *et al.* (2012) also compared aluminium, glass and PET as containers for a given volume of a carbonated soft drink and showed that PET was favourable with respect to global warming potential. However, their research used containers of different sizes, which distorts the comparison significantly. Amienyo *et al.* (2012) used database values for PET production from Gabi. Gabi is LCA software, which contains datasets for a wide range of materials and energy sources and their associated environmental impacts. Amienyo *et al.* (2012) showed that recycling PET at 40-60% could reduce global warming potential of the packaging by 32-48%. Franklin Associates (2009) also demonstrated that recycling has a net beneficial effect.

2.3 Polyester Fibres

Although many studies exist on bottle-grade PET, there are few on fibres. One investigation of fibres compared 100% cotton sheets with sheets made from fibres containing 50% cotton and 50% polyester (Kalliala and Nousiainen, 1999). The results suggested that although cotton fibre requires 40% less energy per unit mass than polyester fibre in manufacture, cotton requires larger quantities of water, in addition to the pesticides and fertilisers used in its cultivation, which have significant negative environmental impacts. It was found that the 50/50 cotton-polyester sheets had a lower impact than sheets made wholly from cotton, owing to greater durability in use and lower laundering energy requirements. Another study (BSR, 2009) confirmed the larger energy requirement for the production of polyester fibre, with cotton requiring ~50 MJ/kg and polyester ~110 MJ/kg. It should be noted that, owing to differences in fibre strength, different masses of fibres would be required to fulfil the same function. Ideally, a functional unit, such as a sheet or t-shirt, should be compared rather than fibres on a basis of unit mass; however, due to the limited information available, a more detailed comparison is not possible.

Collins & Aumonier (2002) undertook a life cycle assessment of two items of male apparel, namely polyester trousers and cotton briefs. The analysis determined the energy footprints for the two products from resource extraction, through production and manufacture, ending with use and disposal. Other environmental impacts were not considered. The study showed that the energy use was dominated by the consumer use phase, with 76% of the total life-cycle energy (~720 MJ in total for the pair of polyester trousers) attributable to washing, drying and ironing. This demonstrates that the phase of consumer use of clothing items contributes significantly to their environmental impact. As noted with other studies, the focus on one indicator (in this case, energy) is insufficient for a complete understanding of the environmental impact. The dominance of the use phase for clothing has been confirmed by other studies, *e.g.* Allwood *et al.* (2006), Steinberger *et al.* (2009) and BSR (2009), but, generally, LCA analyses in the apparel industry are often limited in scope. It is especially difficult to compare a functional unit such as sheets (Kalliala and Nousiainen, 1999) with trousers and briefs (Collins and Aumônier, 2002) because of the difference in function and associated consumer treatment of such articles.

2.4 End of Life Studies

LCAs on waste management for PET feature a range of scenarios including recycling, landfill, and incineration. Most studies suggest that recycling is favourable with regard to energy use and greenhouse gas emissions in comparison to landfill and incineration (Finnveden *et al.*, 2005). Despite the greenhouse gases produced, the next best alternative to recycling is incineration with energy recovery, leaving the worst option as landfill (Moberg *et al.*, 2005). Landfill results in the disposal of an energy-rich waste, whereas for incineration with energy recovery, other fossil fuel use can be avoided. For incineration, some research (Hu *et al.*, 2009; Rieckmann and Völker, 2003) suggests there are significant concentrations of heavy metals in the fly ash, principally manganese and zinc used as catalysts in polymerisation; it was unclear if the concentrations were above toxic levels. For recycling, larger collection systems result in lower energy input requirements per unit mass processed (Song and Hyun, 1999). The best scenario with respect to energy use was a combination of closed loop, *i.e.* bottle-to-bottle, recycling and incineration with energy recovery; however, with incineration, carbon emissions are increased, imposing a trade-off between energy use and global warming potential (Song and Hyun, 1999).

In the fibre sector, Woolridge *et al*. (2006) showed that recycling by reusing the clothing can save 324 MJ/kg polyester clothing compared to using virgin polyester. A more comprehensive study investigated the open-loop recycling of PET bottles to fibres (Shen *et al.*, 2010). The research analysed a wide range of environmental impacts and compared the results with virgin PET fibre and other commodity fibre products. Depending on the recycling technology, mechanical or chemical recycling, and the system boundaries drawn, savings in global warming potential of 25-75% and non-renewable energy of 40-85% could be achieved relative to the use of virgin material (Shen *et al.*, 2010). It is much harder to recycle PET fibre than bottles, because PET fibres are typically blended with other textile fibres and various additives, such as dyes and finishing chemicals, which are difficult to remove to create a clean stream of recycled PET (Shen *et al.*, 2011).

Most studies of waste management compare the use of energy for recycling with that for creating the same product from virgin polymer and generally show energy savings when incorporating recycling. However, because the studies assess different recycling schemes and processes, draw different boundaries and use various allocation mechanisms, it is difficult to summarise the energy savings in a more quantitative manner.

2.5 Biomass Sourcing

Given that some routes investigated in this Dissertation make use of biomass sources, a brief overview covering the potential benefits and drawbacks of using biomass is provided here. Finally, the optimal types of biomass for the production of the raw materials for polyester are identified.

A wide range of commodity chemicals, of which polyester is one, could, in principle, be generated from biomass, sugars and lignocellulose (Holladay *et al.*, 2007; Werpy *et al.*, 2004). Biomass is seen as a good candidate to improve sustainability because it is a renewable resource and it can lead to lower carbon emissions. It is a suitable substitute for fossil-derived feedstock, as it makes use of existing process technologies and established supply chains. There are however many broader considerations to take into account when comparing the use of biomass to traditional feedstocks. Firstly, the biomass needs to be sourced sustainably. This means that important factors, such as use of fertiliser, water and land, must be accounted for in rational comparative studies, such as a life-cycle assessment. There are also social and ethical considerations associated with the use of biomass. For example, the competition between food and biofuels, and the competition for cropland is growing as indicated by the phenomenon of ‘land grabbing’ (Bringezu *et al.*, 2012). 'Land grabbing' occurs when local communities and individuals lose access to land that they previously used, threatening their livelihoods (Friends of the Earth, 2014). The land is acquired by outside investors and typically used for commodity crops, including those used for biofuels. It is important for these social issues to be addressed in addition to economic and environmental concerns, giving rise to the triple bottom line for sustainability (Elkington, 1998).

There are many LCA studies on the production of ethanol from (i) first-generation food crops, *e.g.* sugarcane (Luo *et al.*, 2009a), sugar beet, corn, wheat and potatoes, (ii) from second-generation lignocellulosic materials, *e.g.* willow (Stephenson *et al.*, 2010) and switch grass, and (iii) from waste residues, *e.g.* corn stover, wheat straw, and molasses (Balat, 2011; Larson, 2006; Quirin *et al.*, 2004; von Blottnitz and Curran, 2007). Most studies of bioethanol production show savings in global warming potential and fossil fuel energy use when compared with gasoline. The main factors dominating the performance of bioethanol are crop productivity, climate and the nature of the feedstock (von Blottnitz and Curran, 2007). When assessing studies of bioethanol, the ranges for potential savings are large. This is owing to the different assumptions made regarding the cultivation, conversion and allocation of by-products (Quirin *et al.*, 2004). Few studies, however, fully assess other environmental impacts; for those that do, bioethanol is typically at a disadvantage when compared to fossil fuels, with the key trade-offs being higher levels of acidification, eutrophication, and ozone depletion due to their use of nitrogen compounds in agricultural production (Quirin *et al.*, 2004; von Blottnitz and Curran, 2007).

While it is difficult to compare biomass sources directly, because of their different energy contents and processing requirements, some comparisons have been made on the basis of their performance for producing transport fuels (Balat, 2011; Larson, 2006; Luo *et al.*, 2009a; Quirin *et al.*, 2004; Stephenson *et al.*, 2010; von Blottnitz and Curran, 2007). Sugarcane and willow both showed the largest potential for carbon emissions savings over fossil fuels. The main biomass crops assessed in this Dissertation are therefore sugarcane juice, cellulosic waste (sugarcane bagasse), and finally, lignocellulosic willow (Ecoinvent Centre, 2010; Stephenson *et al.*, 2010).

Three studies have considered biomass as a raw material for PET (Chen and Patel, 2012; Shen *et al.*, 2011; Tabone *et al.*, 2010). Tabone *et al.* (2010) proposed that bioethanol produced from sugarcane in Brazil be dehydrated to ethylene. They qualitatively concluded that ethylene from biomass would provide a saving in greenhouse gas emissions and fossil energy use, over conventional manufacture, but found an increase in other impact categories. The detail in the analysis of Tabone *et al.* (2010) is limited; in particular, the inventory analysis does not include mass and energy balances for the dehydration process, but rather assumed a blanket set of emissions and energy requirements. Accordingly, a conclusive statement about the environmental performance of ethylene derived from biomass cannot be made. Tabone *et al.* (2010) also compared other polymers on a cradle-to-gate basis, which does not account for use and disposal. Finally, Tabone *et al.* (2010) combined the range of LCA impact categories into a single ranking of polymers. As discussed in Chapter 3, combining environmental impact categories has no logical basis, because it imposes priorities by weighting the impacts, which is entirely subjective. Instead the tradeoffs amongst impacts should be considered.

Shen *et al.* (2011) and Chen & Patel (2012) examined bioethanol from both sugarcane in Brazil and corn in the USA to make ethylene. The model for ethanol dehydration used by Shen *et al*. (2011) was based on the simple model of Chen & Patel (2012), which uses a mass balance based on stoichiometric conversion, with the energy required based on the enthalpy of the dehydration reaction. The analysis did not account for energy requirements in other process operations, such as compression and separation, or waste water and gaseous emissions resulting from the processes. Furthermore, neither study is transparent with respect to the assumptions made and there is insufficient detail on the system boundaries. For example, the transportation distances and sources of energy used in production can significantly affect both energy requirements and carbon emissions. That said, Shen *et al.* (2011) and Chen & Patel (2012) reported cradle-to-grave savings on the basis of non-renewable energy use and greenhouse gas emissions, over conventional production of PET, of, respectively, 15-26% and 17-26%. The cradle-to-gate greenhouse gas saving was higher, at 35-53%, because it does not consider the end of life incineration. Even though both studies were based on the same underlying model, their results showed significant variation in the savings predicted, largely owing to differences in the system boundaries.

Both studies (Chen and Patel, 2012; Shen *et al.*, 2011) quantified non-renewable energy use and greenhouse gas emissions only. This is severely limiting given that it overlooks some of the major drawbacks of using biomass which can result in an increase in other environmental impacts, especially eutrophication.

Chen & Patel (2012) also investigated the fermentation of processed corn to isobutanol, which was then converted catalytically to *p*-xylene. The reported cradle-to-grave savings were estimated to be 6-27% and 5-37% for non-renewable energy use and greenhouse gas emissions, respectively (Chen and Patel, 2012). It is therefore possible in principle to produce PET using both ethylene and *p*-xylene derived from biomass, with combined cradle-to-grave savings in the range 21-42% for non-renewable energy use, and 23-55% for greenhouse gas emissions (Chen and Patel, 2012). The variation in these potential savings is large. The lower bounds for non-renewable energy use and greenhouse gas emission savings were reported by Gevo (Chen and Patel, 2012). The larger savings were from calculations by Chen & Patel (2012), which used parameters for the bioconversion to isobutanol provided by Gevo and assumed ideal conditions for the conversion from isobutanol to *p*-xylene using reaction enthalpies; however, no further detail is provided of the analysis. The assumption of ideal conditions is unlikely in practice, and therefore Chen & Patel's (2012) calculation presents the most favourable savings. The boundaries have not been clearly defined and there is no transparency about any further assumptions made in the model. It is therefore not possible to comment further on their analysis. The direct catalytic route to *p*-xylene, investigated in this Dissertation, has not yet been studied in the peer-reviewed literature.

2.6 Conclusion

In summary, although various studies on the sustainability of PET have been undertaken, they do not paint a complete picture of its full life cycle assessment. Also, while there have been previous LCA studies of PET from fossil fuel sources, the impacts of using biomass as a raw material on the polyester value chain have not been investigated rigorously in detail. There is therefore substantial scope to undertake rigorous life cycle assessment on PET production, with clearly stated assumptions, a clear definition of the system boundaries and a standard impact assessment method. The protocol for calculating the latter can have a significant impact on the results, giving inconsistencies when comparing results for the same functional unit between different studies. Through the use of detailed modelling with reference to industrial practice, and by stating and analysing the validity of assumptions made, it is intended that the current research will link the various stages of the value chain into a single comprehensive LCA.

Chapter 3 Methodology

This Chapter outlines the life cycle assessment (LCA) method used for the quantification of environmental impacts. Details relevant to the process modelling and allocation procedures of the studies conducted are discussed in their respective Chapters.

3.1 Life Cycle Assessment

Life cycle assessment (LCA) is a systematic technique for identifying, quantifying and assessing the environmental impacts throughout the entire life of a product, process or service. It should be noted that LCA can be most accurately used as a comparative tool between two equivalent systems; the absolute results from an LCA need to be considered with caution given the difficulty in defining an unequivocal system boundary (Cullen and Allwood, 2009).

The life-cycle stages typically included in a full LCA are: raw materials extraction, processing, manufacturing, transportation, distribution, use and disposal. This is particularly important because many studies claim the largest environmental impact of some products, for example a car, can occur during its use, rather than in its manufacture. This also means that the system under study has to be very carefully defined. For the purpose of LCA, the defined process can be referred to as the economic system (Clift, 1998). The economic system relates to the environment through exchanges of flows of materials, energy, wastes and products, as shown in Figure 3.1. A drawback of LCA is that accurate and detailed studies can be time consuming. However, useful conclusions can often be drawn from the initial stages of LCA, as discussed for some life cycle inventory studies in Chapter 2.

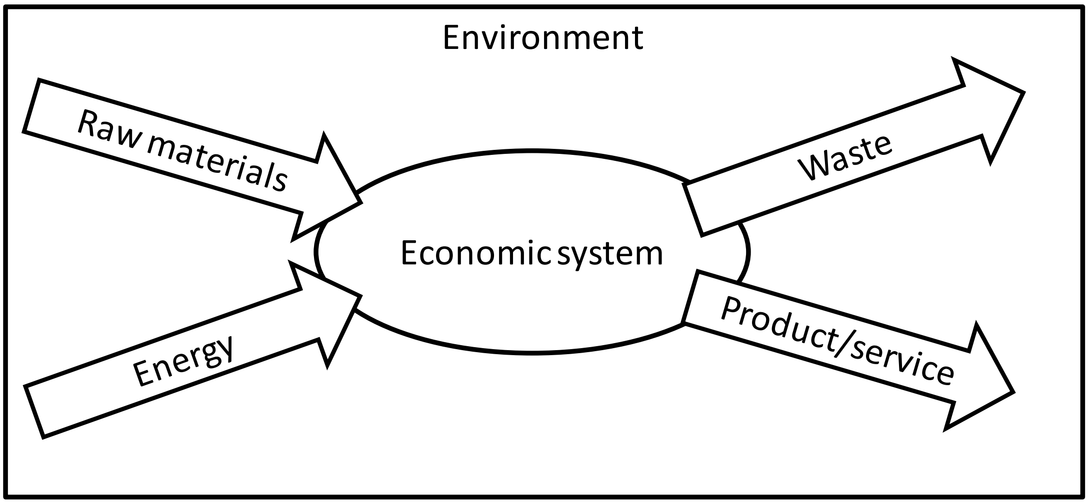

Figure 3.1. Relationship between the economic system of interest and the environment showing flows of materials, energy, wastes and products (Clift, 1998).

The phases undertaken in LCA are: (i) goal and scope definition, (ii) inventory analysis, (iii) impact assessment, and (iv) interpretation (ISO, 2006a, 2006b). It is important to recognise the links between each of the stages: to complete a LCA accurately, each stage must be revisited several times to avoid missing any important parts in the system. The Organisation for International Standards diagrammatically represents each stage in the LCA framework as shown in Figure 3.2 in which the double arrows imply reviewing between each of the stages (ISO, 2006a, 2006b).

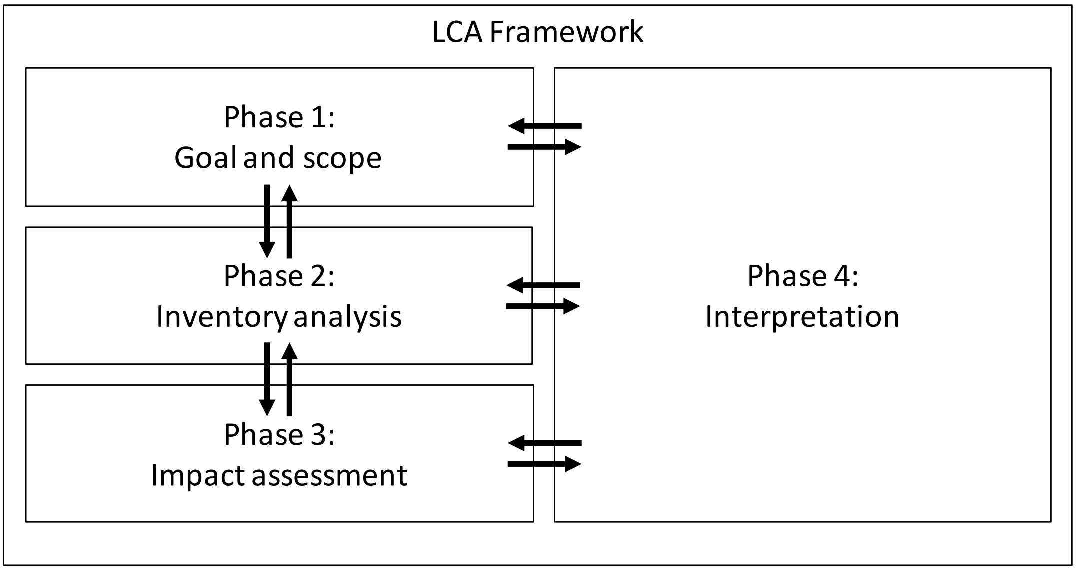

Figure 3.2. LCA framework showing each of the four phases and the reviewing between each stage (ISO, 2006a, 2006b).

3.1.1 Goal and Scope

The goal and scope of LCA must be clearly and consistently defined throughout the analysis. The goal encompasses the intended application and provides the justification for the study. One goal of the LCA in the present research is to identify those processes within PET production having a high environmental impact with the greatest potential for improvement.

The scope of the study defines the economic system, the functional unit and the system boundary. The functional unit is a clearly-defined and measurable quantity of a product or service, which forms a meaningful and consistent basis for quantitative statements of the outcomes of the LCA. It provides a reference to which all other input and output flows are normalised. The functional unit enables comparisons to be made on the same basis amongst different systems. For example, one cotton shirt can be compared with one polyester shirt, which are not necessarily of the same mass, but still serve the same function.

An important part of the scope is defining, carefully, the system boundary. The system boundary determines the processes included within the LCA. In turn the system might be divided into foreground and background systems. The foreground system includes the processes or stages studied and modelled in detail for the LCA, whereas the background system includes processes from other LCA studies and databases required for the full LCA. An example of a background process is electricity from a country's grid, with the environmental impact of the electricity reflecting the mix of fuels used to generate it. The information for background system processes often comes from existing studies or reputable databases, *e.g.* Gabi Professional (PE International, 2013) and Ecoinvent (Ecoinvent Centre, 2010) databases.

Finally, there are two types of LCA, attributional and consequential. An attributional LCA quantifies the burdens associated with the functional unit (Schmidt, 2008). Having quantified the burdens, a comparison can be undertaken comparing two attributional LCAs with equivalent functional units. A consequential LCA quantifies the environmental consequences of a proposed change to the system under study using marginal data (Schmidt, 2008). The research presented in this Dissertation focuses on attributional LCA: it quantifies the impact of producing polyester using conventional processing, and then focuses on the comparison between equivalent LCA systems by investigating the impacts of alternative processing relative to the conventional processing, namely, switching to biomass feedstock. In the latter case, the social and economic implications of the decision need to be taken into account; however, these are only briefly discussed given the focus of this Dissertation is on the environmental sustainability.

3.1.2 Inventory Analysis

The inventory analysis uses detailed process flowsheeting of all the operations in the foreground system to give heat, mass and energy balances for all defined flows. The final outcome of the inventory analysis is usually presented in a tabulated form, showing the net material and energy flows into and out of the system. The details of the operating conditions used are very important, because small changes can sometimes have quite a significant effect on the rest of the process and, consequently, the impact on the environmental impacts. The inventory analysis in this Dissertation uses both Excel and process simulation software Unisim Design Suite R400 (Honeywell, 2010) to model the processes.

3.1.3 Impact Assessment

The impact assessment determines the burden of the system on the environment. The outcomes from the inventory analysis, namely the material, energy, waste and product flows are all assigned to specific impact categories. These categories quantitatively describe the total environmental burden, each with respective standardised units; this is shown in Table 3.1. Each category is also typically provided with timescales. This is because a compound which is quickly removed from the environment may initially have a large effect on a shorter time scale, but over longer periods of time, its relative impact diminishes. The typical time scales used with these indicators are 20, 100, and 500 years. Most studies tend to present the values for 100 years as this time-scale provides a sufficiently long duration over which to observe and measure the environmental impact over a human lifetime.

As explained previously, it is left to the author's discretion as to which environmental impact categories to include, given that there are no set requirements in the LCA guidelines. One of the main environmental impact categories investigated in this Dissertation is the global warming potential. Houghton (2009) describes the greenhouse effect as a combination of the natural and enhanced greenhouse effect The gases nitrogen and oxygen, which make up the bulk of the atmosphere neither absorb nor emit thermal radiation. Water vapour, carbon dioxide and some other minor gases (*e.g.* methane, nitrous oxide) present in the atmosphere absorb some of the thermal radiation leaving the Earth's surface and consequently act as a partial blanket for the thermal radiation. The initial concentrations of these gases in the atmosphere, before anthropogenic emissions, cause a difference of 20-30°C between the actual average surface temperature on the Earth of about 15°C and the temperature that would apply if greenhouse gases were absent. This is known as the natural greenhouse effect. The enhanced greenhouse effect is caused by the additional greenhouse gases present in the atmosphere arising from anthropogenic activities, which result in the increase of global temperature; this is known as global warming (Houghton, 2009). Table 3.1 lists the set of all environmental impact categories considered in this research (Guinée *et al.*, 2002). To find the impact of a specific component in a given process flow, the flow is converted to one of the standard flows given in Table 3.1 using a potency factor. For example, methane contributes to global warming and it has a global warming potential of 34 kg CO_2-eq[1] over 100 years (Guinée *et al.*, 2002). This means that the release of 1 kg of methane to atmosphere is equivalent to releasing 34 kg CO_2 to atmosphere in its effect on global warming. As seen in Table 3.1, the units of kg CO_2-equivalent are the standard units used for global warming potential and so all the components contributing to global warming in a particular process stream can be converted to a single measure.

In order the help rationalise t CO_2-eq and an actual tonne of CO_2 emission, Moura-Costa and Wilson (2000) developed a method for accounting between the radiative forcing effect of CO_2 emissions and carbon sequestration and storage. This was achieved by deriving an equivalence factor between t CO_2-eq and t CO_2-year. Hence, removing 1 t CO_2 from the atmosphere and storing it for 55 years counteracts the radiative forcing effect of a pulse emission of 1 t of CO_2, integrated over a 100-year time horizon.

The environmental impacts listed in Table 3.1 are calculated using the CML impact assessment method (Guinée *et al.*, 2002). Many different methods have been

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[1] kg CO_2-eq = kilogram of carbon dioxide equivalent, other units similarly defined with respect to other elements or chemicals.

developed by different organisations to calculate the impact categories for components, *e.g.* EDIP 2003, Impact 2002+, Impacts ILCD, ReCiPE, TRACI. It is important to note that some impact methods may not use the same categories, whilst others may define additional categories to those specified in Table 3.1; they may also use different units to represent the categories. Furthermore, there are two methods of impact assessment, mid-point and end-point methods. Mid-point methods take a problem-oriented approach, and as such, translate impacts into environmental themes such as those listed in Table 3.1. End-point methods, take a damage-oriented approach, and quantify the environmental impact into issues of concern such as human health, natural environment, and natural resources. End-point methods often have a higher level of uncertainty than mid-point methods, because it is difficult to predict the actual damage with certainty; however, the end-point approach is often easier to interpret as it expresses the results as tangible consequences. Another way to rationalise mid-point methods is to use normalisation. Normalisation is when the quantified impact is compared to a certain reference value, for example, the average environmental impact of a European citizen in one year.

The CML 2001 method (Guinée *et al.*, 2002) was selected for the analysis of the environmental impacts in the present Dissertation, because, apart from giving an assessment of many different environmental impacts, it has been continuously updated, with the latest revision in November 2010 being used by the Gabi software databases used in this work (PE International, 2013). For the impact assessment stage, the inventory analysis findings were imported into Gabi 6, which is life cycle software capable of quantifying the environmental impact from the inventory table using potency factors.

Table 3.1. Environmental impacts assessed using the CML method (Guinée *et al.*, 2002)

Impact category	Units	Definition
Abiotic depletion potential of elements (ADP elements)	kg antimony-eq	The depletion of non-living and non-renewable natural resources such as ores.
Abiotic depletion potential of fossil fuels (ADP fossil)	MJ-eq	The depletion of non-living and non-renewable natural energy resources such as fossil fuels.
Acidification potential (AP)	kg sulphur dioxide-eq	The contribution to acid deposition into soil, groundwater, surface waters, biological organisms, ecosystems and materials (buildings).
Eutrophication potential (EP)	kg Phosphate-eq	The potential impacts of excessively high levels of nutrients, most importantly Nitrogen and phosphorous. Causes undesirable shifts in species composition and elevated biomass production.
Global warming potential (GWP)	kg carbon dioxide-eq	The impact of human emissions to the atmospheric absorption of radiation leading to increase in global temperature. This is frequently characterized for a 100-year time horizon, GWP 100a.
Ozone depletion potential (ODP)	kg chlorofluorocarbon-R-11-eq	Contribution to increase in UV radiation reaching the earth's surface through the depletion of atmospheric ozone.
Photochemical oxidant creation potential (POCP)	kg Ethene-eq	The formation of reactive chemical compounds such as ozone by the action of sunlight on nitrogen oxides and volatile organic compounds. Summer smog can affect human health, ecosystems and damage crops.
Human toxicity potential (HTP)	kg 1,4-Dichlorobenzene-eq	The impacts on human health of toxic substances present in the environment.
Freshwater aquatic ecotoxicity potential (FAETP)	kg 1,4-Dichlorobenzene-eq	The impacts of toxic substances on freshwater aquatic ecosystems.
Terrestrial ecotoxicity potential (TETP)	kg 1,4-Dichlorobenzene-eq	The impacts of toxic substances on terrestrial ecosystems.
Marine aquatic ecotoxicity potential (MAETP)	kg 1,4-Dichlorobenzene-eq	The impacts of toxic substances on marine aquatic ecosystems.

3.1.4 Interpretation

The final phase of the LCA is interpretation, which serves to identify the significant issues based on the outputs of the prior stages. Consideration of the comprehensiveness, consistency and sensitivity of the study enables conclusions and recommendations to be made. This is a crucial stage in the analysis because it brings together each previous stage and draws conclusions from the study. The impact assessment serves to judge the size of the environmental impact. Careful inspection of each different operation allows for processes with a major environmental impact to be identified. Suggestions for targeted improvements can then be made to most efficiently reduce the environmental impacts.

For any changes made to the system, there may be explicit trade-offs to take into account. For example, while a new catalyst may operate at a lower temperature and reduce the global warming potential of a unit operation, it might be that, in the manufacture of the catalyst itself, large quantities of water are used. The trade-off between reduction in global warming and increased use of water accordingly needs to be made in a transparent way at the interpretation stage. This is not trivial given that the impacts are in different units and therefore directly comparing the magnitude of the impacts is not possible.

Whilst it is tempting to group the impact categories from Table 3.1, using a weighting technique to combine them into one overall impact value, this should be avoided. It is not possible to produce one number to represent how well the system performs with respect to the environment, because this would require a weighting system which consequently would place a higher value or priority on one category relative to others. In any case, because the factors have different units, there is no logical basis for combining them. In fact, these categories have been established as being equally important and critical indicators for the environment. For example, trying to attain an economic value, such as an environmental cost of a process, would inevitably place a higher value on some indicators, perhaps global warming potential, either because of subjectivity or because there is unjustified pressure from the government or media to do so.

3.2 Allocation

In the case of multi-output or co-product systems, that is to say the process studied has more than one useful output, it is not always straightforward to distribute accurately the burdens of the system to the respective products. Ideally, wherever possible, the system boundary should be expanded or redefined in order to attain a more accurate representation of the environmental burdens associated with the functional unit. In some cases, a more appropriate functional unit may need to be selected to eliminate this problem.

Where it is not possible to re-define the system boundaries, allocation will be necessary. Allocation is used in order to assign proportions of the inputs and outputs, and hence partitioning the burdens to the different products. If allocation cannot be avoided, then a causal method of allocation should be used. Causal allocation involves apportioning the inputs and outputs amongst the different products to reflect the physical relationships between them, *e.g.* mass and energy requirements. As a last resort, if causal allocation is not possible, other methods of allocation, such as economic value of the products, can be used. It should be noted, that allocation is less rigorous than system boundary expansion and therefore allocation should only be used as a last resort.

Biogenic carbon is a term used to describe carbon stored within biomass during the growth phase of the plant. Carbon allocation is another allocation method. This is defined as the carbon contained in one product divided by the carbon contained by all products from the system. Carbon allocation is different from mass allocation because it does not account for the water content of the biomass source. Water content can significantly distort the mass allocation method, in particular for biomass sources.

Details of the functional unit, system boundary definition, and where required, allocation methods, are described in each respective Chapter.

Chapter 4 The Production of Ethylene from Biomass

This Chapter investigates the environmental impacts of the production of ethylene derived from biomass sources sugarcane and willow, *via* the dehydration of bioethanol. Ethylene is subsequently used within the polyester value chain as the raw material feedstock for ethylene glycol production.

4.1 Introduction

Ethylene glycol accounts for 28 wt% of the final PET polymer. Producing the glycol from biomass has the potential to reduce the greenhouse gas emissions and fossil fuel requirements in PET processing. The route, investigated here, to obtain ethylene glycol from biomass requires the initial fermentation of biomass to ethanol, which is subsequently dehydrated to ethylene and then converted using standard catalytic processes to ethylene oxide and subsequently to glycol. This route will be compared with conventional processing from fossil fuel sources.

As discussed in Chapter 2, the types of biomass giving the largest savings in global warming potential were sugarcane (juice and bagasse) and willow. Sugarcane is conventionally grown in warm temperate to tropical regions; Brazil is the world's largest producer of sugarcane (Luo *et al.*, 2009a). Lignocellulosic biomass is the most abundant reproducible resource on the Earth (Balat *et al.*, 2008) and there are many potential crops for the production of second-generation bioethanol. In the UK, significant attention has recently been paid to the use of the fast-growing perennial energy-crop, willow, which can produce annually high yields of 7-12 dry t/ha and is suitable for cultivation on low-quality land (Stephenson *et al.*, 2010). In this Dissertation, both sugarcane in Brazil and willow in the UK were chosen as starting points for the manufacture of ethanol.

4.2 Analysis

4.2.1 Goal and Scope

As discussed earlier, an important element in LCA is to define the system rigorously and, in particular, to define an appropriate functional unit. The functional unit, the fixed reference quantity used as a basis for comparison between different systems, was defined as one 500 mL carbonated soft drink (CSD) PET bottle after distribution to a supermarket. As noted in Chapter 2, the life cycle impacts of PET fibres are dominated by their use phase, *e.g.* the washing and drying of clothes (Allwood *et al.*, 2006; Collins and Aumônier, 2002). Therefore, this Chapter concentrates on bottle-grade material where changes to the processing have a much greater influence on the product's overall environmental impact. The selection of a bottle also avoids the need to address regional behavioural patterns for washing and drying of clothing, *i.e.* the energy used in washing clothes can vary significantly by region.

The mass of PET in the bottle was assumed to be 23.5 g (Coca-Cola Enterprises, 2012; De Miranda *et al.*, 2011). The scenarios described later explore *inter alia* the effect of changes in geographical location of the final outlet for the bottles and the distances over which material is transported between the processes in the value chain. The boundary of the system studied encompasses all the processes directly involved with the production of the bottles (the foreground system) and also the secondary (background) processes. For background processes, *e.g.* the supply of electricity, existing databases were used, giving geographically-dependent market averages of processes. The scope did not include end-of-life processing, such as recycling or disposal, since the aim was to compare the impact of feedstocks on virgin PET. This is a cradle-to-gate LCA with the gate boundary drawn at the distribution and includes transportation.

4.2.2 Value Chain

The processes involved in the production of PET bottles from (i) conventional fossil-fuel sources and (ii) biomass are shown in Figure 4.1, with the difference between the routes being in the production of ethylene. Bioethanol displaces the naphtha or natural gas requirements for the production of ethylene. Irrespective of whether the ethylene is made from naphtha or bioethanol, it is oxidised to ethylene oxide using the oxygen-based direct oxidation process over a silver catalyst. The resulting ethylene oxide is reacted in excess water to yield ethylene glycol. The manufacturing plants for ethylene oxide and ethylene glycol are often contiguous, leading to energy savings by heat integration, and avoiding the storage and transport of ethylene oxide, which is hazardous.

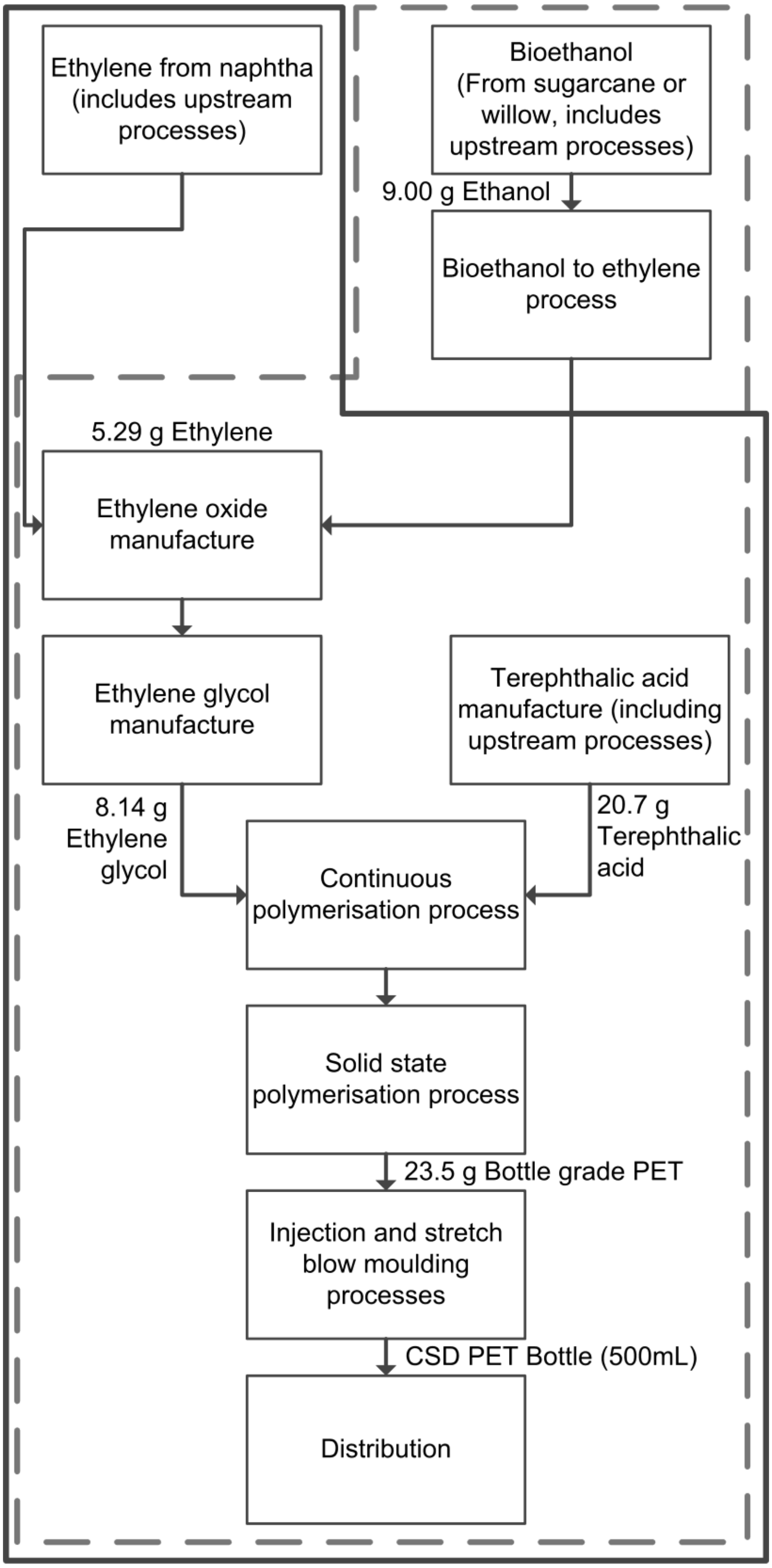


Figure 4.1. Polyester value chain including both conventional and biomass routes, which have been encompassed by their respective system boundaries for the life cycle assessment study.

In Figure 4.1, terephthalic acid is produced from the oxidation of *p*-xylene, which, in turn, is produced from the catalytic reforming of naphtha. As the focus of this study is on the impact of using biomass to produce, ultimately, the ethylene glycol, an existing dataset concerning the environmental impacts of the production of terephthalic acid has been used. Thus, here, terephthalic acid production is considered as a background process. Purified terephthalic acid and ethylene glycol are combined in the continuous polymerisation process.

The processes shown in Figure 4.2 represent the processes included in the system boundary for ethylene production from biomass. The processes, such as the electricity mix and waste water treatment, form part of the background system, processes which are influenced by measures taken in the foreground system.

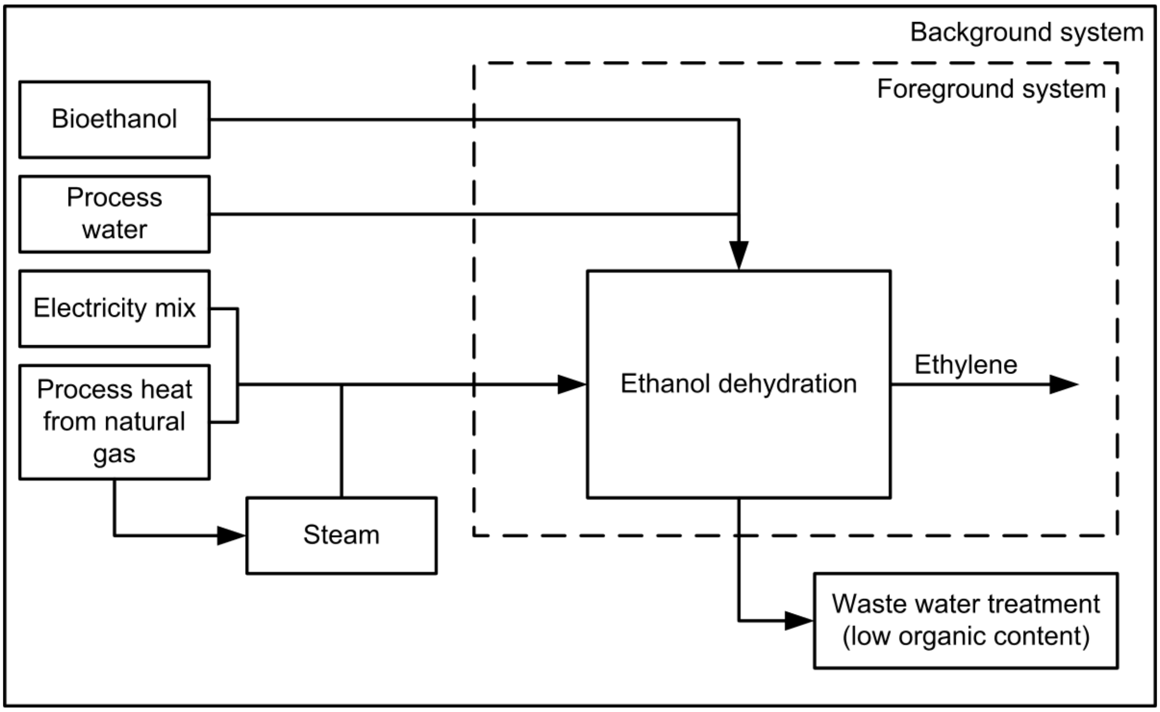


Figure 4.2. The system boundary definition for ethylene production from biomass routes.

As discussed previously, the molecular weight for bottle-grade PET is generally higher than that for fibre products and hence a further solid-state polymerisation stage is required (Culbert and Christel, 2003). The bottle-grade PET is then injection moulded into preforms and stretch blow-moulded to make PET bottles, which are filled and distributed.

For the inventory analysis, quantitative mass and energy balances were performed for the processes within the system. The detailed process flowsheeting is described in Appendix A.

4.2.3 Use of Datasets

Gabi 6 (PE International, 2013) and Ecoinvent version 2.2 (Ecoinvent Centre, 2010) databases with life cycle inventory information for some of the processes were used in conjunction with the process modelling described in Appendix A to complete the value chain. These databases are known to provide industry averages in specific countries. Where the desired location defined in the scenarios did not exist for the desired process, the nearest geographic dataset was employed; this would typically be a region-wide dataset, *e.g.* an EU average. Appropriate, existing databases were also used for the background systems, listed in Table 4.1.

Table 4.1 Datasets used within the study for processes.

Dataset
Ethylene from multi-product steam cracker (PE International, 2013)
Brazilian bioethanol from sugarcane, 95 wt% ethanol (Ecoinvent Centre, 2010)
Bioethanol produced from UK willow, 99.5 wt% ethanol (Stephenson *et al.*, 2010)
Terephthalic acid (PE International, 2013)
Injection and stretch blow moulding (PE International, 2013)
UK, USA, Brazil and The Netherlands electricity grid mix (PE International, 2013)
Process water (PE International, 2013)
Waste water treatment of light organic content (PE International, 2013)
Transportation modes and fuels (PE International, 2013)

The ethanol from willow is at a higher purity 99.5 wt% compared to Brazilian sugarcane bioethanol at 95 wt% purity. Stephenson *et al.* (2010) achieved the higher purification using molecular sieves. Regeneration of the molecular sieves accounted for less than 1% of the total electricity requirements for the process. Using the ethanol of higher purity made from willow does not therefore significantly affect the results and the ultimate comparison with the ethanol made from Brazilian sugarcane.

One concern with the use of biomass is the solid residue left after processing it. Both datasets used have accounted for this. For sugarcane, the bagasse is burnt to generate steam, which is used in the ethanol plant. The excess steam is used to generate electricity. The sugarcane dataset used economic allocation for the co-products ethanol and electricity. The ash resulting from the incineration of the sugarcane bagasse is used as fertiliser for the growing of the cane. Because the ash remains within the boundary of the sugarcane dataset, no further allocation is required. The stillage, the remaining water from after ethanol distillation, is also added to the soil as additional fertiliser, requiring no allocation (Ecoinvent Centre, 2010). For willow, lignin residue was assumed to be combusted at the plant to produce electrical power to satisfy process requirements. In the case where excess electricity was generated, Stephenson *et al.* (2010) allocated the enviornmental burdens using the method of ‘system expansion’, whereby it was assumed that the resulting electricity would displace the corresponding amount supplied by the National Grid.

4.2.4 Allocation

Where there are two or more products from a system, allocation is used to partition the burdens among the products. As discussed previously, where possible in LCA, allocation should be avoided to reduce inaccuracies and improve transparency in the study (Azapagic and Clift, 1999).

In the production of ethylene oxide, allocation was avoided by constraining the process to produce only the ethylene oxide grade required for ethylene glycol formation. An actual plant would produce ethylene oxide for a variety of uses and not just to make glycol. Many of these additional uses require ethylene oxide of higher purity, requiring additional purification steps. Accordingly, the boundaries were drawn around the system to exclude the extra purification operations because they would not be required. As discussed earlier, the ethylene oxide process is a net exporter of heat generated by the exothermic reaction. In this case, allocation was avoided by extending the boundaries to include the ethylene glycol process. The heat was then used for the separation energy requirements in the ethylene glycol process.

The problem of allocation does, however, arise in the production of ethylene glycol, because valuable by-products are formed, such as diethylene glycol and higher glycols, which therefore should also bear their share of the burdens of production. Here, the boundaries were first re-drawn to exclude further purification of the diethylene and higher glycols. This is because the product of interest was ethylene glycol and it would be illogical to assign any of the burdens of refining other glycols to ethylene glycol. Regarding the upstream production and separation up to the point at which nearly-pure ethylene glycol was formed (the operations defined in Figure A.3 of Appendix A); it was not possible to avoid allocation, and therefore, mass-based allocation was chosen. On a mass basis, ethylene glycol production forms 81 wt% of the output and other glycols the remaining 19 wt%. Thus 81% of the burdens for the production were allocated to ethylene glycol. Economic allocation was not chosen because of the price volatility of the products over time skewing the final results as well as outdating these results as soon as trends change. In principle, marginal allocation (Azapagic and Clift, 1999) could be used, but the reaction model was insufficiently refined in this work to investigate how the proportions of products could be changed relative to one another by altering the process conditions.

As mentioned earlier, 1-3 wt% isophthalic acid is added in the continuous polymerisation process for bottle grade PET. The production of isophthalic acid is similar to that of terephthalic acid, yet, industrially, it is typically less efficient owing to the use of older assets and manufacturing in smaller capacities, *e.g.* 150 kt/yr isophthalic acid *cf.* 750-1000 kt/yr terephthalic acid (PCI Xylenes & Polyesters, 2013). There was no isophthalic acid production dataset available within the databases. Given that the final polymer contains 1-3 wt% isophthalic acid, the contribution to the environmental impacts is small. By assuming isophthalic acid production would be similar to terephthalic acid production, the terephthalic acid dataset was therefore used and the environmental impacts were largely incorporated into the analysis.

A final case of allocation was encountered in filling and transporting filled CSD PET bottles to the distribution centres. The filling of the bottles was allocated to the soft drink. Allocation by mass was chosen for transport because the bulk of the functional unit is the liquid. This type of allocation is further justified because heavier packaging containers, *e.g.* glass, have a larger transport requirement. Therefore, in the model, transport of only the bottle mass was calculated.

4.2.5 Scale

The scale of operation for each of the plant designs was 200 kt/y; representative of typical plants midway through their operating life. However, plants being currently built might well exceed 600 kt/y. In the life cycle assessment, production units were scaled on a basis of functional unit. Scale will therefore only have an effect on the LCA if the burdens resulting from the manufacture of plant equipment are taken into account. To examine if the latter is significant, the continuous polymerisation process was studied in detail. Order of magnitude calculations indicated that the contribution of the burdens from the cement and steel used to build the manufacturing facilities would result in less than a 1% increase in the overall environmental impact and energy requirements for a plant operating for 20 years. Thus, the greatest burdens arise from production and not from the construction of the plant.

4.2.6 Comparison with other datasets

In order to verify the modelling undertaken for ethylene glycol production, a comparison with other databases was made. The environmental impacts predicted by the model for ethylene glycol, on a cradle-to-gate basis, were compared with the environmental impacts quoted for ethylene glycol from two different databases in Table 4.2. The environmental impacts assessed were global warming potential (GWP), energy use, eutrophication potential (EP) and acidification potential (AP).

Table 4.2. Comparison of impacts of ethylene glycol from models with other datasets, cradle-to-gate assessment, on basis of 1 kg ethylene glycol.

	GWP (kg CO_2-eq)	**Total energy (MJ)**	**Fossil energy (MJ)**	**EP (kg Phosphate-eq)**	**AP (kg SO_2-eq)**
Current modelling	1.77	51.4	50.1	0.000237	0.00283
Ecoinvent (Ecoinvent Centre, 2010)	1.57	52.2	51.2	0.00238	0.00526
PE International (PE International, 2013)	1.08	40.2	39	0.000327	0.00279

The present work predicts a higher global warming potential, probably owing to the combustion of waste and vented gases for heat recovery in the model, resulting in increased CO_2 emissions. It is, however, difficult to determine further reasons for the differences between the environmental impacts predicted given that the datasets from Gabi and Ecoinvent provide minimal information on the underlying calculations and boundaries drawn.

4.2.7 Scenarios

Two manufacturing locations for PET were considered, namely in the UK and the USA. The following cases were considered.

Case 1: Manufacture of PET in the UK

The manufacture of terephthalic acid, continuous polymerisation and solid state polymerisation were assumed to be collocated in northern England.

- Scenario 1a. It was assumed that ethylene glycol would be manufactured, as at present, from fossil fuel in The Netherlands and transported 600 km by ship to the UK polymerisation plant.

- Scenario 1b. Here, it was envisaged that ethylene glycol would be produced from sugarcane bioethanol in Sao Paulo, Brazil and then transported 10000 km by ship to the UK (scenario 1b). While a 200 kt/y ethanol to ethylene dehydration plant does exist in Brazil, it is currently producing ethylene for polyethylene (Braskem, 2014).

- Scenario 1c. The assumption is that ethylene glycol would be produced in the UK from willow bioethanol, with the willow being grown and processed in the UK.

In all UK scenarios, it was assumed that PET resin would be transported by road an average distance of 300 km to bottle moulding and filling facilities and a further 150 km to supermarkets *via* distribution centres.

Case 2: Manufacture of PET in the USA

The continuous and solid state polymerisation plants were assumed to be located in South Carolina. Terephthalic acid would be transported 650 km by rail from its site of manufacture in Alabama to the polymerisation facilities.

- Scenario 2a. This represents the conventional production of ethylene glycol made from fossil fuel in Texas, with the glycol transported 1500 km to the PET facilities.
- Scenario 2b. This is the same as Scenario 1b, above, except that the glycol is transported 9200 km by ship to South Carolina.

In both US scenarios, it was assumed that PET pellets would be transported on average 1000 km by road to various bottle moulding and filling facilities, and a further 750 km by road to distribution centres for supermarkets.

In practice, owing to the diversity of supply chains, these scenarios (1a, 1b, 1c, 2a, and 2b) are only indicative of a supply chain for a PET CSD bottle. However, the scenarios have been chosen to capture the majority of the environmental impacts associated from the transportation of materials.

4.3 Results

4.3.1 Savings on an Ethylene basis

The savings to global warming potential and non-renewable energy use on the basis of 1 kg of ethylene are first assessed before the investigating the net effect for the entire value chain. For this part of the analysis, ethylene is produced as described for scenarios 1a (from conventional fossil fuels) and 1b (from sugarcane bioethanol).

As can be seen from Figure 4.3, producing ethylene from biomass can deliver significant savings to the measures shown. It is more important, however, to understand the net benefit of such process modifications within the context of the entire value chain; this is discussed next.

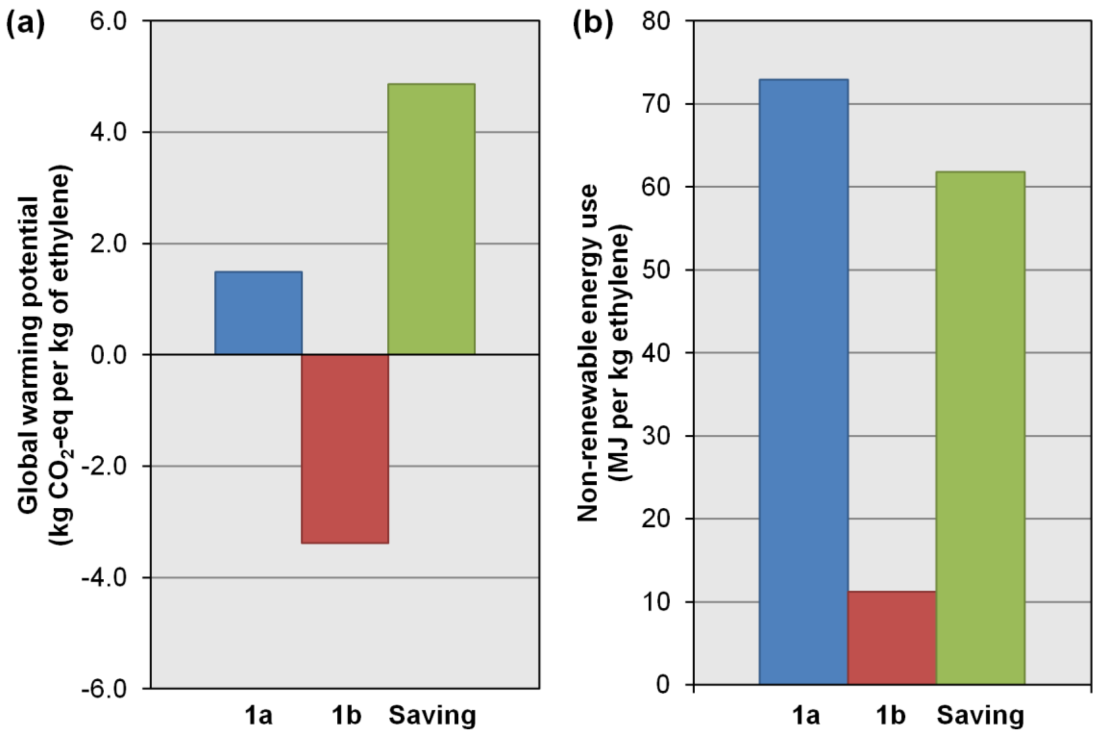


Figure 4.3. Savings to (a) global warming potential and (b) non-renewable energy use on the basis of 1 kg of ethylene. 1a is conventional processing, 1b is ethylene derived from sugarcane.

4.3.2 Energy Flows through the Overall Processes

To understand the overall flows of fossil and renewable fuels through the overall processes, Sankey diagrams were prepared and are shown in Figure 4.4 as energy flows for scenarios 1a and 1b (*i.e.* for PET plants located in the UK). As in all Sankey diagrams, energy is conserved and all the flows in a vertical section add to the same total quantity of energy entering at the left-hand side (Cullen and Allwood, 2010). Figure 4.4 shows the primary sources of energy required for each of the processes as well as the energy content of the intermediates and the final product. The remaining energy from the balance is classified as the processing energy requirements. The results are shown for the functional unit, a 500 mL CSD PET bottle.

It can be seen that the substitution of the naphtha and natural gas by ethanol would result in a reduction of crude oil use and consequently an increase in biomass requirements, as expected. There is a 16% reduction of total fossil fuel requirement. For one 500 mL PET CSD bottle, Figure 4.4 shows that 0.26 MJ of crude oil could be avoided, but instead 0.66 MJ of biomass energy would be required. It can also be seen that scenario 1b, in total, would need 16% more energy to produce the same bottle.

Figure 4.5 shows the total energy requirements in each scenario as well as energy requirements grouped by type, renewable and non-renewable. Comparing the other bioethanol scenarios, 1c with 1a and 2b with 2a, there would be a 16% reduction in fossil fuel use and a 16% increase in the total energy requirements. An important result from Figures 4.4 and 4.5 is that the conversion of bioethanol to ethylene would have, relative to the other processes, a small energy requirement, which would not affect, substantially, the overall energy balance. As a result, the global warming potential of the process converting bioethanol to ethylene is small, accounting for less than 3% of the total global warming potential for scenario 1b, and therefore would not counteract the carbon dioxide savings of using biomass.

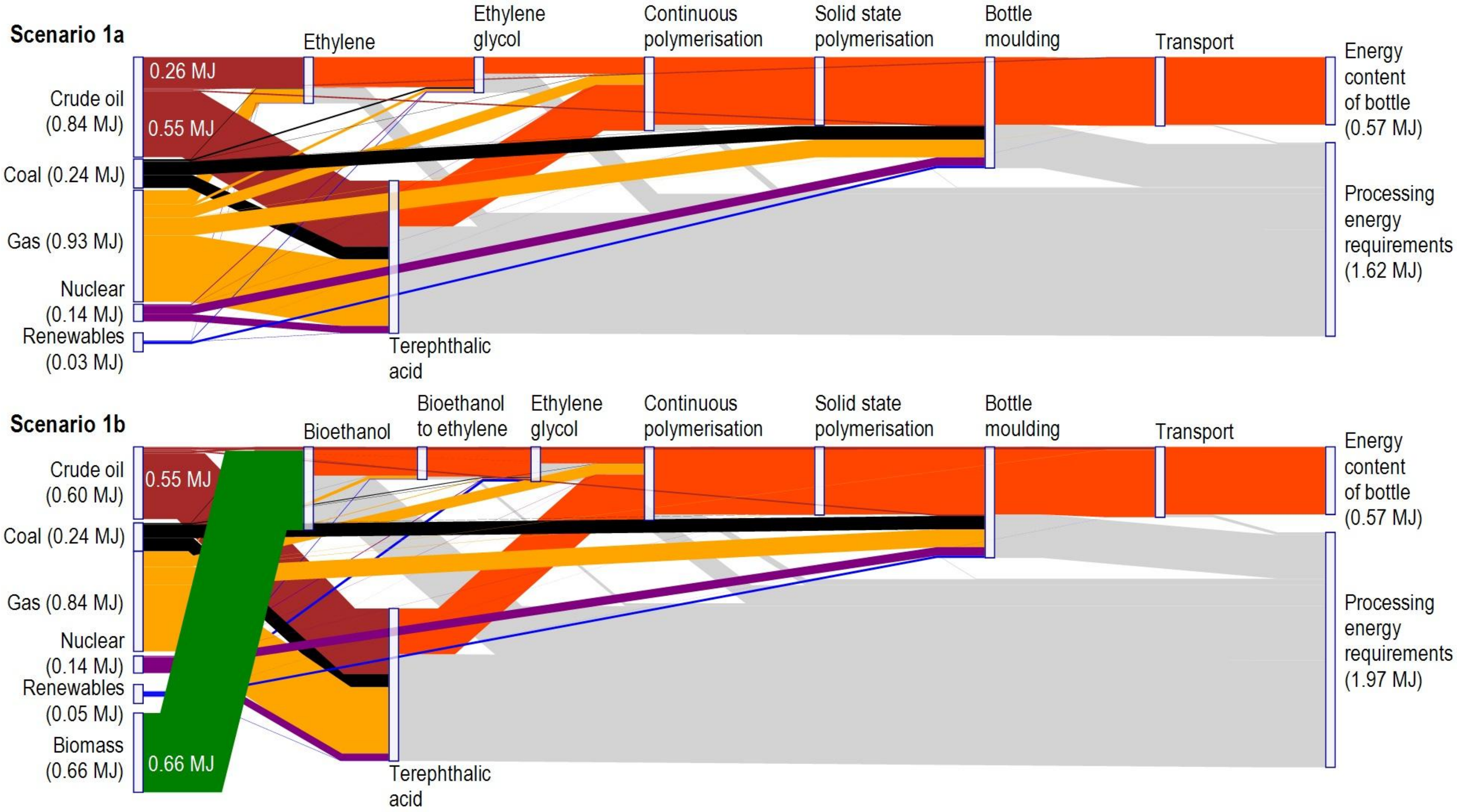


Figure 4.4. Sankey diagram showing the primary source of energy flows to each process for scenarios 1a (conventional processing) and 1b (ethylene derived from sugarcane).

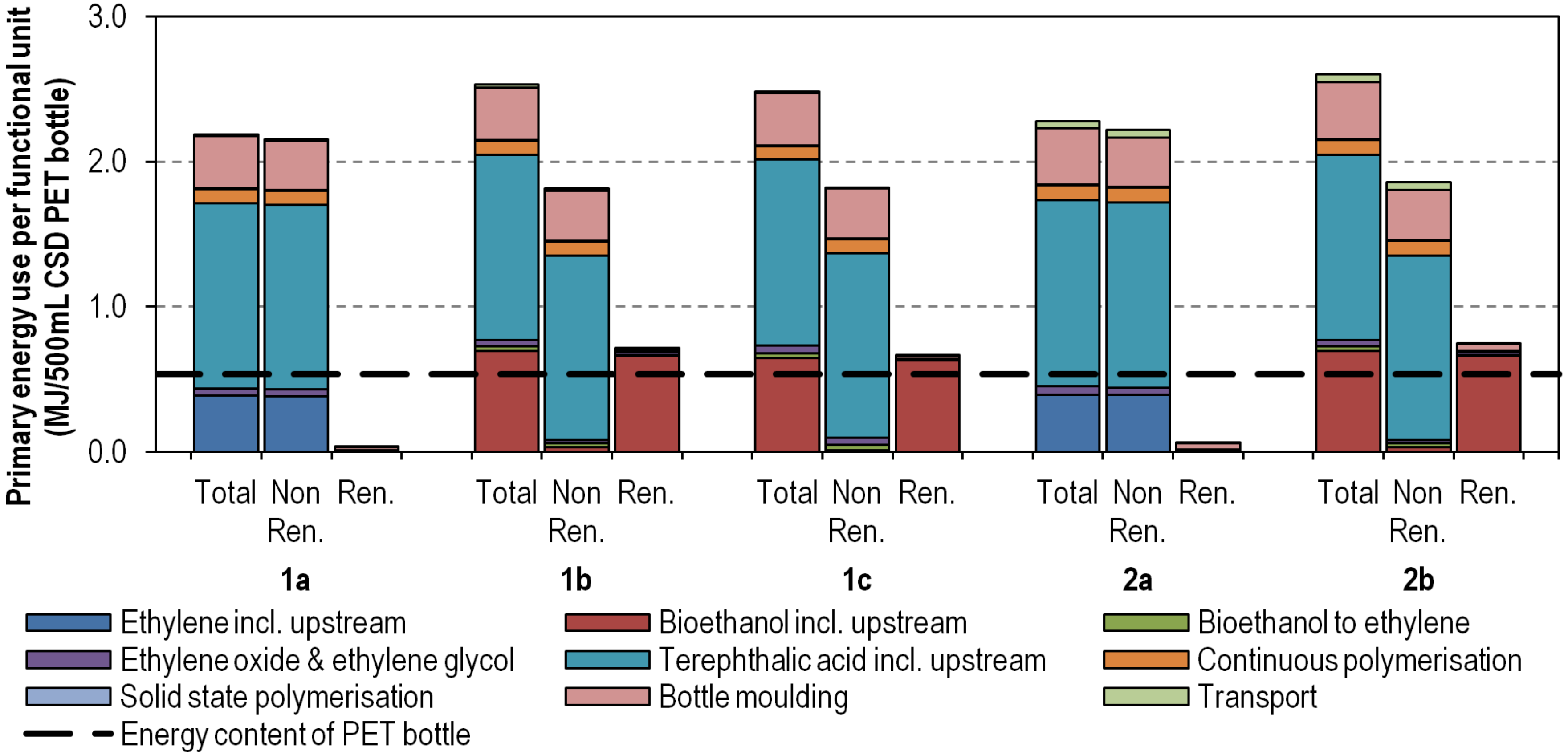
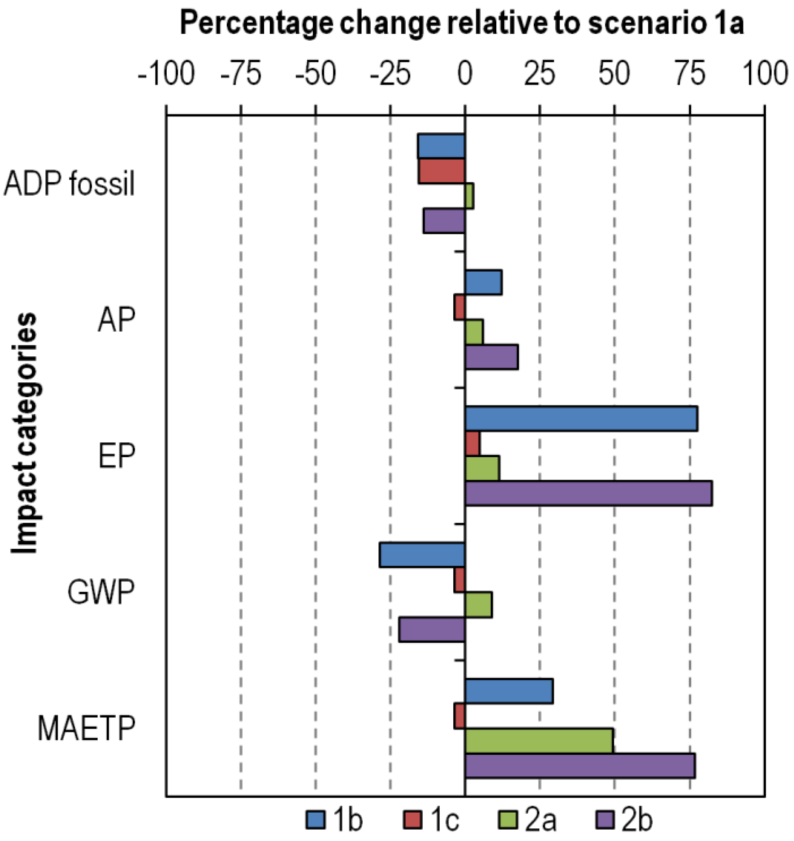


Figure 4.5. Energy use (in MJ/functional unit) for each scenario; total energy requirements for the processes and distribution using renewable (Ren.) and non-renewable (Non Ren.) sources. Scenarios: 1a, conventional processing in the UK; 1b, Brazil sugarcane-derived ethylene used in PET bottle in UK; 1c, Willow-derived ethylene used in PET bottle in UK; 2a, conventional processing in the USA; 2b, Brazil sugarcane-derived ethylene used to make a PET bottle in the USA.

4.3.3 Impact Assessment

The results of the impact assessment are presented on the basis of the functional unit chosen, a 500 mL CSD PET bottle. The impact categories used were defined in Table 3.1. Figure 4.6 shows the performance of scenarios 1b, 1c, 2a, and 2b relative to scenario 1a for the impact categories: fossil abiotic depletion potential, acidification potential, eutrophication potential, global warming potential and marine aquatic ecotoxicity potential. It can be seen that using sugarcane bioethanol would cause a reduction in the impact categories of global warming potential and fossil abiotic depletion potential compared with using ethylene from naphtha and natural gas. However, in every other impact category, there would be an increase were sugarcane bioethanol to be used. For the willow bioethanol, the difference for each impact category when compared to the conventional feedstock would be less significant than with ethanol from cane sugar.



Summary of values for base case, scenario 1a

Impact	Value	Units
ADP fossil	2.00	MJ
AP	3.22×10^{-4}	kg SO_2-eq
EP	2.25×10^{-5}	kg Phosphate-eq
GWP	0.092	kg CO_2-eq
MAETP	5.28	kg DCB-eq

Figure 4.6. Relative performance of scenarios 1b, 1c, 2a, and 2b with the reference scenario 1a for the impact categories: fossil abiotic depletion potential (ADP fossil), acidification potential (AP), eutrophication potential (EP), global warming potential (GWP) and marine aquatic ecotoxicity potential (MAETP). Scenarios: 1a, conventional processing in the UK; 1b, Brazil sugarcane-derived ethylene used in PET bottle in UK; 1c, Willow-derived ethylene used in PET bottle in UK; 2a, conventional processing in the USA; 2b, Brazil sugarcane-derived ethylene used to make a PET bottle in the USA.

The impact categories represented in Table 4.3 were sensitive to small changes in parameters characterising elements of the value chain. For example, the differences in electricity grid mix and transport distances between the UK and US for the conventional fossil fuel systems caused large changes in impact categories. Comparing the scenarios, the bioethanol process often made the largest contribution to these impact categories. For example, Figures 4.7(a-c) shows for each scenario, respectively, the global warming potential, acidification potential and eutrophication potential. Figure 4.7(a) shows the breakdown of global warming potential contributions by stage in the value chain shown in Figure 4.1. The total global warming potential for the production and distribution of a 500 mL CSD PET bottle using conventional fossil fuel, in the UK scenario 1a, would be 0.092 kg CO_2-eq and, in the US scenario 2a, 0.10 kg CO_2-eq. The use of bioethanol from Brazil would result in a reduction of global warming potential of 28% for both the UK (1b) and the US (2b). This reduction can be seen in Figure 4.7(a) to come from the carbon absorbed in the growth phase of the sugarcane biomass, *i.e.* biogenic carbon. The biogenic carbon is contained within the bioethanol produced which substitutes for the fossil fuel carbon used to produce ethylene glycol. Scenario 1c uses bioethanol from willow in the UK and while this feed has a similar energy saving to sugarcane bioethanol, the saving in global warming potential is much lower. In part, this is because in the study by Stephenson *et al.* (2010), there were significant emissions in some of the processing stages, *e.g.* enzyme processing. Furthermore, the method of quantifying the emissions used by Stephenson *et al.* (2010), did not quantify the biogenic carbon contained within the willow and instead quantified global warming potential of bioethanol combustion relative to gasoline combustion. The biogenic carbon content of willow is estimated in Chapter 5, where a more detailed analysis on the basis of the willow composition has been made. Hence, given the lack of inclusion of the biogenic carbon, the savings for global warming potential of the willow bioethanol bottle are underestimated.

Table 4.3. Absolute values for the other impact categories assessed for each scenario. Acronyms for environmental impacts are listed in Table 3.1.

Scenario	**ADP** elements 10^{-9} kg Sb-eq	**ODP** 10^{-12} kg CFC R11-eq	**POCP** 10^{-5} kg Ethene-eq	**HTP** 10^{-3} kg DCB-eq	**FAETP** 10^{-4} kg DCB-eq	**TETP** 10^{-4} kg DCB-eq
1a	7.51	2.69	5.38	9.51	2.66	32.4
1b	27.4	379	16.2	45.3	33.4	47.5
1c	54.2	41.0	5.05	9.41	2.51	33.2
2a	17.0	10.8	5.16	7.65	1.89	3.23
2b	31.3	386	16.1	43.5	32.7	18.5

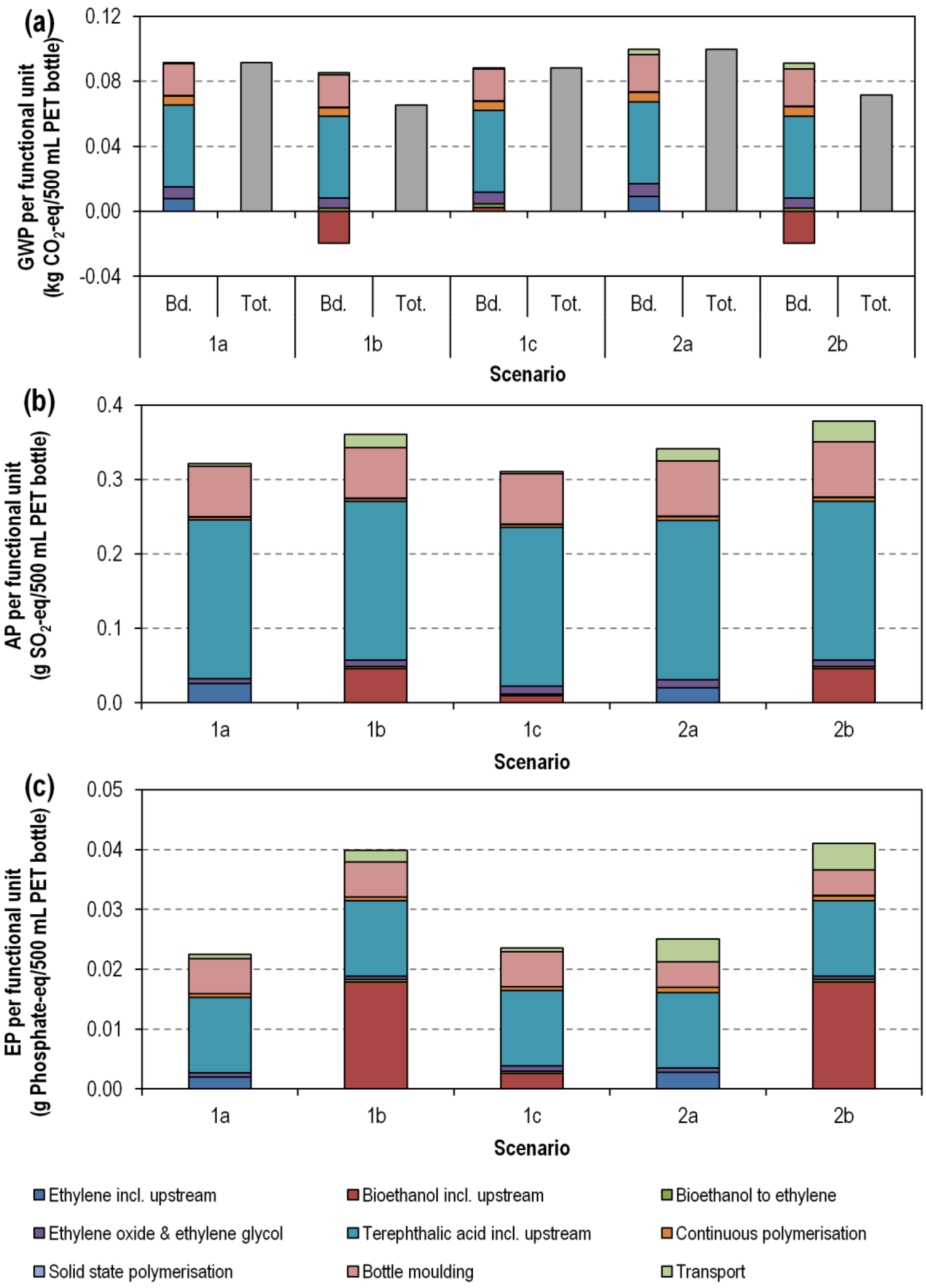


Figure 4.7. For each scenario, detailed breakdown of the contribution from processes to (a) global warming potential (GWP) where Bd.=Breakdown, Tot.=Total., (b) acidification potential (AP), and (c) eutrophication potential (EP). Scenarios: 1a, conventional processing in the UK; 1b, Brazil sugarcane-derived ethylene used in PET bottle in UK; 1c, Willow-derived ethylene used in PET bottle in UK; 2a, conventional processing in the USA; 2b, Brazil sugarcane-derived ethylene used to make a PET bottle in the USA.

4.4 Discussion

4.4.1 Interpretation

From the Sankey diagram in Figure 4.4, the substitution of the conventional feedstock resulted in a reduction of crude oil and natural gas use and consequently an increase in biomass requirement. Further, the sugarcane biomass route requires about 16% more energy in total to produce the same bottle, 2.53 MJ compared to 2.19 MJ for scenario 1a. So, whilst there is a beneficial reduction of fossil fuel use by using sugarcane biomass, there is also lower net energy efficiency in the conversion processes from biomass relative to the conversion from naphtha and natural gas. One limiting factor is the efficiency of the conversion of sugars from sugarcane to ethanol, *e.g.* maximum theoretical yield of 0.51 kg ethanol per kg glucose. Because biomass is a renewable energy source, this does not affect the reduction in fossil fuel energy but it does mean that more biomass needs to be grown. This in turn results in larger impacts related to agronomy, as well as larger land areas devoted to sugarcane. Figures 4.4 and 4.5 also reflect the large energy requirements in terephthalic acid production and bottle moulding, which are energy intensive processes. As a consequence, Figure 4.7(a) shows that these processes also make relatively large contributions to the global warming potential. Accordingly, because of the other processes involved, the global warming potential and fossil fuel energy savings of using biomass are lost to some extent when considering the end product, particularly in view of the fact that only 28% by mass of PET is ethylene glycol.

Figures 4.5 and 4.7(a) also demonstrate that transporting materials would contribute only in a minor way to the total global warming potential and energy requirement. This important result demonstrates that global-scale supply chains for biomass would be possible without significantly reducing the environmental impact savings made, provided the energy dense products, *e.g.* ethylene glycol, are transported. However, transport has other impacts, as discussed below.

A problem with using sugarcane ethanol would be an increase in all of the impact categories, other than global warming potential. Two categories, acidification potential and eutrophication potential, are examined in more detail in Figures 4.7(b) and (c). Figure 4.7(b) shows that the acidification potential would increase for the sugarcane bioethanol scenarios (1b and 2b) compared to the conventional processes (scenarios 1a and 2a). The increase is attributable to both the bioethanol process and the transport of ethylene glycol over the long distance from Brazil. The contribution from the bioethanol processes arises in agronomy and particularly in the manufacture of the required fertilisers. Quirin *et al.* (2004) also observed this impact for cultivated biomass. The willow bioethanol, scenario 1c, has a lower acidification potential; the study of Stephenson *et al.* (2010) suggested that synthetic fertilisers could be avoided in growing willow by using organic sludge from local water companies.

Figure 4.7(c) examined changes in eutrophication potential, arising largely as a result of the leaching of fertilisers into natural water courses. Figure 4.7(c) shows that growing sugar cane would be particularly troublesome in this respect. However, in contrast to sugarcane, the willow biomass does not need high applications of synthetic fertiliser and consequently its growth would not contribute significantly to eutrophication. Transport is taken to affect eutrophication as a result of the release of nitrogen oxide emissions from engines and so the large transportation distances from Brazil to UK or US also contribute to the eutrophication category for sugarcane ethanol. The process of conversion of bioethanol to ethylene, however, makes a negligible contribution to the acidification and eutrophication potentials.

4.4.2 Sensitivity

The sensitivity of using two different sources of bioethanol – from sugar cane and willow – has been demonstrated with scenarios 1b and 1c in the results. Another study also showed that deriving ethylene from corn bioethanol, results in an increase in global warming potential when compared with ethylene from naphtha (+35%) or natural gas (+60%) (Ghanta *et al.*, 2013). The key difference is the crop used, in this case, corn, which has fertiliser requirements approximately three times higher than sugarcane (corn: 149 kg/ha *cf.* sugarcane: 55 kg/ha) (Ecoinvent Centre, 2010; Patzek *et al.*, 2005). Furthermore, sugarcane bioethanol has a much higher ratio of bioenergy energy output (energy contained in bioethanol) to fossil energy input (energy required to make the bioethanol, including agriculture) when compared to corn bioethanol, which means that corn is an energy intensive crop and it is therefore difficult to accomplish the desired reductions in carbon footprint (von Blottnitz and Curran, 2007).

As described earlier, there can also be significant variation amongst bioethanol studies because of the boundaries chosen and the assumptions made. Quirin *et al.* (2004) summarised this variation with an upper and lower bound for the global warming potential for sugarcane bioethanol studies. The sensitivity of this variation on the savings of scenario 1b can be investigated. The results from scenario 1b were therefore recalculated using the upper and lower bounds of global warming potential from Quirin *et al.*'s (2004) review. Table 4.4 shows the uncertainty in the global warming potential savings relative to scenario 1a. While the savings on an ethanol basis can vary widely, the effect is substantially reduced when considering the end product (500 mL CSD bottle), because other processes in the value chain also contribute to the carbon footprint, thereby reducing the sensitivity of the final results to the bioethanol study used.

Table 4.4. Sensitivity of the sugarcane bioethanol study used to calculate the GWP savings.

	GWP Saving (kg CO_2-eq per kg ethanol)	**GWP scenario 1b** (kg CO_2-eq per 500 mL CSD bottle)	**GWP *cf.* scenario 1a** (%)
Ecoinvent	-2.19	0.065	-28
Lower (Quirin *et al.*, 2004)	-1.80	0.069	-25
Upper (Quirin *et al.*, 2004)	-2.87	0.059	-35

Two further sensitivities investigated concerning the difference between scenarios 1a and 1b are the conversion of bioethanol to ethylene, and the distance over which ethylene glycol is imported. These sensitivities were assessed with respect to fossil-energy required, global warming potential, acidification potential and eutrophication potential as shown in Table 4.5. From this analysis, it can be deduced that the results are not very sensitive to the changes made, with respect to the base case, scenario 1b. However, lower conversion would result in more bioethanol being wasted, and it might be valuable to modify the process in to include an ethanol recovery stage. As previously discussed, the results are insensitive to the distance over which ethylene glycol is transported.

Table 4.5. Sensitivity of LCA results to process parameters

Sensitivity	Details		Change of impact category *cf.* base case (%)			
	Base case (scenario 1b)	Change made (*cf.* base case)	Fossil-energy required	Global warming potential	Acidification potential	Eutrophication potential
Bioethanol to ethylene conversion	98.4%	93.4% (-5%)	+0.2	-1.4	+0.7	+2.3
Ethylene glycol transport distance	10000 km	11000 km (+10%)	+0.1	+0.1	+0.4	+0.3

4.4.3 Wider Considerations

If PET packaging production worldwide were to use ethylene glycol derived from bioethanol instead of from fossil fuel, it would utilise 11% of the 1.0 × 10^8 m^3 annual bioethanol production capacity estimated for 2015 (Sarkar *et al.*, 2012). World PET production in 2015 was estimated from the amount for 2011, 60 Mte/yr, by inflating it using an average 6% annual growth rate projection (PCI Xylenes & Polyesters, 2013), assuming that 30% of PET use for packaging remained constant.

Considering sugarcane bioethanol production in Brazil, the average harvests are 6.0 kg of sugarcane/m^2 and the estimated bioethanol conversion rate used in this Dissertation was assumed to be 14.9 kg sugarcane per kg bioethanol (Ecoinvent Centre, 2010; Lapola *et al.*, 2009). Therefore, to produce the ethanol for the total quantity of PET produced for packaging in 2011, 18 Mt/y, approximately 17,000 km^2 of land would be needed to grow sugarcane. This land requirement amounts to 18% utilisation of the 96,170 km^2 cultivated sugarcane land area in 2011 in Brazil (Unica, 2013). This crude estimate gives only a rough order of the amount of land required; of course, there are many conflicting requirements for such land, ranging from the need to produce ethanol for other industries wishing to switch from fossil-based feedstock, to requirements for food production and the need to maintain the eco-system. Such considerations are beyond the scope of the present research.

Water use is an important consideration for sustainability studies. The water used to make ethanol from sugarcane and willow is, respectively, 15.5 kg and 27.4 kg per kg bioethanol (Ecoinvent Centre, 2010; Stephenson *et al.*, 2010). The water required to process lignocellulosic biomass is larger, primarily owing to the pre-treatment stages prior to fermentation. In both cases, no irrigation is required during cultivation. When comparing scenarios 1b and 1c, with 1a, the total water used was found to be similar, and the processes for bioethanol accounted for < 10% of the total water used in their respective scenarios. For scenario 1b, the water use was assessed by excluding the Brazilian electricity grid mix given that a significant quantity of water is used in hydroelectric power generation.

A basic economic assessment was performed, based on a reported capital investment of $278 million by Braskem to construct a plant to produce 200 kt/y ethylene from bioethanol (Schill, 2010). A capital depreciation allowance, deductable before tax, of 15% on the total capital investment and a scrap value of 10% of the capital investment at the end of the 20 years' plant lifetime was assumed. Corporation tax, without tax breaks, was estimated at 30% of profit, payable 1 year in arrears. Based on the process modelling and inventory analysis, 1.7 kg of bioethanol forms 1.0 kg of ethylene. With current bioethanol and ethylene prices at $674/t bioethanol and $1,246/t ethylene respectively, the feedstock to product margin made would be $99/t ethylene (Platts, 2013; Unica, 2013). Other operating expenses were approximated based on the process modelling and typical costs of the utilities; however, the analysis showed that these operating expenses would be insignificant compared to the feedstock costs. The resulting net present value showed a breakeven point after 20 years of production with a very low interest rate of 3%, giving no incentive from the industry to invest. The most sensitive parameters in the analysis were the feedstock and product prices. A hypothetical case can be calculated to determine the conditions required for such an investment to be profitable at a desired interest rate of 10% and also deliver an overall rate of return on the investment of 10%. Increasing the value added margin, by artificially reducing bioethanol price and increasing ethylene price, both by 22%, would result in the desired investment criteria being met. Under these conditions, a positive net present value and payback time would be achieved after 4 years of production.

Such an assessment has illustrated that the economics are sensitive to feedstock and product price fluctuations owing to the small value-added margins. Incentives such as tax cuts and grants would be necessary because the 22% change in prices is artificially high and unlikely to occur in the near future. These strategies are necessary unless the total investment cost can be reduced through further process integration and economies of scale.

4.4.4 Further Process Improvements

Currently, the production of bioethanol and its conversion to ethylene have been studied as independent processes. In the former, the ethanol is distilled to a purity of 95 wt%, but in the latter the ethanol would be diluted with water as discussed in Appendix A. Integration of these processes could therefore reduce the distillation energy requirements if, for example, a 50 wt% ethanol stream were sent directly to the ethylene glycol process.

The functional unit defined was a 500 mL CSD bottle made of 23.5 g of PET. There is potential to reduce the mass to 18 g while maintaining the same performance (De Miranda *et al.*, 2011). Thus, using 23% less polymer material results in a commensurate reduction of 23% in all impact categories. With no tradeoffs, this technique delivers global warming potential reductions similar to those provided by substituting bioethanol from sugarcane. However, there is a limit to making lighter bottles without compromising the strength of the bottle. Combining the benefits of lighter bottles with bioethanol from Brazil, total savings in global warming potential and use of fossil fuel energy of, respectively, 45% and 35% are possible.

4.5 Conclusion

In this Chapter, the environmental impacts of producing a PET bottle using ethylene glycol derived from biomass, both sugarcane and willow, were investigated and compared to conventional ethylene glycol production. The sugars contained in sugarcane juice were fermented to bioethanol and the cellulosic sugarcane bagasse was burnt for electricity generation. It was found that, by using sugarcane bioethanol as a feedstock, the global warming potential and non-renewable resource use for a PET bottle could be reduced by 28% and 16%, respectively. The main drawback of using sugarcane as a feedstock is an increase in other environmental impacts, such as acidification and eutrophication potential. This is largely caused by the cultivation of the sugarcane, requiring fertilisers. Willow biomass was first deconstructed from cellulosic biomass to fermentable sugars. Using willow bioethanol as a feedstock could potentially reduce non-renewable resource use by 16%, and did not increase other environmental impacts as significantly as sugarcane. From the scenario analysis, the transportation of ethylene glycol from Brazil only resulted in a minor increase of the environmental impacts.

Chapter 5 The Production of *p*-Xylene from Biomass

Biomass can be used as the principal raw material feedstock for the production of *p*-xylene. This Chapter quantifies the environmental impacts of using biomass-derived *p*-xylene within the polyester value chain for the production of a PET bottle.

5.1 Introduction

Chapter 4 has shown that producing PET from ethylene glycol derived from sugarcane reduces fossil carbon emissions by ~28%. The objective of this Chapter is to study the environmental impact and economic feasibility of using *p*-xylene manufactured from biomass, rather than from naphtha, in the production of PET. For this analysis, a LCA has been undertaken to compare (i) the conventional process route (*viz.* with raw materials made from fossil fuel) and (ii) a modified process route (*viz.* using *p*-xylene made from biomass).

Processes have been developed to hydrolyse cellulose and hemi-cellulose biomass to sugars. Along with sugars already present in the biomass, these hydrolysed sugars can be catalytically reformed to a range of paraffins, olefins, and aromatics of similar composition to reformate (Blommel and Cortright, 2008) from which *p*-xylene can be isolated using conventional separation techniques (PCI Xylenes & Polyesters, 2013). Reformate is a key intermediate from a catalytic reforming process, typically containing high octane hydrocarbons, which can either be used in gasoline or as the main feedstock for an aromatics unit, because it contains a high proportion of benzene, toluene, and xylene. In the present research, it has been assumed that the subsequent conversion of *p*-xylene to terephthalic acid would continue to use the conventional oxidation process. The principal advantage of using biomass to produce upstream chemicals, such as *p*-xylene, is that no changes are needed in the existing downstream processes.

Terephthalic acid accounts for the larger proportion of PET, ~72 wt% of the total polymer. Given that using biomass for the ethylene glycol, which accounts for the remaining ~28 wt%, resulted in ~28% reduction of global warming potential and ~16% reduction of fossil fuel use, then bio-sourced terephthalic acid is likely to make a substantial reduction in carbon emissions for the polymer, provided the savings are not outweighed by additional emissions from the conversion of biomass to *p*-xylene.

Generally, the cradle-to-gate emissions for the conventional production of terephthalic acid from naphtha results in carbon emissions of the order of 2.4-3.1 kg CO_2-eq per kg of purified terephthalic acid (Boustead, 2005; Li *et al.*, 2014). The range reflects the differences between studies and, particularly, system boundaries used. In total, ~60 MJ of energy is required to produce one kg of purified terephthalic acid, almost exclusively (~99.5% of the total energy) from fossil fuel sources (Boustead, 2005); this includes both processing energy and energy contained within terephthalic acid. It has been shown (Li *et al.*, 2014) that improvements in terephthalic acid processing can reduce cradle-to-gate carbon emissions by between 4% and 24% from the upper 3.1 kg CO_2-eq; however, a substantial part of the emissions is associated with the preparation of the raw materials for the terephthalic process associated with resource extraction and the production of naphtha and *p*-xylene. Of course, if the starting material were biomass, significant processing would also be required to convert this to the raw materials needed for terephthalic acid production.

The research presented here investigates, for the first time, the environmental impacts of converting the biomass to sugars and subsequent catalytic reduction of the sugars to reformate. There are differences in the unit operations required to produce sugars from different types of biomass. Accordingly, a number of different crops have been investigated, namely sugarcane juice, cellulosic wastes, sugarcane bagasse, corn stover and willow. As stated in Chapter 2, sugarcane and willow both show the largest potential for savings in emissions of carbon. Corn stover was also included in this study because it is an abundant source of biomass in the USA. US corn bioethanol is one of the world's largest sources for bioethanol, at 57% of global bioethanol production. However, its performance with respect to different environmental impacts is worse than sugarcane in a number of categories (Quirin *et al.*, 2004).

5.2 Analysis

5.2.1 Goal and Scope

For the reasons explained in Chapter 4, the analysis in the present Chapter concentrates on bottle-grade material. The LCA undertaken in this Chapter also does not include recycling or disposal, since the aim was to compare the impact of different raw materials for the production of terephthalic acid on virgin PET. End-of-life scenarios for PET are assessed separately in Chapter 7. The functional unit was defined as one 500 mL CSD PET bottle after distribution to a supermarket. The mass of PET used to make the bottle was assumed to be 23.5 g.

5.2.2 Value Chain

The processes involved in the production of PET bottles from (i) conventional fossil-fuel sources and (ii) using *p*-xylene derived from biomass, are shown in Figure 5.1, with the difference between the routes being in the production of *p*-xylene. Using conventional technology, *p*-xylene is one of several products formed from the catalytic reforming of naphtha. Biomass is, in the case of cellulosic biomass, first converted to a solution of sugars (Davis *et al.*, 2013), and then catalytically reformed to a product of similar composition to reformate derived from naphtha in conventional *p*-xylene production (Blommel and Cortright, 2008). The same separation processes as used in conventional *p*-xylene production can then be used to isolate a stream rich in *p*-xylene. The *p*-xylene, irrespective of starting material, is then oxidised to terephthalic acid. The second raw material, ethylene glycol, is, in the initial analysis, produced using conventional techniques, from naphtha and natural gas, oxidation to ethylene oxide and hydrolysed to ethylene glycol, as described in Chapter 4.

Purified terephthalic acid and ethylene glycol are combined in the continuous polymerisation process, which is followed by the solid-state polymerisation stage. The bottle-grade PET is used to make bottles, which are filled and distributed. As the focus of this study is the impact of using biomass to produce, ultimately, the *p*-xylene, the models from Chapter 4 concerning the environmental impacts of the production of ethylene glycol, polymerisation and bottle moulding have been used.

For the inventory analysis, quantitative mass and energy balances were performed for the processes defined within the system. The detailed process flowsheeting and sample calculations for the methods of allocation are described in Appendix B.

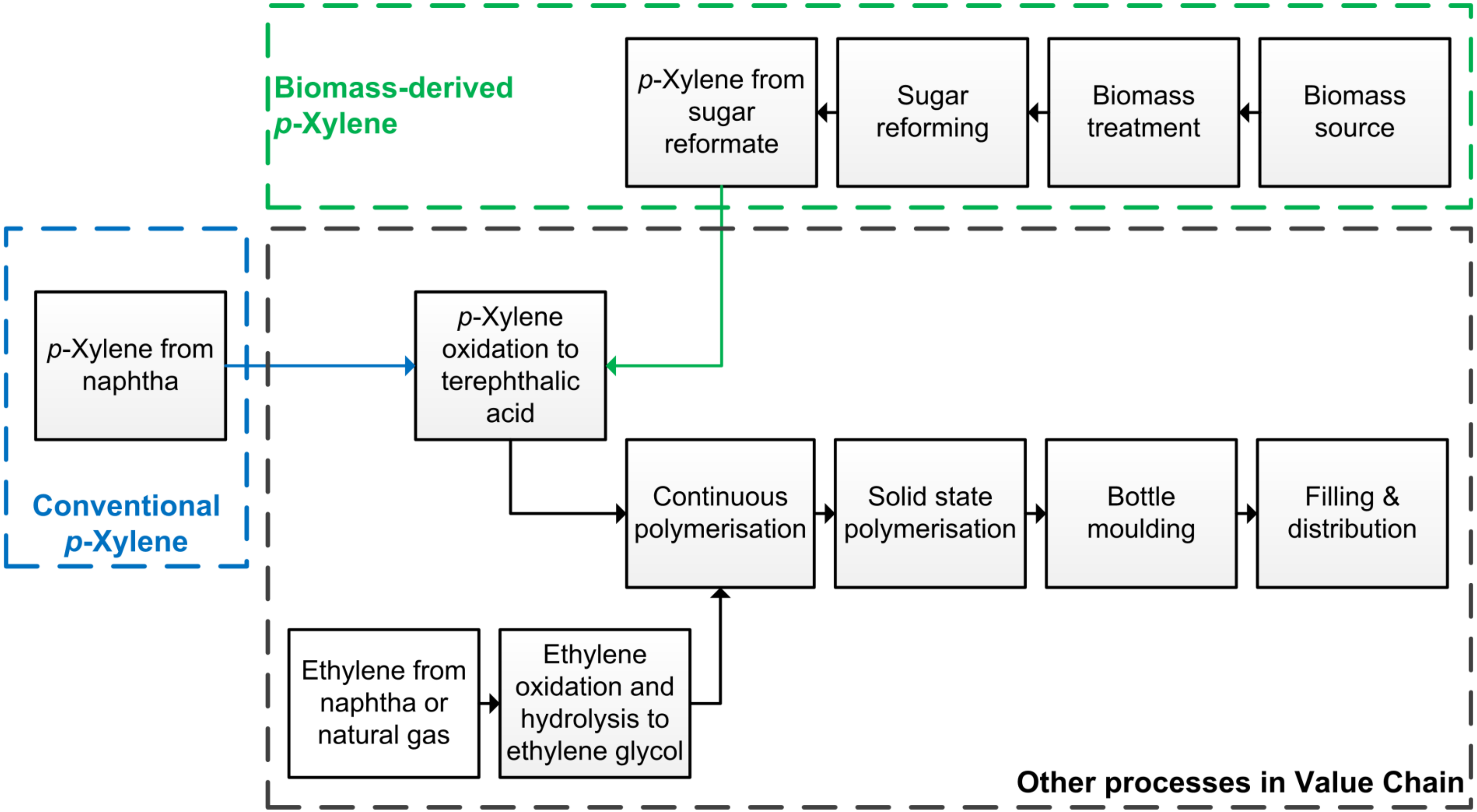


Figure 5.1. Polyester value chains for both conventional and biomass routes.

The processes shown in Figure 5.2 represent the processes included in the system boundary for *p*-xylene production from biomass. The processes, such as the electricity mix and waste water treatment, form part of the background system, processes which are influenced by measures taken in the foreground system.

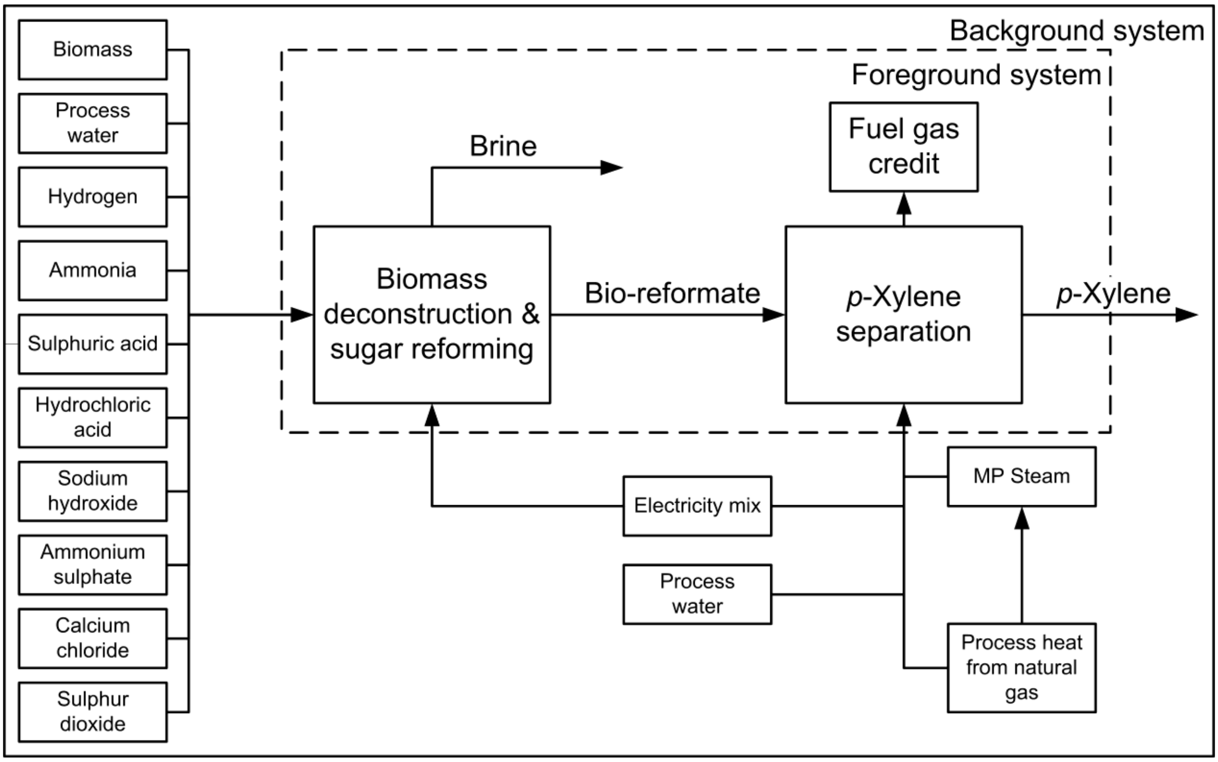


Figure 5.2. The system boundary definition for *p*-xylene production from biomass.

5.2.3 Allocation

Some of the processes described in Appendix B required allocation. While the details of, and sample calculations on, the allocation methods can be found in Appendix B, the rationale for using allocation is described here.

The conventional production of *p*-xylene from naphtha is a multi-product process. There is a high level of integration within the process, *e.g.* heat integration, such that it is not possible to identify the relationships between the products and feeds. It was also not possible to redraw or expand the system boundaries for this analysis (the preferred method). Allocation was therefore required. Economic and mass-based allocation methods were used so that the sensitivity to the method of allocation could be investigated later. Mass-based allocation makes use of the mass balances for the process. The allocation fraction can be calculated by dividing the mass of one product by the total mass of all products. For economic allocation, the allocation fraction is calculated based on product value, such that the value of one product is divided by the total value of all products. Price fluctuations are an issue for economic allocation, therefore, the average price for each product over a five year period (2010-2014) was used.

Two of the agricultural systems studied, sugarcane and corn, are multi-product systems. Sugarcane bagasse is a by-product of sugarcane juice production. Similarly, corn stover is a by-product of corn production. Adjusting the system boundaries to include both agricultural products is possible and has been investigated in Section 5.3.3 for sugarcane. However, it is desirable for biomass processes that they can only make use of second generation biomass, such as agricultural wastes, sugarcane bagasse and corn stover. For this reason, it is necessary to investigate the environmental impacts of using these agricultural by-products independently. One method of doing so is called the cut-off approach. The cut-off approach assumes that none of the environmental impacts associated with agriculture should be allocated to the sugarcane bagasse or corn stover because these by-products are waste residues. Thus, the full agricultural burden is allocated to the primary product, sugarcane juice or corn. It was decided in the present work that drawing the system boundaries in this way would be incorrect because sugarcane bagasse and corn stover are actually valuable by-products and should consequently bear part of the burdens associated with agriculture. It was not possible to change the system boundaries in any other way given the inherent integration of primary crop product (corn and sugarcane juice) growth and the agricultural waste (corn stover and sugarcane bagasse). Furthermore, given the lack of information within the datasets used for corn and sugarcane, it was not possible to identify relationships between the inputs and outputs of the agricultural processes. For this reason, allocation of the burdens for the by-products was considered. In addition to mass and economic allocation methods described previously, carbon allocation was also used. Carbon allocation was defined as the carbon contained in one product divided by the carbon contained by all products from the system. Carbon allocation is different from mass allocation because it does not account for the water content of the biomass source. Water content can significantly distort the mass allocation method. Again, several allocation methods were used so that the sensitivity could be investigated in Section 5.3.2. As described in Chapter 3, given that allocation methods are not as rigorous as system boundary expansion, it is especially important to consider the sensitivity.

5.2.4 Use of Datasets

Gabi 6 (PE International, 2013) and Ecoinvent version 2.2 (Ecoinvent Centre, 2010) databases with life cycle inventory information for some of the processes were used in conjunction with the process modelling described in Appendices A and B to complete the value chain. One process in the value chain was not modelled, the oxidation of *p*-xylene to terephthalic acid. For this process, a dataset from Ecoinvent (Ecoinvent Centre, 2010) was used. The terephthalic acid dataset from PE International (2013), used in Chapter 4, was not suitable because it did not allow modification of the source of *p*-xylene.

5.2.5 Scenarios

In all the scenarios considered, ethylene glycol and its upstream production, *p*-xylene oxidation to terephthalic acid, polymerisation and bottle moulding would take place in the USA. In detail, the continuous and solid state polymerisation plants would be located in South Carolina. The production of ethylene glycol would be located in Texas and the feedstock was assumed to be transported by ship 1500 km to the polymerisation facility. Terephthalic acid would be transported 650 km by rail from its manufacturing plant in Alabama to the PET plants.

The location for the production of *p*-xylene varied depending on the source of the raw material. In the conventional scenario, where *p*-xylene is produced from napththa, *p*-xylene production was assumed to be located in Texas and would then be transported 1000 km by ship to Alabama. Transport is especially important for biomass because it is bulky and of low energy density, factors which would cause significant environmental impacts if transported long distances. Biomass is best utilised where it is produced, with the refined, energy-dense products being shipped. Thus, in this analysis, sugar reforming facilities were assumed to be scattered across the biomass cropping area such that biomass feedstocks would be transported by road an average distance of 500 km. The bio-reformate would then be transported by sea to the conventional *p*-xylene separation units, which would be located in Texas.

The feedstock source, production locations and transport distances for *p*-xylene are summarised in Table 5.1 for each scenario.

Table 5.1. Summary of raw materials for *p*-xylene production and respective locations.

Feedstock	Cargo	From → To	Distance and Mode
Conventional (Naphtha)	Naphtha	Collocated	Included in dataset
	p-Xylene	Texas → Alabama	1000 km by ship
Corn stover	Corn stover	Farm → Reforming	500 km by truck
	Bio-reformate	Middle USA → Texas	1000 km by train
	p-Xylene	Texas → Alabama	1000 km by ship
Willow	Willow	Woodland → Reforming	500 km by truck
	Bio-reformate	Georgia (Stephenson and MacKay, 2014) → Texas	1000 km by train
	p-Xylene	Texas → Alabama	1000 km by ship
Sugarcane	Sugarcane	Farm → Reforming	500 km by truck
	Bio-reformate	São Paulo (Brazil) → Texas (USA)	10000 km by ship
	p-Xylene	Texas → Alabama	1000 km by ship

The willow dataset, representing the use of woody biomass, although originally calculated for production in the UK, has been modified for the USA. The background datasets based in the UK, *e.g.* electricity and fuel production, have been substituted with US based datasets. The underlying model from Stephenson *et al.* (2010) for the agriculture of willow has not been modified. The reason for this assumption is that the yields reported by Stephenson *et al.* (2010), 7-12 dry te/ha, averaged at 10 dry te/ha in the model are similar to those for willow agriculture in the USA (Volk *et al.*, 2011).

As noted previously, in practice, owing to the diversity of supply chains, the transport routes and distances are only indicative of possible supply chains. The scenarios have been selected to capture most of the environmental impacts associated from the transport of materials.

5.3 Results

5.3.1 Feedstock Comparison

Figure 5.3(a) shows the global warming potential and Figure 5.3(b) the primary energy use for a range of scenarios using conventional naphtha and biomass as a feedstock for *p*-xylene for the functional unit of a 500 mL CSD PET bottle, defined earlier. For these results, economic allocation has been used across all scenarios. For the conventional processing, the results from the 2008 and 2013 process designs can be compared with the *p*-xylene dataset from Gabi. All three scenarios have similar levels of fossil energy requirements at 2.4-2.5 MJ per bottle; however, the conventional 2008 and 2013 models feature global warming potentials ~20% lower than the dataset. Because details of the inventory analysis of the *p*-xylene dataset from Gabi are not in the public domain, it is difficult to determine the exact reason for this discrepancy. The differences could arise due to different boundary conditions, allocation methods, or due to process conditions, *e.g.* efficiency and catalysts. Comparing the 2008 and 2013 plant designs, the energy requirements were similar.

Given the similarities in the results from the 2008 and 2013 designs, the biomass scenarios shown in Figure 5.3 only used the separation model from the 2013 design to separate *p*-xylene from the bio-reformate. The four biomass sources are now compared with the conventional 2013 processing. Referring to Figure 5.3(b) first, it is immediately obvious that a significant quantity of fossil energy is required to process the biomass feedstock into bio-(*p*-xylene). Both corn stover and willow require 96-98% of the fossil fuel used by the conventional 2013 scenario. While the sugarcane scenarios require 85-87% of the conventional fossil fuel requirements, this is primarily attributable to the effect of the Brazilian electricity grid, which uses a larger proportion of hydroelectric power than the USA (grid mixes are country averages from the Gabi database). The largest fossil energy requirement for the biomass scenarios is the bio-reformate process. This includes both the biomass deconstruction and sugar reforming processes. In detail, hydrogen production accounts for ~40% and electricity accounts for ~46% of the fossil energy requirements of the bio-reformate process. The largest electricity requirements are the operations of biomass milling, mechanical vapour recompression (MVR) evaporation, and hydrogen recovery and compression. The process heating requirements are satisfied by waste burning and heat integration. The separation of *p*-xylene from the bio-reformate requires, in comparison to other processes, very little fossil energy. The total energy for the biomass scenarios is much greater. A large quantity of biomass energy goes into the process and requires energy-intensive processing. Overall, in terms of saving fossil fuel, there is very little benefit in using biomass to make *p*-xylene.

It is important to note that the renewable biomass energy content of the corn stover and sugarcane bagasse scenarios are not accurately represented. This is owing to the economic allocation factor for corn stover and sugarcane bagasse being very small at 11% and 7% respectively. Thus the biomass energy is being largely allocated to the higher priced corn and sugarcane juice. Due to this, the sugarcane juice scenario, with an allocation factor of 93%, has an overestimated renewable biomass energy content. The same argument applies to the global warming potential results where the CO_2 emission savings for corn stover and sugarcane bagasse are underrepresented while the savings for sugarcane juice are overrepresented in Figure 5.3(a). The sensitivity of allocation method is investigated later. The scenario most accurately represented in Figure 5.3 is therefore the willow scenario because it avoids the issue of allocation caused by agricultural co-products. The willow scenario gives a CO_2 emission reduction of 32% by using bio-(*p*-xylene), but only a 2% reduction of fossil fuel energy. The bio-reformate process is the largest contributor to global warming potential because of the emissions from the energy intensive operations listed earlier, as well as the emissions from the waste burning (*i.e.* burning lignin, biogas from waste water treatment, and waste gases from reforming) to generate heat and electricity.

Regarding transport, the impact and energy requirement for each scenario is relatively small because the transporting of bulky biomass was minimised by having decentralised bio-reformate production facilities. Energy-dense bio-reformate was then transported over larger distances.

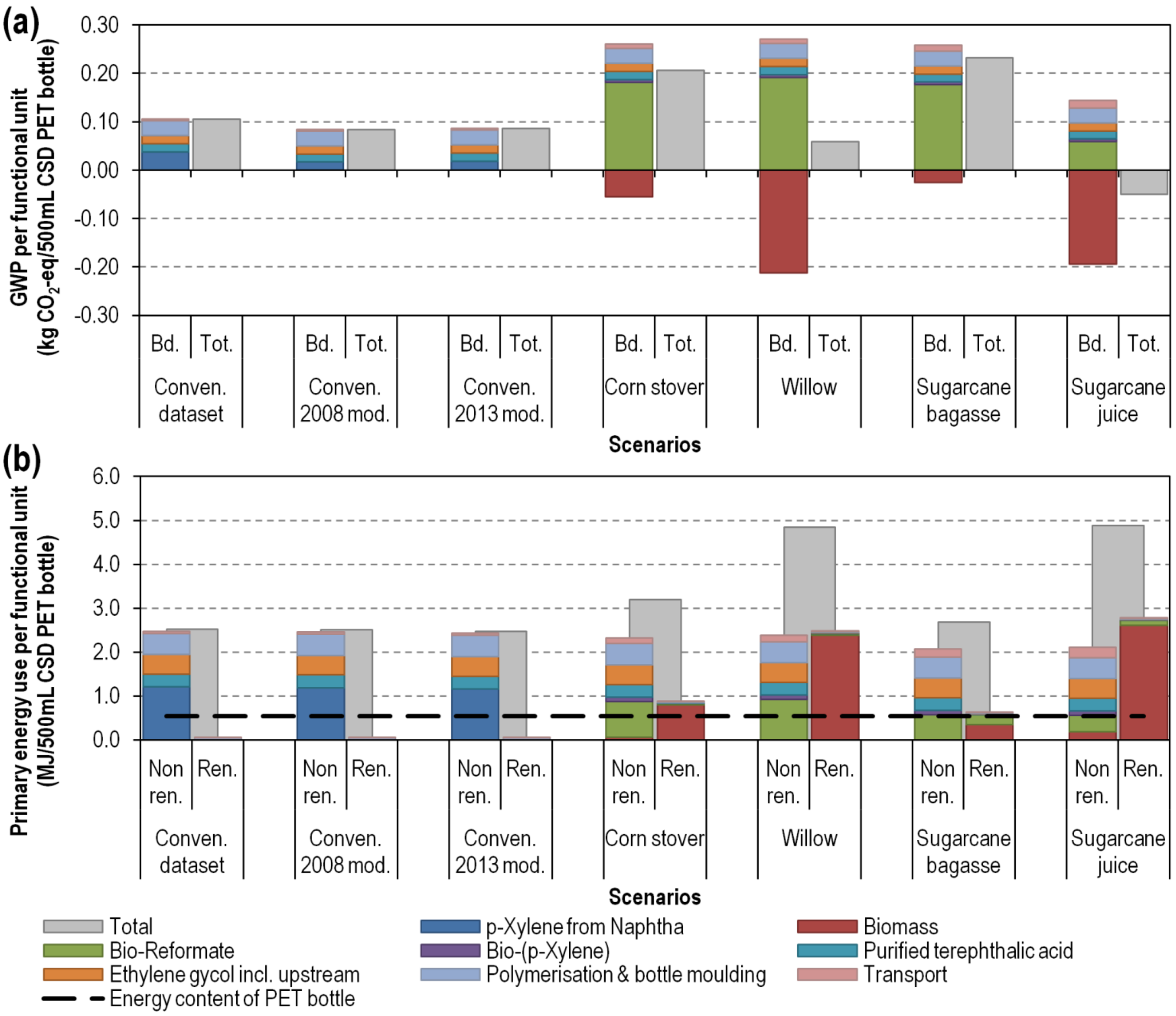


Figure 5.3. (a) Global warming potential, in kg CO_2-eq, for conventional (conven.) processing with a dataset or models (mod.) for 2008 and 2013 *p*-xylene processing. Bio-(*p*-xylene) is also shown for feedstock types corn stover, willow and sugarcane bagasse and juice. Bd.=Breakdown, Tot.=Total. (b) Breakdown of primary energy use, in MJ, from both non-renewable (non. ren.) and renewable (ren.) sources for scenarios described in (a).

5.3.2 Sensitivity to Method of Allocation

Figure 5.4 represents the sensitivity of using different allocation methods in this LCA on the basis of (a) global warming potential and (b) primary energy use. As discussed earlier, for the conventional scenario, economic and mass allocation methods were used. There is very little variation between the economic and mass allocation results for the conventional scenario, meaning that the results presented in Figure 5.3 using the economic allocation method are robust. For the willow dataset there is no allocation issue, as noted earlier.

According to Figure 5.4(b), regardless of allocation method, the fossil energy requirements are mostly unaffected by method of allocation. However, as shown in Figure 5.4(a), changing the allocation method can tell a very different story about greenhouse gas emissions. Using mass-based allocation, the corn stover scenario appears to make a reduction of 18% to the carbon emission when compared to conventional processing, yet an increase in carbon emission when using economic and carbon allocation schemes. The fundamental problem here is that the allocation method fails to represent accurately the reality of the causal relationship between CO_2 absorbed by the corn and corn stover. The same argument applies to sugarcane juice and sugarcane bagasse. It is interesting that even with the least favourable allocation method, using 50% carbon allocation; sugarcane juice presents a favourable scenario with a 53% reduction in global warming potential and a 17% reduction of fossil fuel use when compared to the conventional scenario. These savings are significantly larger than the savings made by using willow biomass discussed earlier.

A final sensitivity unrelated to allocation was also tested. It was thought that the cellulase enzyme loading would be significant change in the impact assessment. The enzyme loading was increased from 10 g of cellulase per kg of cellulose to 26 g of cellulase per kg cellulose, which was used in the NREL report (Davis *et al.*, 2013). The sensitivity was investigated for the corn stover scenario using economic allocation. For a 2.6 fold increase in enzyme loading, the global warming potential and fossil energy use both increased by ~2%, so enzyme loading does not have a large effect.

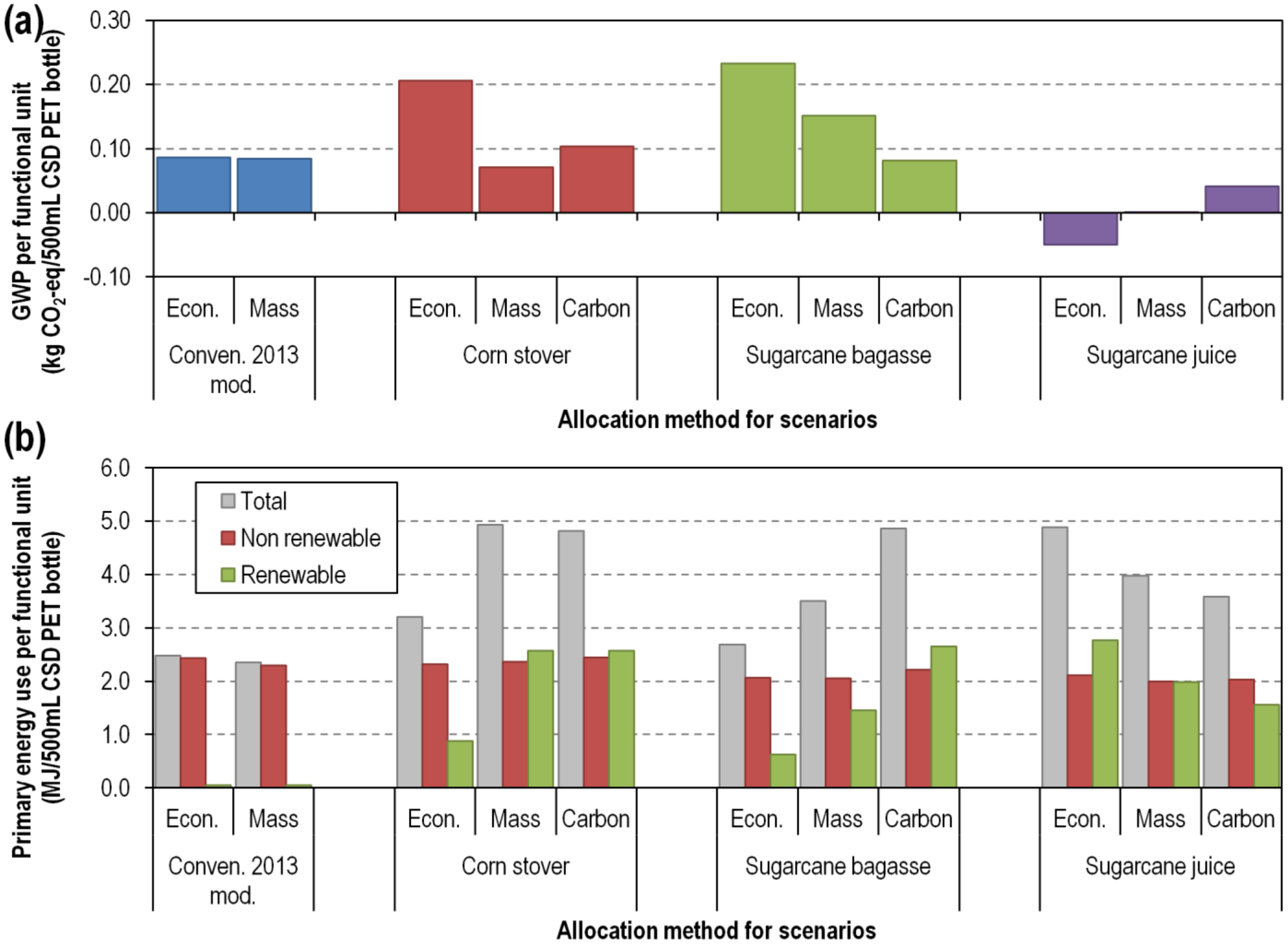


Figure 5.4. (a) Global warming potential, in kg CO_2-eq, for conventional (conven.) 2013 model (mod.) and biomass sources corn stover, sugarcane bagasse and sugarcane juice using different methods of allocation: economic (econ.), mass, and carbon. (b) Primary energy use for scenarios and allocation methods described in (a).

5.3.3 Improved Scenarios by Avoiding Allocation

In order to avoid allocation, three additional sugarcane scenarios were investigated and compared to the conventional 2013 scenario and willow scenario.

- The first sugarcane scenario involves deriving bio-reformate from the whole sugarcane crop, *i.e.* both 0.72 kg sugarcane juice and 0.28 kg sugarcane bagasse are used to form bio-reformate. While the sugarcane bagasse would still require the biomass deconstruction process, the sugarcane juice would be fed directly into the evaporator to concentrate the sugars before reforming.

- The second sugarcane scenario uses sugarcane juice only to form the bio-reformate, but the sugarcane bagasse is burnt and used to generate electricity in Brazil with a conversion efficiency of 35%. This scenario receives an electricity credit equivalent to the grid mix in Brazil.

- The third sugarcane scenario uses the second sugarcane scenario described above (bio-reformate produced from sugarcane juice and electricity generated from the combustion of sugarcane bagasse), but it also incorporates the manufacture of bio-(ethylene glycol) from sugarcane bioethanol studied in Chapter 4. This final scenario represents the impact of generating a ~100% biomass-sourced bottle from sugarcane.

By using both sugarcane juice and sugarcane bagasse all three of these scenarios manage to avoid allocation issues between the juice and bagasse by instead expanding the system boundary thereby reflecting the causal relationships transparently.

The results of these scenarios are shown in Figure 5.5 for the production of a 500 mL CSD PET bottle for (a) global warming potential, (b) primary energy use, and (c) eutrophication potential. Each sugarcane scenario presents increased savings in global warming potential and fossil fuel energy use when compared with the conventional scenario. The savings become substantial for the case of burning bagasse, giving an overall 87% reduction global warming potential and 26% reduction to fossil fuel energy use. Coupled with deriving ethylene glycol from sugarcane bioethanol, the overall reduction in global warming potential is 114%, *i.e.* the system, as defined, is effectively sequestering CO_2 from the atmosphere. There is also a reduction of 39% in fossil fuel energy use. However, it is important to realise that total energy efficiency is much lower when using biomass: a 100% biomass-sourced bottle uses 81% more energy in total than the conventional route. This is because biomass enters the processing partially oxidised, typical formula of $C_nH_{2n}O_n$, which requires a substantial amount of energy to effectively hydrogenate and also incurs a loss of ~30% of the carbon in the sugars to CO_2 during the reforming (see Appendix B).

The overall flows of fossil and renewable fuels through each of the processes in Figure 5.1 are best understood using the Sankey diagrams, shown in Figure 5.6. Two scenarios are represented here, the conventional processing and the 100% biomass bottle from sugarcane. From the Sankey diagrams, the total energy, represented by the scale of each flow, and energy conversion efficiency for each process is clear. The burning of bagasse generates 0.48 MJ of electricity, which resulted in a credit based on the Brazilian electricity grid mix. The large blue renewable flow represents the substantial amount of hydroelectric power generation in Brazil.

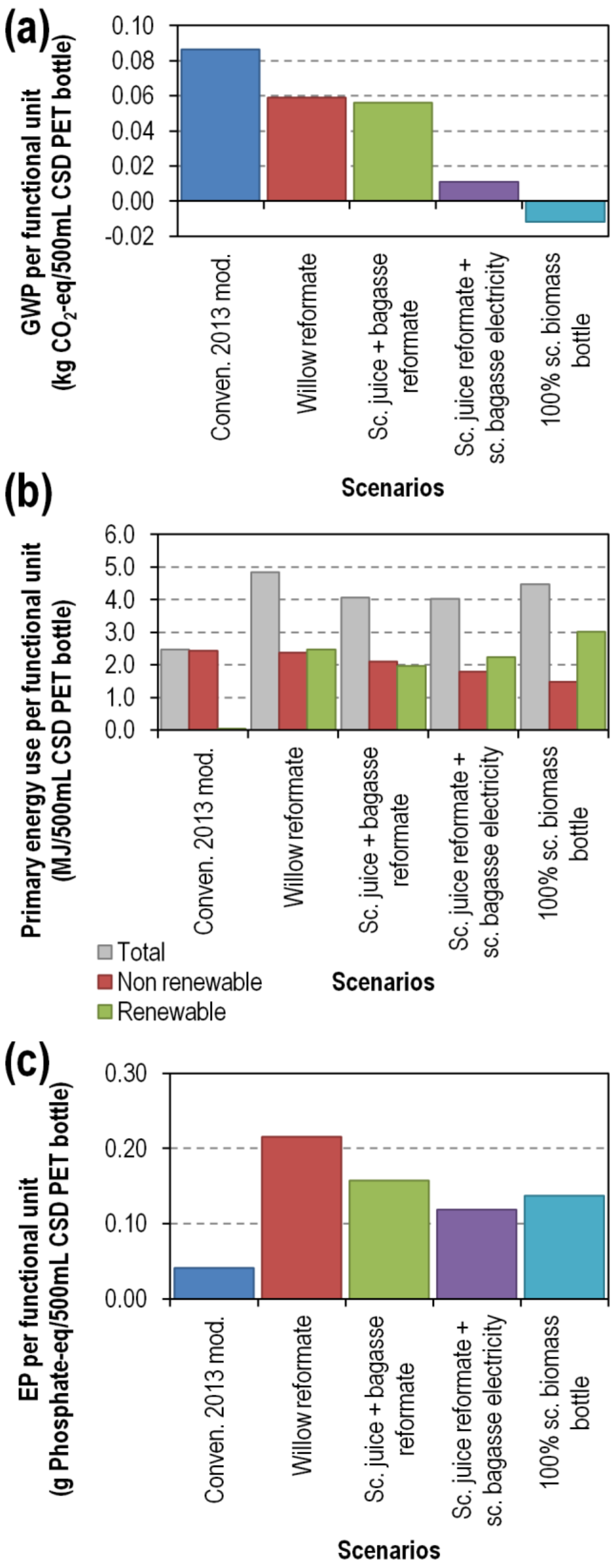


Figure 5.5. For the scenarios: conventional (conven.) 2013 model (mod.), willow and various sugarcane (sc.) scenarios, performance is shown on the basis of three metrics is compared (a) Global warming potential in kg CO2-eq (b) Primary energy use in MJ (c) Eutrophication potential in g Phosphate-eq

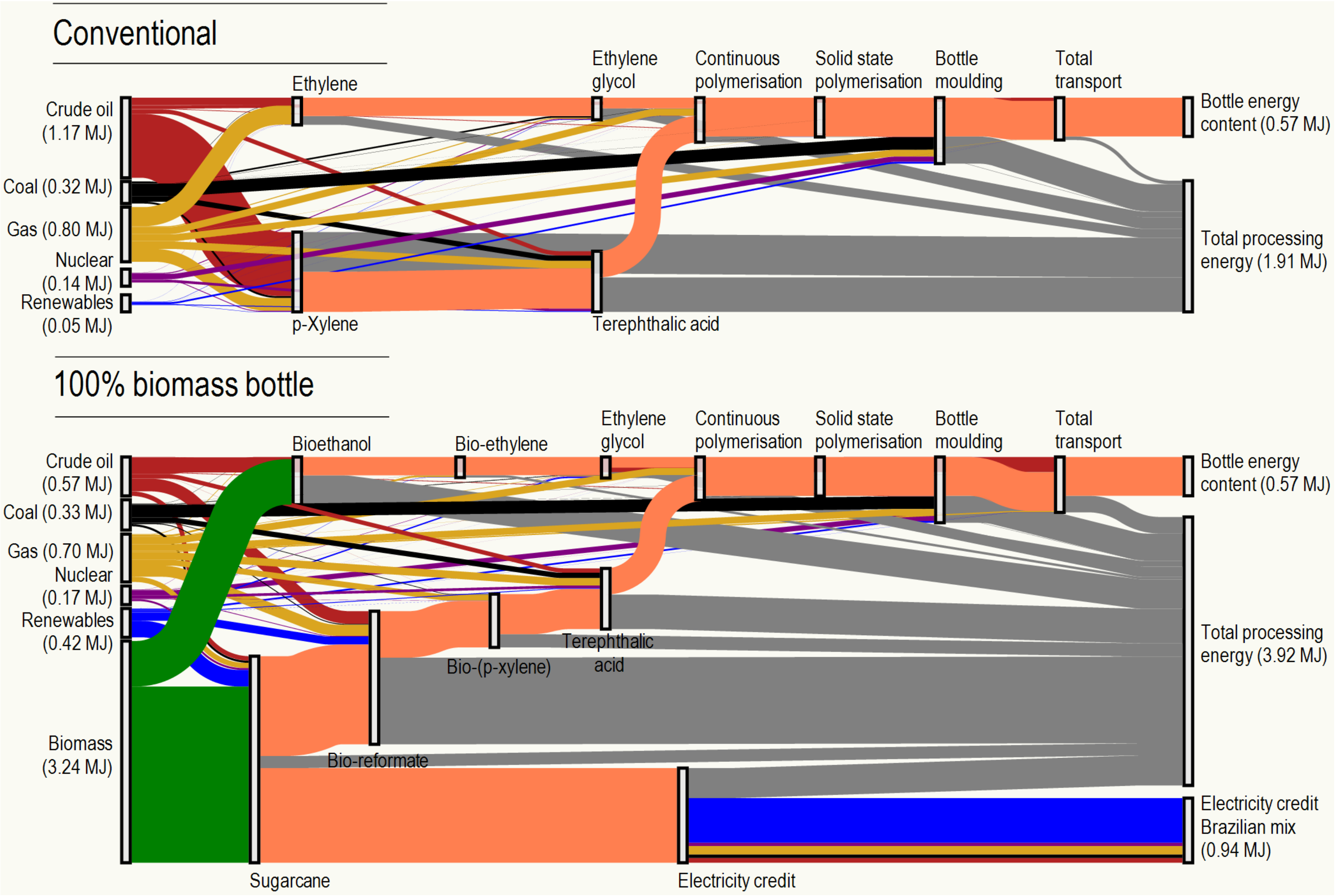


Figure 5.6. Sankey diagram showing the primary source of energy flows to each process for conventional polyester and a 100% biomass polyester for the functional unit of a 500mL CSD PET bottle.

Figure 5.5(c) shows the eutrophication potential for each scenario. Eutrophication is measured in g Phosphate-equivalents and represents the impact of nutrients such as nitrogen and phosphorous compounds which can cause a shift in species composition and biomass growth, *e.g.* algal bloom, which affects the survival of other species and biodiversity.

In LCA, emissions, for example, small quantities of nitrogen compounds from the burning of fossil fuels can contribute to eutrophication. For this reason, the conventional scenario has a small ‘base line’ eutrophication potential. However, it is the increase which is of interest. For the willow scenario, the production of willow contributed only 5.5% to the total eutrophication; however, the combustion of biomass waste in the biomass deconstruction process contributes 72% of the total impact. For the sugarcane juice and bagasse reformate scenario, growing the sugarcane contributed 21% to the total eutrophication, and nitrogen compound emissions from waste combustion contributed to 49% of the impact. While normally for agricultural products the eutrophication levels are significantly higher due to fertiliser use, both willow and sugarcane use low quantities of fertilizer. The willow dataset specifies the use of sewage sludge, which is applied once every three years (Stephenson *et al.*, 2010). Sugarcane cultivation contributes significantly more to eutrophication signifying a higher use of fertilizers for this biomass feedstock. The largest impact of eutrophication in this case, is caused by the burning of the wastes from the biomass deconstruction process. Nitrogen contained within the biomass and cells from waste water treatment is released on combustion and contributes to eutrophication. The overall sugarcane scenarios are lower in eutrophication compared to the willow scenario due to the use of sugarcane juice which does not go through the biomass deconstruction phase.

The totals for other environmental impacts categories assessed using the CML method, which have not been described in detail, are shown in Table B.8 of Appendix B.

5.4 Discussion

Producing a 500 mL CSD PET bottle only from sugarcane biomass feedstocks and using the sugarcane bagasse to generate electricity 0.48 MJ of electricity requires a total of ~0.63 kg sugarcane. At average harvests of 6.0 kg sugarcane/m^2, each bottle with the above scenario requires ~0.1 m^2 of land (Lapola *et al.*, 2009). For scale, hypothetically, if all PET packaging in 2013 (65 Mt/y × 30%) was made using sugarcane, this would require ~520 Mt/y of sugarcane and a land equivalent of ~86,000 km^2. To put this in perspective, total sugarcane production in 2013 from Brazil was ~650 Mt/y. This crude estimate serves to give some order of the respective amounts of biomass and land required, which would result in significant competition with food, other land and fuel uses, and biodiversity.

Water use in the production of bioethanol for bio-(ethylene glycol) has been discussed in the previous Chapter. Regarding agriculture, both sugarcane and willow are not irrigated and rely on rainfall (Ecoinvent Centre, 2010; Stephenson *et al.*, 2010). Water use for the biomass deconstruction and sugar reforming processes to produce bio-reformate from both sugarcane and willow has been assessed. Although in the biomass deconstruction a significant amount of water is added for the caustic wash and the acid and enzyme hydrolysis most of this water is recovered in the later stages of waste water treatment and evaporation. Furthermore, water produced in the sugar reforming stage can also be recycled into the biomass deconstruction after separation from the product. Overall, no additional process water is required for the production of bioreformate.

The production capacity of new conventional *p*-xylene facilities in 2013-2014 ranged between 400 and 1000 kt/y (PCI Xylenes & Polyesters, 2013). World *p*-xylene production capacity in 2013 is estimated to be ~38 Mt/y and production capacity is expected to grow by ~15% in 2014 as new units are commissioned, while the demand growth for *p*-xylene is ~6% (PCI Xylenes & Polyesters, 2013). Based on supply and demand growth ratios, in 2014, *p*-xylene will be in over-supply; this trend is expected to continue over the next five years as older assets close. Currently, there are no commercial scale bio-reformate facilities in existence. Given the projected over-supply of *p*-xylene, new biomass routes, which typically operate at significantly smaller scales and are therefore unlikely to benefit from the same economies of scale, will face significant barriers to entering the current *p*-xylene market.

5.5 Conclusion

This Chapter, focused on an alternative route for producing *p*-xylene. Conventionally *p*-xylene is derived from naphtha, however, new technologies have enabled *p*-xylene to be derived from biomass. In the analysis, cellulosic biomass sources, willow, sugarcane bagasse and corn stover, would first be deconstructed to a sugars solution. Sugarcane juice could skip the deconstruction step. All sugar solutions would then be concentrated prior to entering an aqueous reforming phase in the presence of hydrogen. In the process, the sugars would form a range of hydrocarbons similar in composition to reformate. From the reformate, *p*-xylene could be extracted and used as a feedstock in PET production.

From the various feedstocks assessed, only willow and sugarcane, with both sugarcane juice and bagasse included in the system boundary, could be reliably assessed due to LCA allocation issues. Producing a PET bottle, using *p*-xylene derived from willow, could reduce the global warming potential and non-renewable energy use by 32% and 2% respectively. Using sugarcane juice for *p*-xylene production and burning bagasse for electricity generation, resulted in larger savings to global warming potential (87%) and non-renewable energy use (26%) when compared with conventional bottle production. The use of biomass within the value chain did increase all other impact categories, most notably, those for eutrophication and acidification.

Chapter 6 Alternative Uses of Biomass within the PET Value Chain

This Chapter investigates how biomass can be used most efficiently in order to reduce the global warming potential and non-renewable energy use. Routes examined are the use of biomass in the production of raw material feedstocks, ethylene or *p*-xylene, or the use of biomass as a fuel source for process heat or electricity production.

6.1 Introduction

Chapters 4 and 5 have shown that the feedstock for the manufacture of PET, ethylene glycol and *p*-xylene, can be produced from various types of biomass, such as sugarcane, willow and corn stover, with the potential for reduced fossil fuel use and greenhouse gas emissions. The objective of the present Chapter is to investigate ways in which biomass could be introduced into the polyester value chain, other than to make ethylene glycol or *p*-xylene. In particular, the use of biomass as a source of fuel for (i) process heat or (ii) electricity has been studied. The resulting savings in global warming potential and fossil fuel have been quantified and compared with those predicted in Chapters 4 and 5. Conclusions are drawn about the most effective use of biomass within the polyester value chain.

6.2 Analysis

6.2.1 Goal and Scope

In earlier Chapters, the functional unit was defined as a 500 mL carbonated soft drink (CSD) PET bottle after distribution to a supermarket. In the present analysis, for convenience in expressing the quantities of biomass involved, the functional unit has been scaled up to 1 tonne of PET in bottle form, *i.e.* the functional unit is ~42,553 CSD PET bottles of 500 mL capacity, with each bottle weighing 23.5 g. The LCA did not include recycling or disposal, since the aim was to examine virgin PET production. A consideration of the recycling and disposal of PET is deferred until Chapter 7.

When considering the most effective use of biomass, the parameter of interest is quantity of biomass used per unit of saving. As discussed in Chapter 5, the different types of wet biomass have various energy contents, principally owing to their differing contents of moisture. Here, the base unit for comparison across all types of biomass is therefore the total energy content of the wet biomass used per unit of saving. The energy content of the biomass was assumed to scale with cost.

6.2.2 Value Chain

The processes involved in the production of PET bottles from conventional fossil-fuel sources are compared in Figure 6.1 with the following modifications:

(i) ethylene, only, made from biomass,

(ii) *p*-xylene, only, made from biomass,

(iii) biomass used only for process heating, and

(iv) biomass used solely to generate electricity for the overall process.

Items (i) and (ii) have been considered in Chapters 4 and 5, respectively. As shown in Figure 6.1, for (iii) and (iv), the background system for process heating or electricity has been modified from the conventional sourcing to using biomass instead. Two simple models have been assumed for the generation of process heat or electricity from biomass. Both models for the combustion of biomass for process heat or electricity are based on the same underlying assumptions. Biomass was assumed to combust to near completion; 99.7% of the moles of carbon in the biomass are converted to carbon dioxide. It is more difficult to assess the quantity of other emissions such as, SO_2 and NO_x. An average from typical biomass burners was assumed for these emissions per MJ of fuel input (Biomass Energy Centre, 2014). When comparing with other datasets, emission levels were of the same order of magnitude, but there was considerable variation, even among emissions predicted by the databases (Ecoinvent Centre, 2010; PE International, 2013). The assumptions used are summarised in Table 6.1.

Finally, process heat was assumed to be extracted from the burner at an efficiency, $\eta = \frac{\text{Heat Output}}{\text{Biomass Energy Input}} = 90\%$. Electricity was assumed to be generated from the biomass combustion at an efficiency of 35%, meaning that, $\eta = \frac{\text{Electricity Output}}{\text{Biomass Energy Input}} = 35\%$. The efficiency estimates were guided by those predicted by other databases (Ecoinvent Centre, 2010; PE International, 2013).

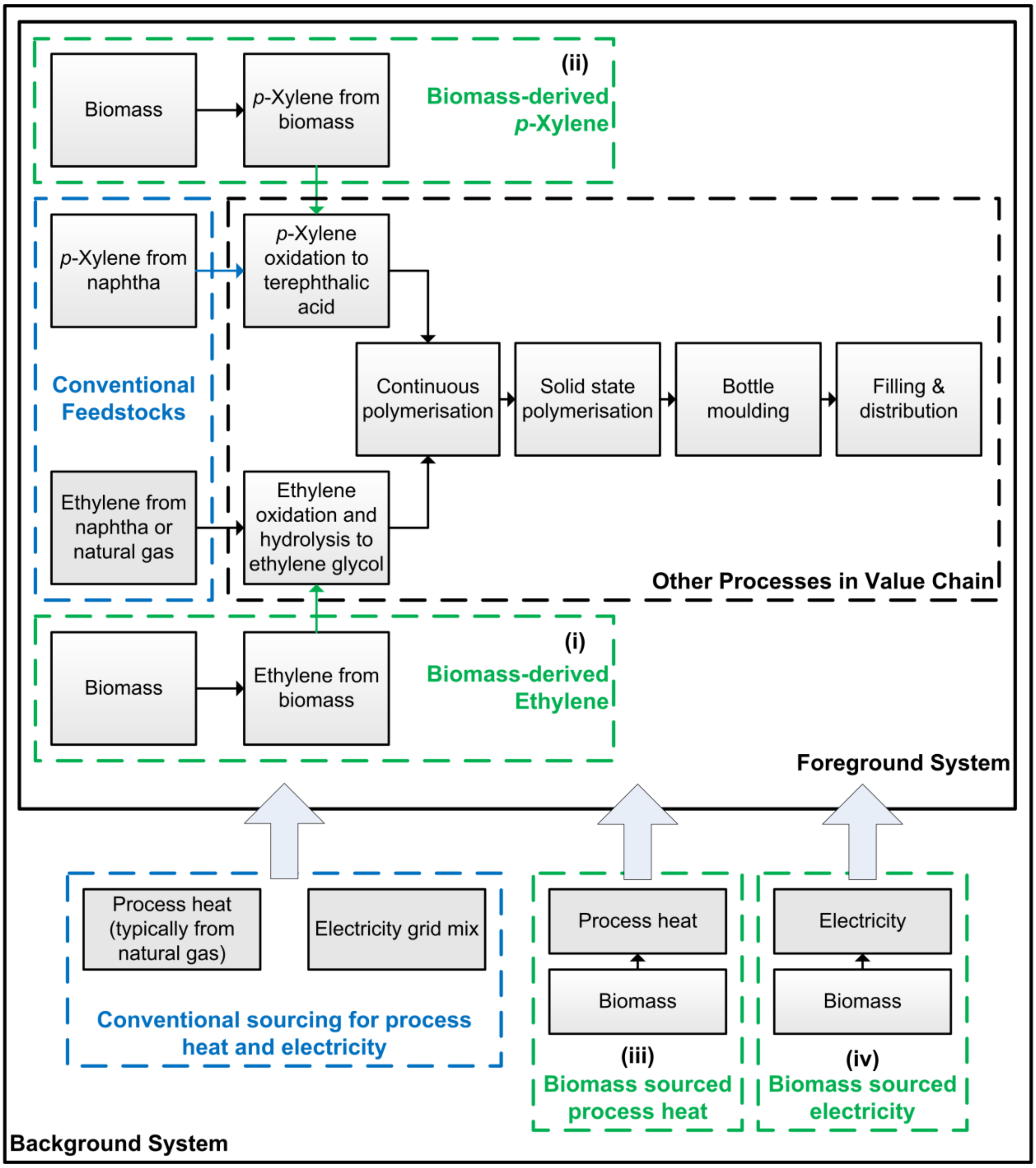


Figure 6.1. Overview of the various possible uses of biomass within the polyester value chain.

Table 6.1. Assumptions made for the combustion of biomass

Parameter	Value
Combustion, molar conversion to CO_2	99.7%
SO_2 emissions (mg/MJ fuel input)	20
NO_x emissions (mg/MJ fuel input)	150
Particulates (mg/MJ fuel input)	30
Process heat extraction efficiency	90%
Electricity generation efficiency	35%

The contents of energy and moisture for two types of biomass, sugarcane and willow, have been quantified in Chapter 5. These values are reproduced below in Table 6.2 for reference. Sugarcane juice and bagasse are considered separately. As described earlier in Section 6.2.1, for each use of biomass, the energy content of the biomass required is the basis of the comparison. As stated in Chapter 5, each kg of sugarcane produces 0.72 kg sugarcane juice and 0.28 kg bagasse, the total sugarcane energy content is therefore: (3.3×0.72)+(10.0×0.28)=5.2 MJ/kg of sugarcane.

Table 6.2. Summary of energy content for biomass sources

Parameter	Sugarcane juice	Sugarcane bagasse	Willow
Dry energy content (MJ/kg)	17 (sucrose)	19.3	19.9
Moisture content (wt%)	80	48	35
Energy content (MJ/kg)	3.3	10.0	12.9

Combined heat and power (CHP) has not been investigated, as such, in this analysis. In CHP, the high temperature heat is first used for electricity generation and the resulting lower temperature heat is used in the process for heating. The main benefits of CHP are therefore improved thermal efficiency. However, because the simplified models, described above, only used an efficiency parameter, rather than temperatures, they would not accurately reflect a CHP process.

6.2.3 Scenarios

For this comparison, all analyses were assumed to take place in the USA. For each type of biomass, sugarcane and willow, a cradle-to-gate LCA was performed quantifying the global warming potential and non-renewable energy requirements. The following cases were considered:

Feedstock 1: Sugarcane

- Scenario 1a, process heat would be supplied by the combustion of sugarcane bagasse. Sugarcane juice would not be burnt.
- Scenario 1b, electricity would be generated from the combustion of sugarcane bagasse. Again, sugarcane juice would not be burnt.
- Scenario 1c, production of ethylene from sugarcane bioethanol, *i.e.* analysis from Chapter 4, scenario 2b. Sugarcane juice would be used for ethanol production; sugarcane bagasse would be burnt for energy recovery.
- Scenario 1d, production of *p*-xylene from sugarcane; both sugarcane juice and bagasse would be used to produce reformate, *i.e.* analysis from Chapter 5.
- Scenario 1e, production of *p*-xylene from sugarcane juice only; sugarcane bagasse would be burnt for energy recovery resulting in an electricity credit, *i.e.* analysis from Chapter 5.

The first two sugarcane scenarios, process heat or electricity from sugarcane bagasse, require allocation, because the sugarcane juice cannot be burnt. Based on the analysis in Chapter 5, the allocation method selected was carbon allocation because it was most representative of the carbon content of the sugarcane bagasse.

Feedstock 2: Willow

- Scenario 2a, process heat would be supplied from the combustion of willow.
- Scenario 2b, electricity would be generated from the combustion of willow.
- Scenario 2c, production of ethylene from willow bioethanol.
- Scenario 2d, production of *p*-xylene from willow, *i.e.* analysis from Chapter 5.

The emissions involved with shipping raw materials and product for all scenarios were based on the analyses using US sugarcane and willow in Chapter 5.

To quantify the effectiveness of each scenario, the possible savings in global warming potential and non-renewable energy use were quantified relative to the base case. The *base case* was defined as PET production from conventional feedstocks and conventional fuel sources.

6.3 Results

6.3.1 Abatement Performance

Here, 'abatement' refers to the potential reduction of an environmental impact, *i.e.* Abatement = Base case impact – Scenario impact. The two environmental impacts considered in this Chapter are the abatement of global warming potential and the abatement of non-renewable energy resources. The biomass energy input is divided by the abatement in order to compare the performance for each scenario and type biomass. The abatement performance for each scenario is summarised Table 6.3. It should be noted that primary energy values are used here, allowing heat and electricity to be compared across the same basis.

Table 6.3. Performance of each scenario at abating non-renewable energy and global warming potential (lower values of MJ biomass input per unit abated are better).

Scenario	Non-renewable energy use		Global warming potential	
	Performance (MJ biomass input per MJ of non-renewable energy abated)	Absolute abatement (GJ non-renewable energy per tonne PET)	Performance (MJ biomass input per kg CO_2-eq abated)	Absolute abatement (tonne CO_2-eq abated per tonne PET)
Sugarcane				
1a, sugarcane bagasse process heat	0.84	17.8	15.5	0.97
1b, sugarcane bagasse electricity generation	1.06	21.5	17.7	1.29
1c, ethylene derived from sugarcane juice, sugarcane bagasse combustion for electricity generation	1.94	15.3	24.8	1.20
1d, *p*-xylene derived from both sugarcane juice and bagasse	4.78	14.2	52.3	1.30
1e, *p*-xylene derived from sugarcane juice only, sugarcane bagasse combustion for electricity generation	4.28	25.4	36.0	3.02
Willow				
2a, willow process heat	0.80	18.8	13.7	1.09
2b, willow electricity generation	0.99	23.0	15.3	1.49
2c, ethylene derived from willow	1.22	14.3	10.4	1.69
2d, *p*-xylene derived from willow	48.2	2.1	85.8	1.18

For comparison, the abatement performance metrics were plotted against one another in Figure 6.2. In Figure 6.2, scenarios in the bottom left of the chart have a lower biomass energy input requirement and scenarios in the top right require more biomass energy, *e.g.* the production of *p*-xylene from willow is costly relative to other options. Producing *p*-xylene from willow requires a considerable amount of energy in order to break down the cellulose and hemicellulose components. Scenarios 1d and 1e perform better than scenario 2d given that sugarcane juice does not require the intensive pre-processing. A more detailed comparison of scenarios in the bottom left of Figure 6.2 is given in Figure 6.3.

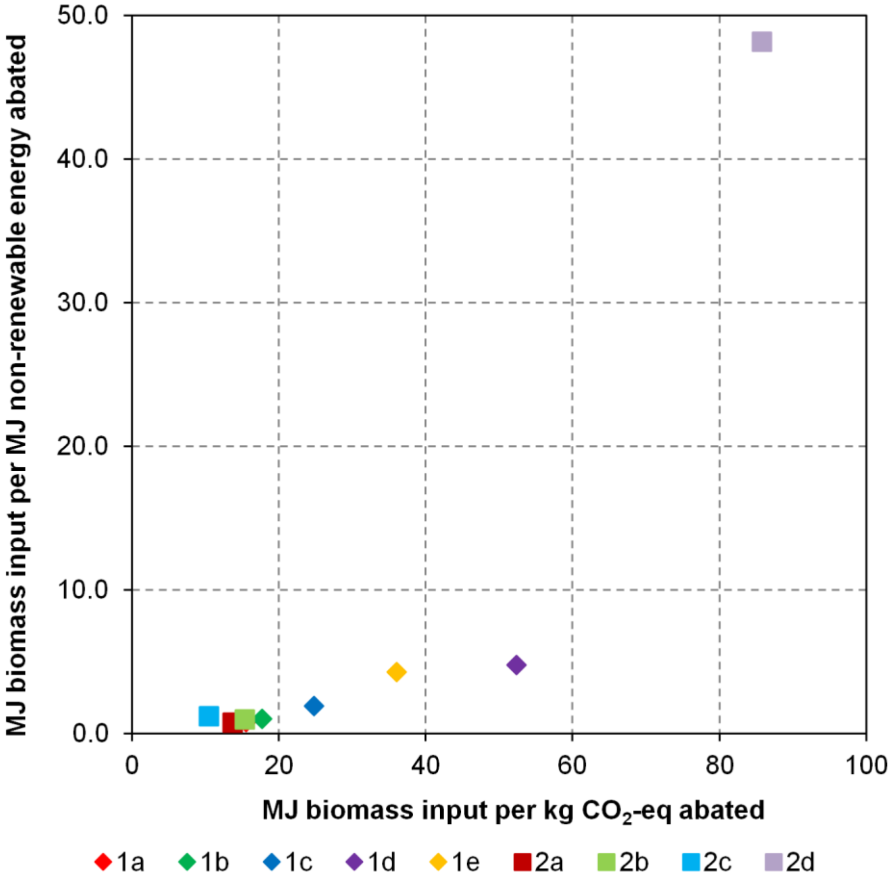


Figure 6.2. Performance of each scenario on the basis of biomass energy input.

From Figure 6.3, it is clear that the combustion of sugarcane bagasse and willow for process heat or electricity are the most favourable options with respect to reducing non-renewable energy use (scenarios 1a, 1b, 2a, and 2b). The production of ethylene from willow results in the best savings in global warming potential, but provides a lower reduction in the use of non-renewable energy.

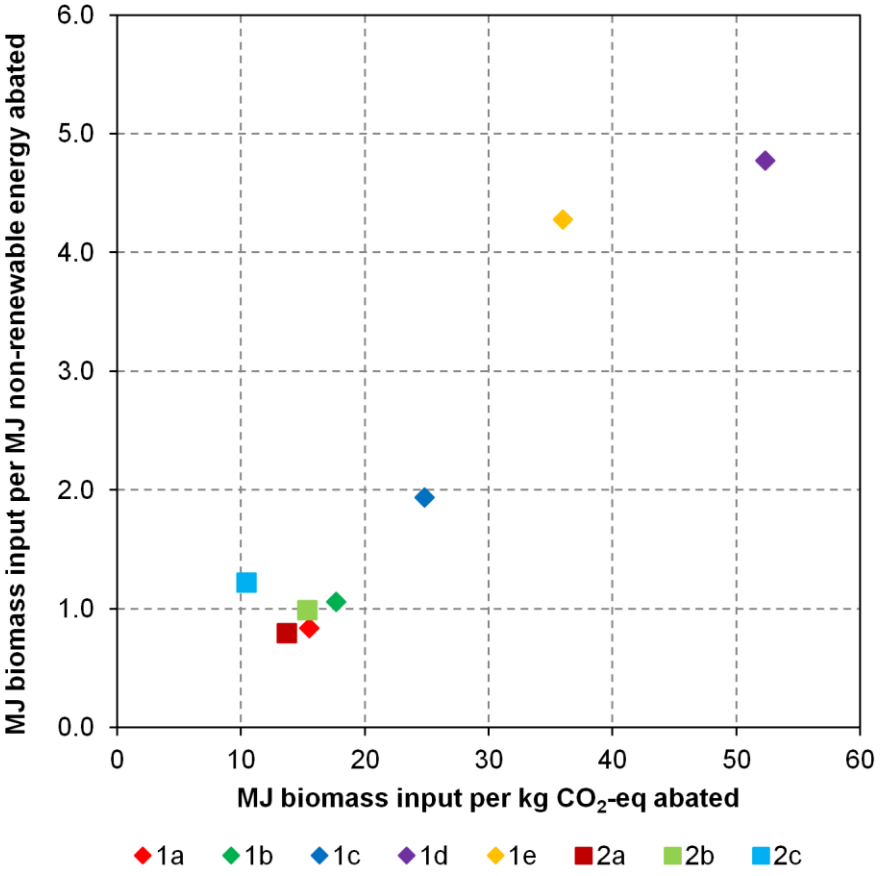


Figure 6.3. Performance of each scenario on the basis of biomass energy input. The scenario, 2d, which has the worst performance, has been removed, *i.e.* magnified version of cluster from Figure 6.2.

The best case, in order to reduce fossil fuel use most efficiently is the combustion of biomass for process heat, scenarios 1a and 2a. When considering non-renewable energy use, the total abatement for process heat or electricity from both biomass sources are larger than scenarios 1c and 2c, thereby having a larger capacity to reduce non-renewable energy use. Of course, one could also consider substituting biomass produced heat or electricity into other processes outside the foreground system, denoted in Figure 6.1, thereby increasing the capacity for abatement for these scenarios (1a, 1b, 2a, 2b) even further. As described earlier, scenario 2c performs better with respect to abating global warming potential, appearing as the best option in this respect.

6.4 Discussion

6.4.1 Interpretation

From the above results, it appears to be preferable to use biomass primarily as a source of process heating, followed by using it for process electricity, rather than for making the raw materials. This is largely because to convert the biomass, a significant amount of additional energy is required, as described in Chapters 4 and 5. In the case of biomass combustion, no additional processing is required, resulting in lower energy consumption. While there are still greenhouse gas and fossil fuel savings to be made by using biomass-derived chemical raw materials when compared with the conventional base case, biomass could be used most effectively throughout the value chain to provide process heating or electricity.

Of course, it should be noted that, in all cases, the abatement is dependent on the counterfactual. If, for example, the generation of heat or power from the conventional system had much lower greenhouse gas emissions and fossil fuel use, then the abatement values of using biomass would consequently be lower, and it would possibly be more favourable to use biomass as a feedstock source for the chemicals ethylene and *p*-xylene.

6.4.2 Sensitivity to Conversion Efficiency

In Section 6.2.2, the most significant assumption was thought to be the conversion efficiencies of the biomass combustion to heat or electricity. The sensitivity of the results to changes in the assumed efficiency was therefore investigated. Efficiency and process emissions are related, because a decrease in efficiency means that more biomass needs to be burnt to produce an equivalent quantity of heat or electricity. To test the sensitivity, the conversion efficiencies were both lowered by 5%. The effect on the abatement was measured and the sensitivity is shown in Table 6.4.

Table 6.4. Sensitivity of results to reduced conversion efficiency in biomass combustion processes.

Efficiency	Value	**Non-renewable energy** MJ biomass input per MJ of non-renewable energy abated (% change)	**Global warming potential** MJ biomass input per kg CO_2-eq abated (% change)
Sugarcane			
Thermal	85%	0.89 (+6%)	16.5 (+7%)
Electrical	30%	1.25 (+18%)	21.2 (+20%)
Willow			
Thermal	85%	0.84 (+6%)	14.5 (+6%)
Electrical	30%	1.16 (+17%)	17.9 (+17%)

From Table 6.4, it is clear that efficiency is a sensitive parameter. Lower efficiency requires more biomass, increasing cost, and results in larger emissions. However, even with a 5% reduction in efficiency, the overall results above remain unchanged, *i.e.* it is still more efficient to burn biomass than to produce biomass-derived chemicals in order to reduce greenhouse gas emissions and non-renewable energy use. Typical conversion efficiencies for biomass electricity generation are estimated between 30-40% (IEA Bioenergy, 2007).

6.4.3 Sourcing All Processes from Biomass

If chemical feedstocks, ethylene and *p*-xylene, and the process heat and electricity were to be fully sourced from sugarcane biomass the cradle-to-gate carbon footprint and non-renewable energy use for the production of a single 500 mL CSD PET bottle is shown in Figure 6.4. In this example, the sugarcane bagasse was burnt and the sugarcane juice was used in the process for ethylene and *p*-xylene. The conventional value chain is also included for comparison. As can be seen, some non-renewable energy is still required, for example, in the generation of hydrogen required for hydrodeoxygenation of the biomass sugars.

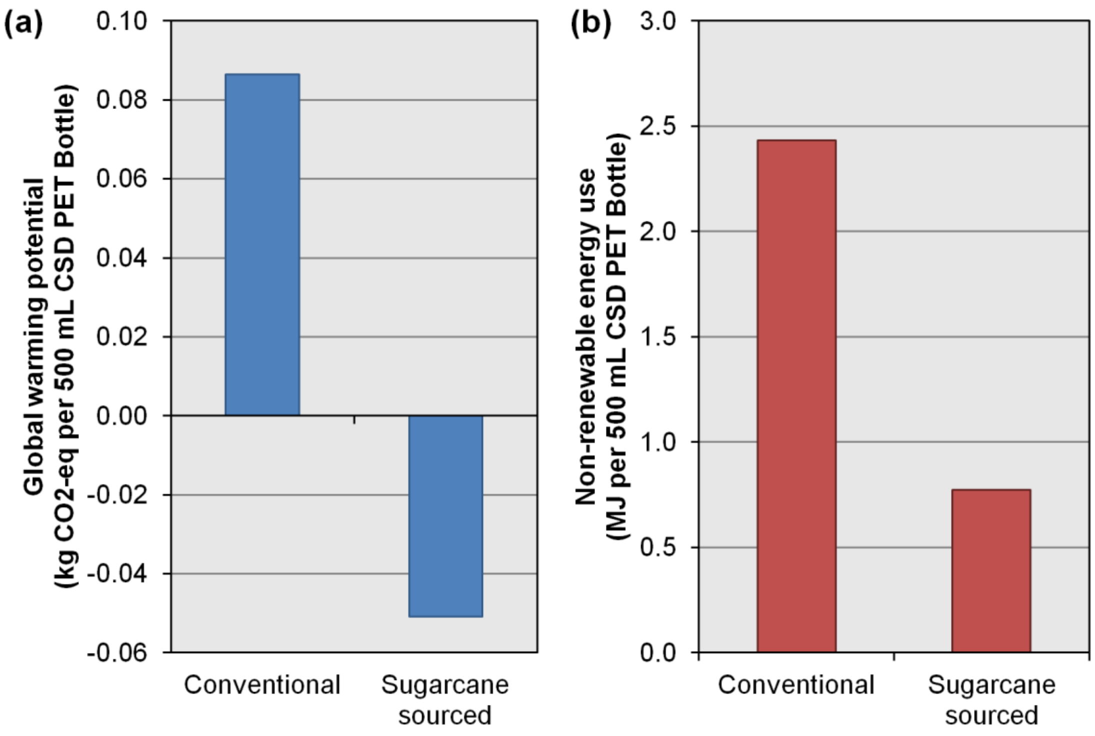


Figure 6.4. Global warming potential and non-renewable energy use for fully sourced

6.5 Conclusion

This Chapter has compared the potential uses of biomass within the polyester value chain, whether as a feedstock for chemicals (ethylene or *p*-xylene) production, or for generating process heat or electricity. The various uses were assessed in terms of the biomass energy input that would be required to reduce the global warming potential and non-renewable energy use. In conclusion, the best possible use of biomass within the value chain is by combustion for process heat. The next best use is for electricity generation. Only in one scenario, ethylene derived from willow, and for one measure, global warming potential, was producing a chemical from biomass better then combustion for process heating. A sensitivity analysis showed that the results were sensitive to conversion efficiency; however, with a 5% reduction of heat and electricity conversion efficiency, the overall conclusions remain unchanged.

Chapter 7 Recycling, Landfill and Incineration

This Chapter focuses on the end-of-life routes of polyester, which includes recycling, landfill and incineration. Open and closed loop recycling routes have been investigated, in addition to the international transport of polyester waste for recycling.

7.1 Introduction

So far, in this Dissertation, the environmental impacts associated with various processing routes to PET have been assessed without considering what happens to articles made from PET at the end of their life. There are three main routes when considering the end of life for PET: (i) recycling, (ii) landfill, and (iii) incineration.

The primary objective of this Chapter is to determine, for a variety of cases, the global warming potential arising from, and energy used in, recycling. It is important to note that this Dissertation investigates post consumer recycling to generate new products, *i.e.* the polymer has two consumer life cycles. This is different from industrial recycling because in industrial recycling, *e.g.* cut-offs, waste is recycled internally within the processes, thereby not generating a second product life for the consumer. The literature reviewed in Chapter 2 has discussed the advantages of recycling PET. As outlined in Chapter 1, there are two main options: closed loop recycling, *i.e.* bottles used to make new bottles, and open loop recycling, *i.e.* bottles used to make fibre. Regarding the actual processing of waste bottles, these can either be mechanically recycled to flake, or chemically processed to monomer. Chemical recycling allows greater control of the polymer quality, because the resulting monomer can be re-polymerised to the desired specifications (Shen *et al.*, 2010). For chemical recycling, three major routes exist: (i) hydrolysis, (ii) methanolysis, and (iii) glycolysis (Datye *et al.*, 1984; Lorenzetti *et al.*, 2006; Paszun and Spychaj, 1997). Hydrolysis of the polyester, either *via* acid, base or steam, is slow and energy-intensive and recovery of the monomer is difficult, requiring numerous purification stages (Bartolome *et al.*, 2012). Methanolysis yields dimethyl terephthalate, the feedstock used in older batch polymerisation technologies (Bartolome *et al.*, 2012). Dimethyl terephthalate has been replaced with terephthalic acid in the continuous polymerisation process (Bartolome *et al.*, 2012). Therefore, glycolysis is a preferred route, yielding the bis(2-hydroxyethyl) terephthalate monomer, which can be directly added to the continuous polymerisation process reducing the requirement for both terephthalic acid and ethylene glycol feedstock (Macdowell, 1961; Ostrowski, 1970). Chemical recycling using glycolysis is investigated in this Chapter along with mechanical recycling. Chapter 2 also identified that fibre recycling, other than re-use, is much more challenging, because the PET fibres are often blended with other textile fibres and the various additives, *e.g.* dyes and finishing chemicals are difficult to remove. Therefore, in this Chapter, consideration will be given only to PET bottles being recycled into new PET bottles and into new PET fibres.

When considering recycling from an LCA perspective, in order to account for the environmental impacts associated with the PET waste entering the recycling system, three techniques are commonly used (Shen *et al.*, 2010):

- System expansion. As shown in Figure 7.1, the LCA boundary includes the production of virgin PET, which is then recycled. This method is by far the most transparent and accurate approach given that the environmental impacts of producing virgin PET are included in addition to the impacts from recycling.

- Cut-off approach. The production of virgin PET, which is to be recycled, is not included within the LCA boundary, dashed line in Figure 7.1. For this approach the PET entering the recycling system is ‘seen’ as a waste product and therefore all environmental impacts associated with the virgin PET production are to be allocated to the virgin PET system and not the recycling system. This method effectively separates both virgin and recycling processes into individual systems. Results from this method are favourable to recycled PET, given that the feedstock, *i.e.* PET waste, has no associated environmental impacts.

- Waste valuation is a weighting method which allocates a fraction of the environmental impacts from manufacturing virgin PET to the PET waste entering the recycled system. The allocation factors are typically based on the economic value of virgin PET and the value of baled bottles, *i.e.* PET bottles collected and sorted for recycling. This method is not transparent, because, by using allocation factors, the causal relationships between processes are not accurately reflected.

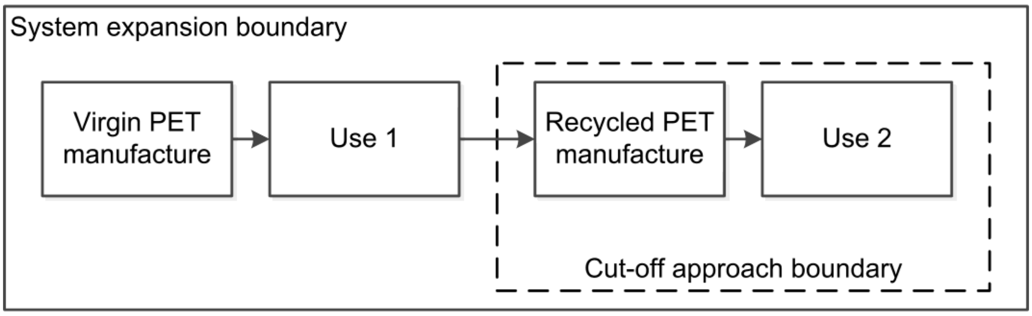


Figure 7.1. Comparison of the LCA boundaries for the system expansion and cut-off methods when considering recycling.

The method selected in this Chapter is the system expansion method because it most accurately reflects all the environmental impacts associated with a recycling system.

A secondary objective of this Chapter is to investigate the environmental impacts of other end of life routes, *viz.* landfill and incineration, for polyester.

7.2 Analysis

7.2.1 Goal and Scope

It is necessary to select different functional units depending on whether closed loop or open loop recycling is being considered. The recycling system boundaries and these functional units, using the method of system expansion, are described below.

Closed loop recycling:

Here, bottles are recycled to form new bottles. As shown in Figure 7.2, the functional unit for each system is 1000 CSD PET bottles, each of 500 mL capacity and weighing 23.5 g. The bottles can be produced either from new feedstock, the virgin system, or from a combination of virgin and recycled material. Losses are encountered in the recycling processes meaning that more virgin bottles must be produced. The recycling losses for both mechanical and chemical recycling are described later in Section 7.2.2.

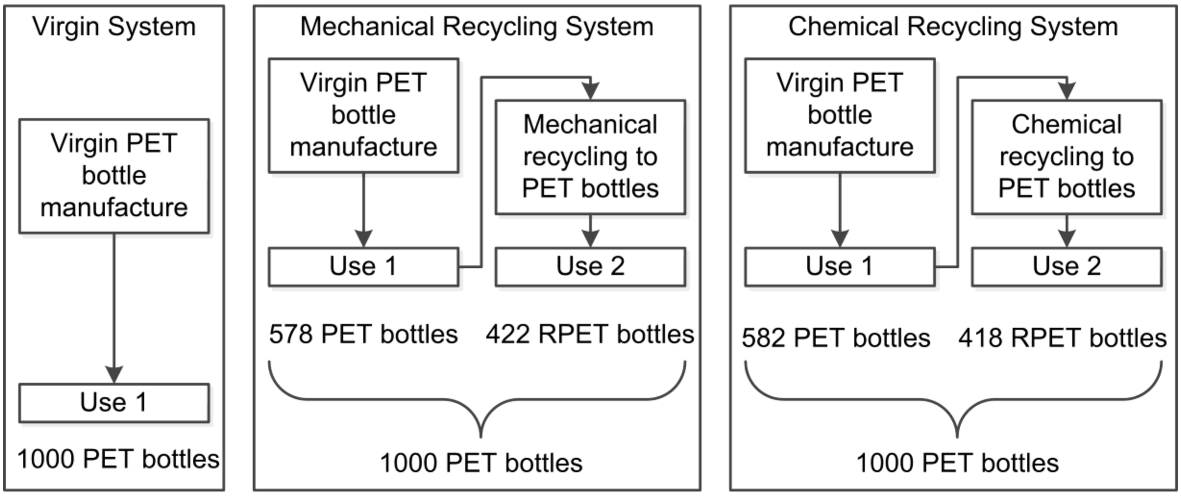


Figure 7.2. Closed loop recycling product systems and the equivalent virgin product system, each producing 1000 PET bottles.

Open loop recycling:

Here, bottles are recycled to form polyester fibres instead of bottles. The polyester fibre product selected was a 175 g polyester t-shirt. From the modelling described in Section 7.2.2, it was found that recycling 1000 CSD PET bottles to fibres could produce ~68 polyester t-shirts. Therefore, given that the comparison of each system is based on the same functional unit output, as shown in Figure 7.3, in addition to producing 1000 CSD PET bottles, each system also manufactures ~68 polyester t-shirts.

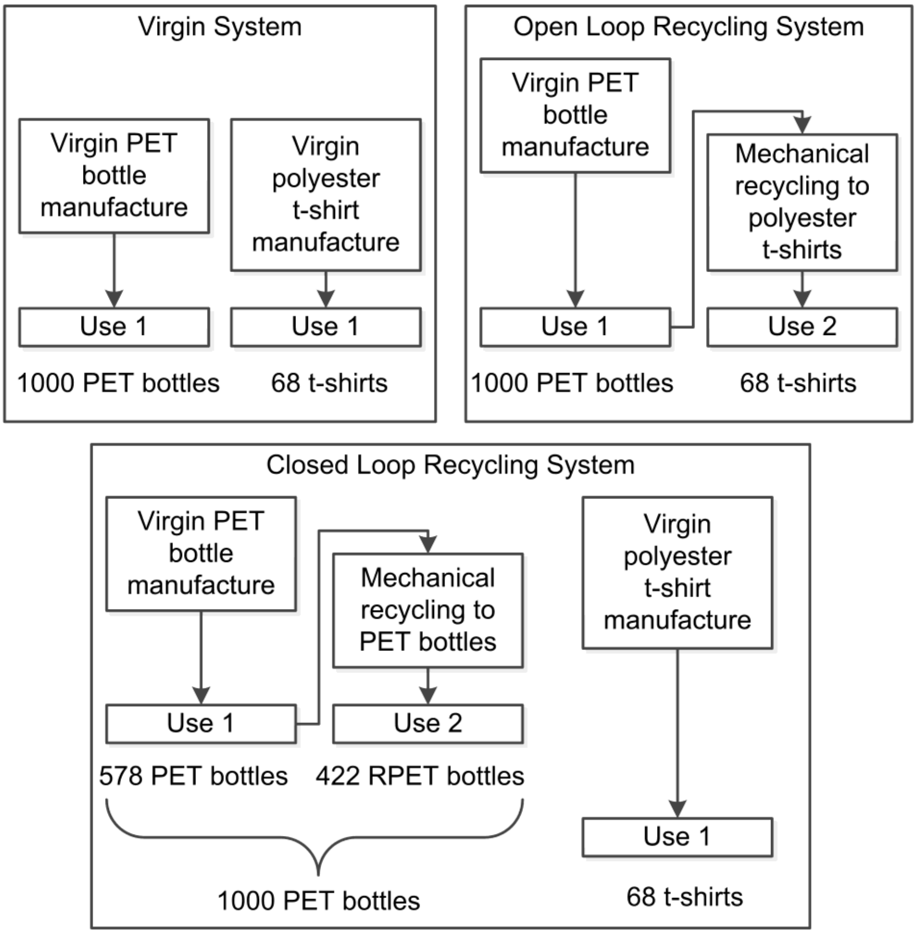


Figure 7.3. Virgin system, open loop system, and closed loop system each producing 1000 PET bottles and ~68 polyester t-shirts.

Whilst the environmental impacts associated with the use phase of a PET bottle are small, as described in Chapter 2, this is not the case for clothing, so that the use phase of fibres is the dominant contributor to the impacts (Collins and Aumônier, 2002; Smith and Barker, 1995). However, there are many different methods of washing and drying clothing, varying significantly by region around the world, and giving widely different environmental impacts. It is therefore difficult to capture an average in-use impact and so this Chapter focuses only on the processing aspects of polyester fibres.

7.2.2 Value Chain

The systems to be analysed have been depicted in Figures 7.2 and 7.3. The processes involved with each recycling mechanism are shown in Figure 7.4. All recycling chains require bottle collection, sorting & baling, as well as washing and mechanical crushing to PET flake.

- In closed loop, mechanical recycling, PET flake can be used in the bottle moulding process to create new bottles which can then be filled and distributed.

- In closed loop, chemical recycling, the PET flake is broken down to the monomer, bis(2-hydroxyethyl) terephthalate, in the glycolysis process. The monomer is then added to the continuous polymerisation process, followed by the solid state polymerisation, bottle moulding and finally, filling and distribution.

- In open loop recycling, the PET flake undergoes fibre processing which involves: preparation, spinning, weaving, dyeing, finishing and make-up into polyester t-shirts, which are then distributed.

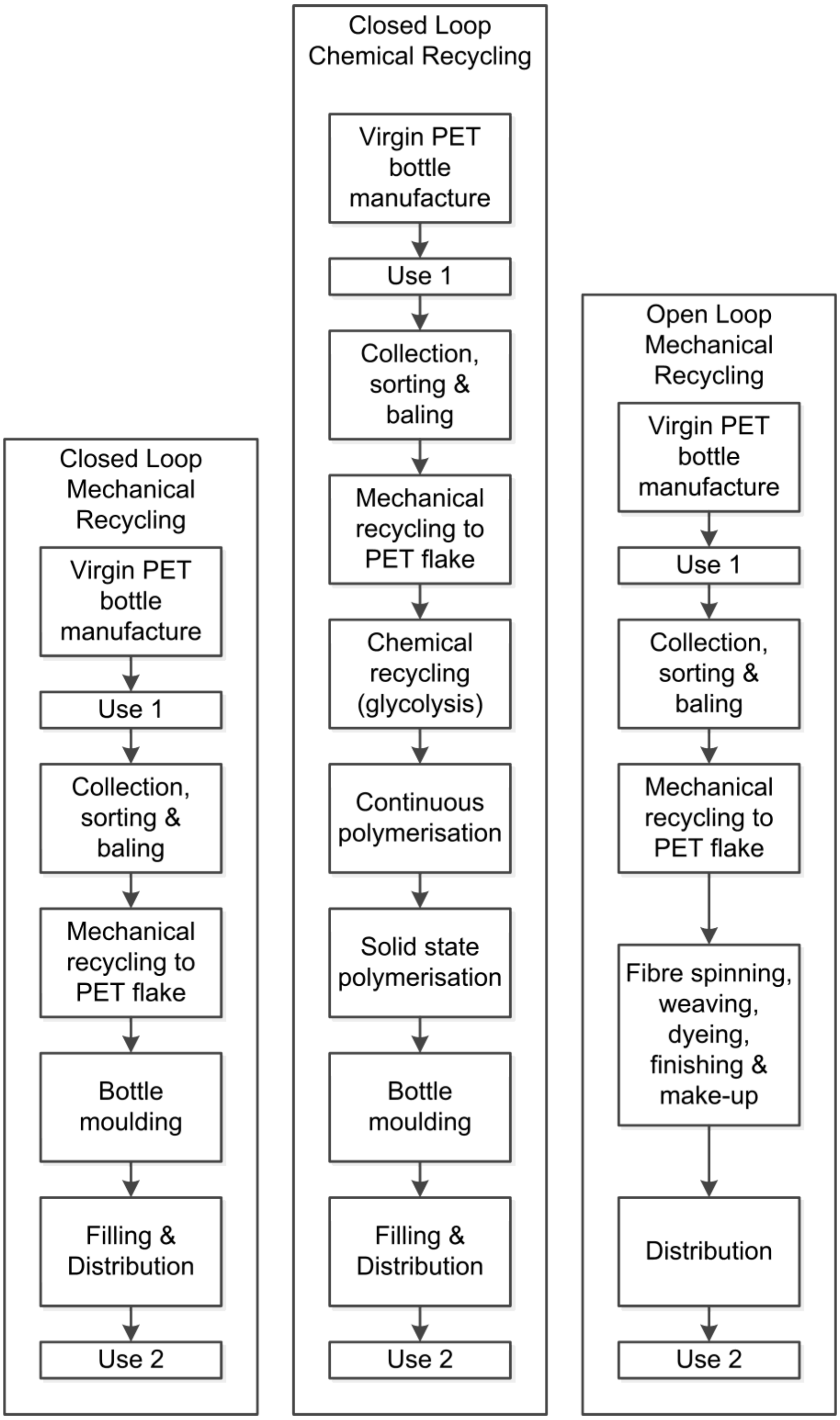


Figure 7.4. Recycling process chains for closed loop, mechanical and chemical, recycling to bottles and open loop mechanical recycling to t-shirts.

Franklin Associates (2011b) collected process information on sorting, baling and mechanical recycling and the resulting values were used for the inventory analysis. The inputs and outputs of each process are listed in Table 7.1 per tonne of PET waste entering the process. Material losses refer to the fraction of PET waste entering the system unsuitable for recycle, typically because the polymer may be of poor quality, contains impurities, or unwanted colours. Electricity is sourced from the local grid. Carbon emissions from the combustion of the fuels are estimated in Table 7.2.

Once PET waste has been collected, it must be separated from other materials and plastics. Most sorting operations take place at recovery facilities, where sorting operations range from manual sorting on a conveyor to highly automated systems using magnets, air classifiers, optical sorters, and a range of other technologies to separate the incoming waste (Franklin Associates, 2011b). PET bottles, once separated, are typically baled for transporting to mechanical recycling.

At mechanical recycling facilities, the bales of bottles are broken open and the material sorted to remove any further non-recyclable wastes. The sorted materials are then granulated to flake and washed, typically using a solution of sodium hydroxide (Franklin Associates, 2011b). The product from mechanical recycling is clean PET flake, which is transported to the next stage in the value chain. Although small quantities of surfactants, defoamer and wetting agents are added in the wash, there are no datasets available to account for the LCA impacts. However, these chemicals are added in very small quantities, relative to the caustic, and their effect on the environmental impacts was therefore assumed minimal.

Table 7.1. Inputs and outputs for sorting, baling, and mechanical recycling operations.

Process	Parameter	Value
Sorting and Baling		
	Material losses (to landfill)	8.7 wt%
	Electricity	59 MJ/tonne PET waste
	Natural gas	0.093 MJ/tonne PET waste
	Diesel fuel	81 MJ/tonne PET waste
	Propane	76 MJ/tonne PET waste
Mechanical recycling		
	Material losses (to landfill)	20 wt%
	Caustic (Pure NaOH)	19.0 kg/tonne PET waste
	Surfactant	0.61 kg/tonne PET waste
	Defoamer	1.78 kg/tonne PET waste
	Wetting agent	0.70 kg/tonne PET waste
	Water	316 kg/tonne PET waste
	Electricity	2.9 MJ/tonne PET waste
	Natural gas	5.5 MJ/tonne PET waste
	Liquefied petroleum gas (LPG)	0.012 MJ/tonne PET waste
	Propane	0.002 MJ/tonne PET waste

Table 7.2. Carbon emissions for combustion of fuels used in sorting, baling, and mechanical recycling.

Fuel	Carbon dioxide emissions (kg CO_2/MJ fuel)
Natural gas	0.050
Diesel fuel	0.069
Propane	0.060
Liquefied petroleum gas (LPG)	0.060

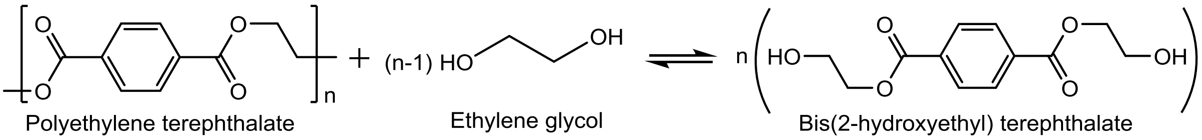
The non-renewable energy requirements and global warming potential predicted by the inventory from Franklin Associates (2011b) were compared with studies of mechanical recycling conducted by Shen *et al.* (2010) and Arena *et al.* (2003) in Table 7.3. The values presented in Table 7.3 are results for flake production, which includes the processes: sorting, baling, and mechanical recycling to flake. The results predicted by the inventory from Franklin Associates (2011b) are within the range of those reported in the literature.

Table 7.3. Comparison of non-renewable energy requirements and global warming potential predicted by model used from Table 7.1 with other published studies.

Parameter	**Model**	**Arena *et al.* (2003)**	**Shen *et al.* (2010)**
Non-renewable energy use (GJ/tonne PET flake)	7.5	8.3	2.5-6.0
Global warming potential (kg CO_2-eq/tonne PET flake)	587	635	310-720

A more detailed level of modelling was required for the chemical recycling by glycolysis. While Shen *et al.* (2010) performed an analysis of several chemical recycling routes, including glycolysis, details of the actual process inputs and outputs were not quoted. For the present analysis, two key operations were modelled for chemical recycling by glycolysis, depolymerisation and filtration.

As shown for continuous polymerisation in Appendix A, the depolymerisation reaction is the forward step of (Carta *et al.*, 2003):



In depolymerisation, ethylene glycol is added, in excess by 12.5% of the stoichiometric requirement (Ostrowski, 1970), at ~0.36 kg ethylene glycol per kg PET flake in a stirred tank reactor. PET dissolves in boiling ethylene glycol at atmospheric conditions (Ostrowski, 1970). Reactor temperatures are usually between 180-250°C, and in this model, a temperature of 197°C was used (Ostrowski, 1970), *i.e.* the boiling point of ethylene glycol at atmospheric pressure. At this temperature, the most commonly used catalyst, zinc acetate, added at 0.01 kg zinc acetate/kg PET flake, was shown to give a yield of 85.6 wt% of bis(2-hydroxyethyl) terephthalate (Bartolome *et al.*, 2012). A small quantity of water, 0.02 kg water per kg PET flake, is also added, to reduce the formation of glycol ether (Datye *et al.*, 1984). The depolymerisation reaction is exothermic and no additional heat is required for the reactor. The specific heat required to bring the reactants to a temperature of 197°C can be supplied by the reaction enthalpy. At this temperature, the ethylene glycol boils off from the reaction mixture and is condensed and recycled. The stirring power was quantified using the same method as used for the esterification reactor modelled in Appendix A.

The next stage is filtration, which separates unconverted PET flake and oligomers from the monomer, bis(2-hydroxyethyl) terephthalate. PET flake and oligomers are recycled back into the depolymerisation reactor. A filtration differential pressure of 5 bar was assumed. A simple pump calculation, $\frac{\Delta \text{Pressure} \times \text{Volumetric Flowrate}}{\text{Pump Efficiency}}$, was performed on the reactor outlet to estimate the electricity requirement for this operation. The filtrate contains the monomer and a small quantity of ethylene glycol. Ethylene glycol was removed by vacuum distillation and recycled back to the reactor. It was assumed that the bis(2-hydroxyethyl) terephthalate from the glycolysis plant could be added directly to the continuous polymerisation process for repolymerisation (Macdowell, 1961; Ostrowski, 1970). For this to occur, the glycolysis plant would be located close to the continuous polymerisation plant so that further operations, *e.g.* crystallisation of bis(2-hydroxyethyl) terephthalate for transportation, would not be required.

For the bis(2-hydroxyethyl) terephthalate produced by glycolysis, an ethylene glycol and terephthalic acid credit was applied, as shown in Figure 7.5. For every mole of bis(2-hydroxyethyl) terephthalate, a feedstock credit of one mole of terephthalic acid and two mole of ethylene glycol was applied. The primary saving made by recycling *via* glycolysis is that the requirement for virgin terephthalic acid in continuous polymerisation is reduced. Hence, as shown in Figure 7.5, by expanding the boundary and adding virgin PET polymer production the feedstock saving is included. With the addition of bis(2-hydroxyethyl) terephthalate, it is unclear whether the inclusion of this recycled feedstock would result in significant savings in the energy requirements of the continuous polymerisation process. The continuous polymerisation process was therefore assumed to remain unchanged other than having a reduced terephthalic acid and ethylene glycol feedstock requirement. This approach was considered reasonable because in Chapter 4 the continuous polymerisation processing only made a small contribution to the environmental impacts for virgin polymer.

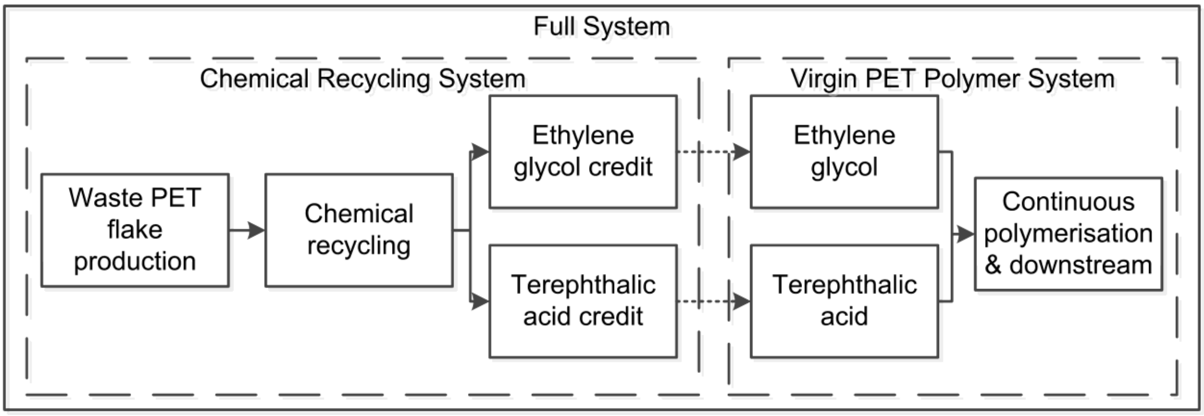


Figure 7.5. Flow diagram for the feedstock credit applied to bis(2-hydroxyethyl) terephthalate generated from chemical recycle by glycolysis.

Finally, fibre production has not yet been considered in this Dissertation. The main operations required to produce a polyester t-shirt are (Collins and Aumônier, 2002; Smith and Barker, 1995):

- The production of polyester fibres, typically by melt spinning, *i.e.* the polymer is melted for extrusion.

- Weaving to produce fabrics.

- Dyeing and finishing the fabric, which once dyed, is sent through a chemical wash.

- Cutting and make-up: the final creation of the clothing item. The most significant polyester losses are incurred here.

The energy requirements and material losses for each operation are summarised in Table 7.4. The values were selected from Collins and Aumonier’s (2002) study for polyester, considering the energy requirements based on British textile technology standards. The fibre analysis is limited to energy use and greenhouse gas emissions because details of the dyes and chemicals used were not available within Gabi and Ecoinvent databases. In order to estimate, to some degree, the energy use and global warming potential for dyes and chemicals, the same assumption made by Collins and Aumonier (2002) was used, whereby, 350 kg of chemicals per tonne of fabric, equally split between organic and inorganic chemicals, were used. The Ecoinvent database has generic datasets for both organic and inorganic chemical manufacture. The energy requirements for fibre manufacture were found to be 15% higher than those determined by Smith and Barker (1995).

Table 7.4. Energy requirements and material losses for each stage of polyester fibre production

Operation	Energy requirements (MJ/kg polyester input)	Average material losses from polyester input (wt%)
Preparation	6.0 (100% electricity)	6
Spinning	18.7 (100% electricity)	4
Weaving	10.6 (100% electricity)	5.5
Dyeing and finishing	11.4 (10% electricity, 90% heat)	6.5
Cutting and makeup	2.0 (100% electricity)	12.5

Regarding the final end of life analysis for PET, two options were considered, landfill and incineration. For both operations, existing Gabi datasets were used to represent the environmental impacts. For the incineration dataset, which generates both heat and electricity, a credit for both useful outputs was taken into account.

7.2.3 Scenarios

Scenarios are analysed for PET production in the USA, UK and China. As described earlier, closed loop recycling systems were defined using the system expansion method shown in Figure 7.2 In the USA and UK, the proportion of open loop recycling is small; however, in China, bottle to fibre recycling is common (PCI Xylenes & Polyesters, 2013). With reference to Figure 7.3, open loop recycling can be compared to closed loop recycling. Finally, landfill or incineration were assessed for the USA. The details of each scenario assessed in this Chapter are discussed below:

Case 1, Production of PET in the USA:

Each system for the USA produces 1000 PET bottles.

- Scenario 1a, virgin PET bottles
    - *p*-Xylene would be transported by ship for 1000 km from its point of manufacture in Texas to a plant in Alabama for terephthalic acid production
    - Terephthalic acid would be transported 650 km from Alabama to PET plants in South Carolina
    - Ethylene glycol would be produced in Texas and transported 1500 km by ship to the PET plants
    - Continuous and solid state polymerisation plants were assumed to be contiguous. PET pellets would be transported on average 1000 km by road to various bottle moulding and filling facilities, and a further 750 km by road to distribution centres for supermarkets.
- Scenario 1b, closed loop mechanical recycling
    - Virgin PET bottles would be produced as described in scenario 1a.
    - PET waste bottles would be collected and transported an average of 50 km by truck to sorting stations
    - Baled bottles from the sorting stations would then be transported 600 km by rail to a mechanical recycling facility.
    - PET flake would be transported a further 1000 km by truck to bottle moulding facilities. Finally, recycled bottles would be transported 750 km by road to distribution centres.
- Scenario 1c, closed loop chemical recycling
    - Virgin PET bottles would be produced as described in scenario 1a.

    - PET waste bottles would be collected and transported an average of 50 km by truck to sorting stations
    - Baled bottles from the sorting stations would then be transported 600 km by rail to a mechanical recycling facility.
    - PET flake would be transported a further 1000 km by truck to chemical recycling facilities.
    - Bis(2-hydroxyethyl) terephthalate, the monomer produced from chemical recycling, would be directly added to continuous polymerisation, *i.e.* the plants were assumed adjacent. Finally, PET pellets would be transported on average 1000 km by truck to various bottle moulding and filling facilities, and a further 750 km by road to distribution centres for supermarkets.

Case 2, Production of PET in the UK:

Each system for the UK produces 1000 PET bottles.

- Scenario 2a, virgin PET bottles
    - It was assumed that ethylene glycol would be manufactured from fossil fuel in The Netherlands and transported 600 km by ship to the UK polymerisation plant.
    - The terephthalic acid, continuous polymerisation and solid state polymerisation were assumed to be located together in northern England. PET pellets would be transported on average 300 km by truck to various bottle moulding and filling facilities, and a further 150 km by road to distribution centres for supermarkets.
- Scenario 2b, closed loop mechanical recycling
    - Virgin PET bottles would be produced as described in scenario 2a.
    - PET waste bottles would be collected and transported an average of 50 km by truck to sorting stations

    - Baled bottles from the sorting stations would then be transported 400 km by rail to a mechanical recycling facility.
    - PET flake would be transported a further 300 km by truck to bottle moulding facilities. Finally, recycled bottles would be transported 150 km by road to distribution centres.

Case 3, Production of PET in China:

Scenarios 3a and 3b have the functional unit of 1000 PET bottles

- Scenario 3a, virgin PET bottles
    - One half of the *p*-xylene requirements would be imported 10000 km by ship from the Middle East, the other half produced locally in China.
    - Ethylene glycol would be transported 500 km by rail to the PET plants.
    - The terephthalic acid, continuous polymerisation and solid state polymerisation were assumed to be grouped in an industrial cluster, *i.e.* no transport of intermediate products would be required. PET pellets would be transported on average 1000 km by truck to various bottle moulding and filling facilities, and a further 500 km by road to distribution centres for supermarkets.
- Scenario 3b, closed loop mechanical recycling
    - Virgin PET bottles would be produced as described in scenario 3a.
    - PET waste bottles would be collected and transported an average of 50 km by road to sorting stations
    - Baled bottles from the sorting stations would then be transported 400 km by rail to a mechanical recycling facility.
    - PET flake would be transported a further 1000 km by road to bottle moulding facilities. Finally, recycled bottles would be transported 500 km by road to distribution centres.

Scenarios 3c, 3d, and 3e have the functional unit of 1000 PET bottles and 68 polyester t-shirts, see Figure 7.3.

- Scenario 3c, virgin PET bottles and virgin polyester t-shirts
    - Virgin PET bottles would be produced as described in scenario 3a.
    - Virgin PET for polyester t-shirts would also be produced as described in scenario 3a, with the exception that the solid state polymerisation step and bottle moulding are not required. Instead, PET from the continuous polymerisation process would be transported 1000 km by truck to fibre manufacture. Finally, polyester t-shirts would be distributed an average of 500 km by road.
- Scenario 3d, closed loop mechanical recycling and virgin polyester t-shirts
    - Virgin PET bottles and closed loop recycling would be produced as described in scenario 3b. Virgin polyester t-shirts added to this system would be produced as described in scenario 3c.
- Scenario 3e, open loop mechanical recycling
    - Virgin PET bottles would be produced as described in scenario 3a.
    - PET waste bottles would be collected and transported an average of 50 km by road to sorting stations
    - Baled bottles from the sorting stations would then be transported 400 km by rail to a mechanical recycling facility.
    - PET flake would be transported a further 1000 km by truck to fibre manufacturing facilities. Finally, recycled polyester t-shirts would be transported 500 km by road.

Case 4, End of life scenarios in the USA:

Collection of PET waste ~50 km by road and landfill or incineration.

- Scenario 4a, after collection, all PET waste would be sent to landfill.

- Scenario 4b, PET waste sent to incineration, an electricity credit would be applied to the energy released from incineration.

- Scenario 4c, PET waste would first be recycled using closed loop mechanical recycling, *i.e.* scenario 1b, the recycled bottles would be sent to landfill.

- Scenario 4d, PET bottles would be recycled using closed loop mechanical recycling, *i.e.* scenario 1b, the recycled bottles would then be incinerated with an electricity credit applied.

7.2.4 Use of Datasets

For case 3, the analysis in China, a dataset for the generation of electricity did not exist within available databases. The sources of primary energy assumed for the production of electricity in China is shown in Table 7.5 (EIA, 2014).

Table 7.5. Energy mix for the production of electricity in China.

Source	Contribution (%)
Coal	66
Hydropower	22
Nuclear	1
Wind	5
Solar	0.2
Biomass and waste	1
Oil	2
Natural Gas	3

Compared with electrical power generation in the USA and UK (PE International, 2013), Chinese power has a larger carbon footprint owing to the larger contribution from coal to the energy mix, as shown in Figure 7.6.

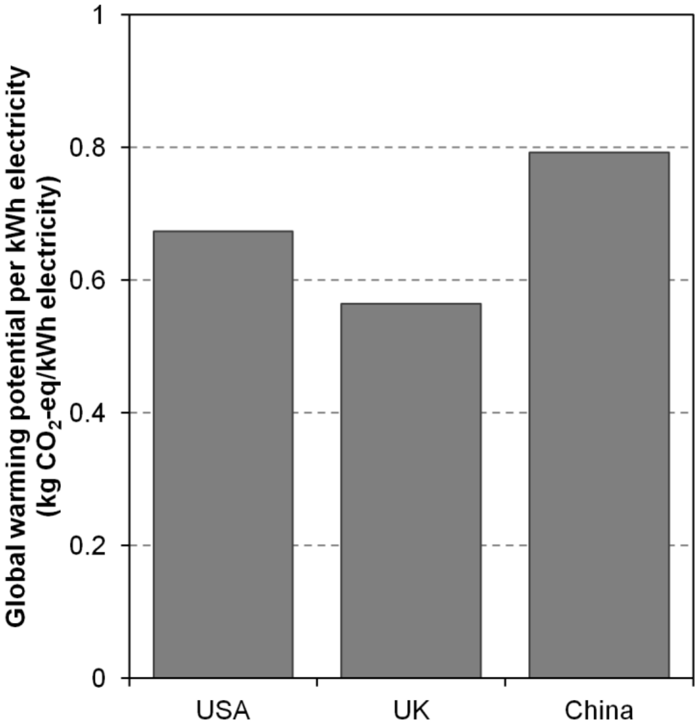


Figure 7.6. Global warming potential for electricity generation in the USA, UK and China (PE International, 2013).

7.3 Results

7.3.1 Closed Loop Recycling

The global warming potential and energy use for Scenarios 1a, 1b, 1c, 2a, 2b, 3a and 3b are shown in Figures 7.7 and 7.8 respectively. Considering Figure 7.7, closed loop mechanical recycling of PET bottles in the USA, scenario 1b, can result in a 22% reduction of the global warming potential relative to producing virgin PET bottles, scenario 1a. Similar savings are possible for closed loop mechanical recycling in the UK and China. Closed loop chemical recycling in the USA, scenario 1c, has the potential to reduce global warming potential by 17% relative to scenario 1a.

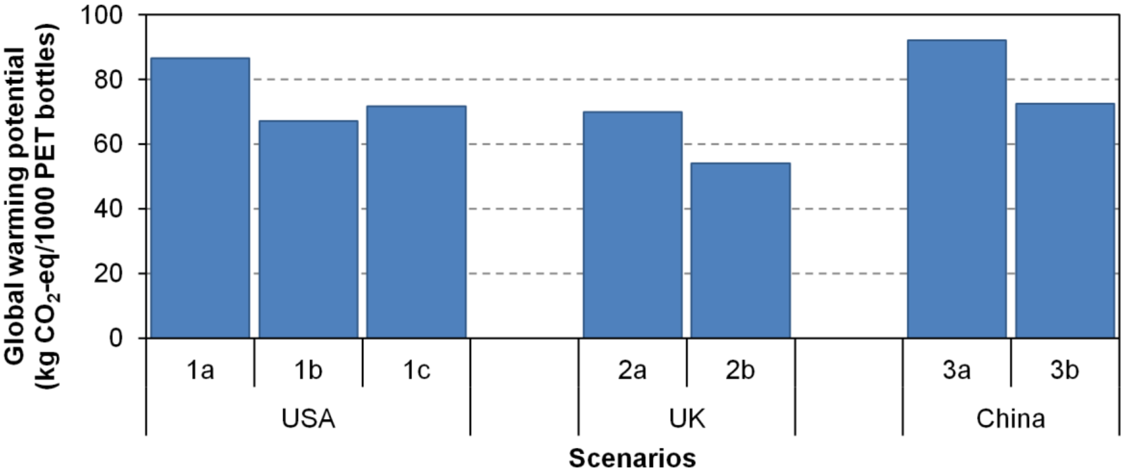


Figure 7.7. Global warming potential for closed loop recycling compared with virgin PET bottle production, scenarios 1a, 1b, 1c, 2a, 2b, 3a and 3b. Scenarios: 1a, 2a, and 3a are virgin polymer only; 1b, 2b, and 3b are mechanical closed loop recycling; 1c is chemical closed loop recycling.

Considering the energy requirements, shown in Figure 7.8 for all scenarios, the use of renewable energy is minimal, less than 2% for the USA and UK; it is slightly higher in China, ~4%, because of the larger proportion of hydroelectricity. For all three countries, closed loop mechanical recycling can reduce the total energy use by 31%. Closed loop chemical recycling, scenario 1c *cf.* scenario 1a, can reduce the total energy use by 27%.

The savings possible in global warming potential and energy use when using chemical recycling are smaller than the potential savings from mechanical recycling. This is because of the additional processing stages required for chemical recycling, which would not have been required for mechanical recycling.

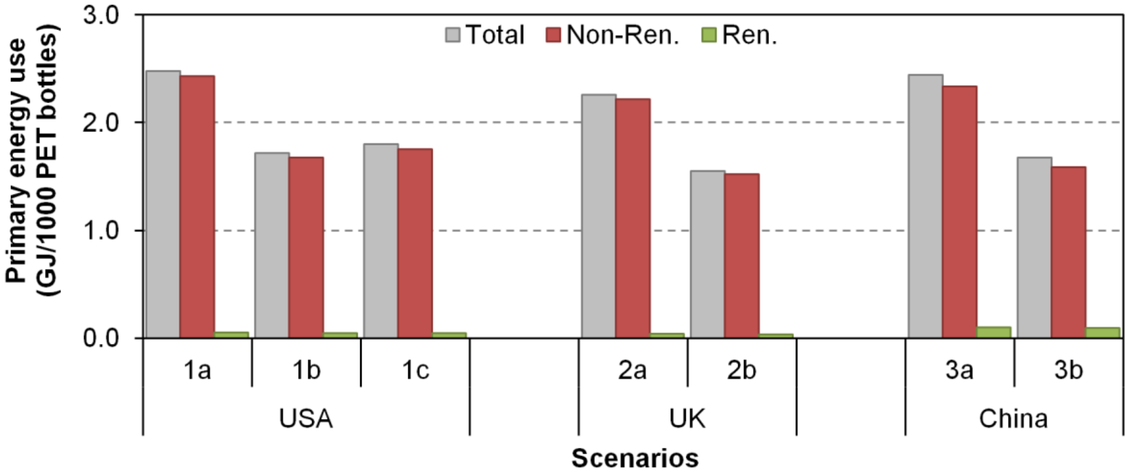


Figure 7.8. Energy use for closed loop recycling compared with virgin PET bottle production, scenarios 1a, 1b, 1c, 2a, 2b, 3a and 3b. Scenarios: 1a, 2a, and 3a are virgin polymer only; 1b, 2b, and 3b are mechanical closed loop recycling; 1c is chemical closed loop recycling.

A further analysis of total energy requirements is shown in Figure 7.9 for scenario 1b. Of the total 1.72 GJ energy used for 1000 bottles, the 578 virgin PET bottles required ~84% of the total energy; recycling and producing a further 422 PET bottles required the ~16% of the total energy. Clearly, the largest energy requirement is associated with the virgin polymer production because this includes the energy content of the feedstocks required to manufacture the polymer, in addition to the energy required for polymerisation and bottle moulding. The energy requirement for the transport of recycled PET is small. Finally, the actual recycling operations account for ~5% of the total energy use, whereas the bottle moulding of recycled bottles requires 10% of the total energy.

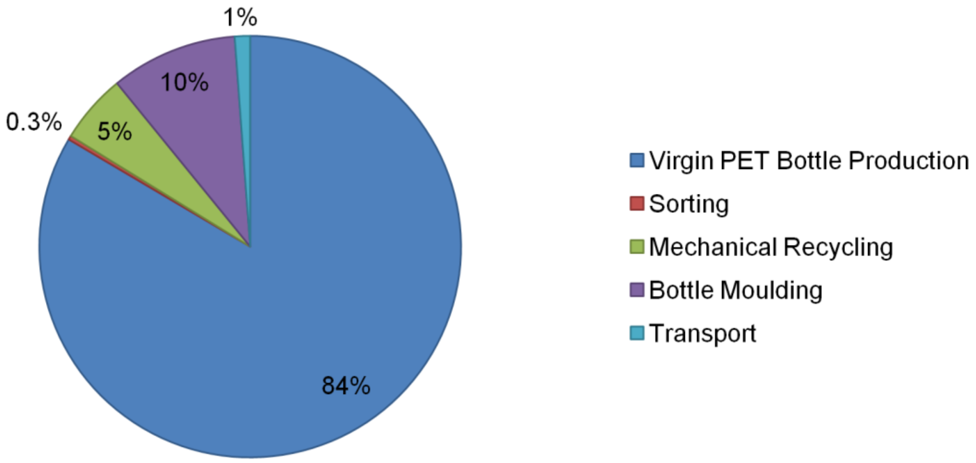


Figure 7.9. Distribution of energy requirements for scenario 1b

7.3.2 International Recycling: Trading Baled Bottles

The closed loop recycling systems assessed in Section 7.3.1 have shown the potential for reduced carbon footprint and energy use. However, as shown in Table 7.6, a proportion of baled bottles is either imported or exported; China is the largest importer of baled PET bottles globally (PCI Xylenes & Polyesters, 2013).

Table 7.6. Imports and exports of baled bottles, in Mt, in USA, West EU and China.

Source	USA	West EU	China
Locally collected and recycled	0.52	1.35	2.49
Imported and locally recycled	0.21	0.09	1.88
Locally collected and exported	0.26	0.16	0

Both the USA and Western EU are exporting baled bottles to China (PCI Xylenes & Polyesters, 2013). The closed loop scenarios 1b and 2b were modified to represent the export of baled PET bottles to China, in order to investigate how transporting the PET waste from the USA and the UK to China, compared with recycling locally-produced bottles in China. The assumptions were:

- Baled bottles from the USA are transported an average distance of 16000 km to China by ship.
- Baled bottles from the UK are transported 20000 km to China by ship.

In Figure 7.10, a comparison of recycling in China, using local PET bottles from China, or imported PET bales from the USA or the UK, is shown for global warming potential. It is interesting to note that the global warming potential for recycling imported PET bales from the USA or the UK is in fact lower than locally recycling PET bottles produced in China. This is because the global warming potential of producing virgin PET in China is greater than producing virgin PET in the USA or the UK, as shown in Figure 7.7.

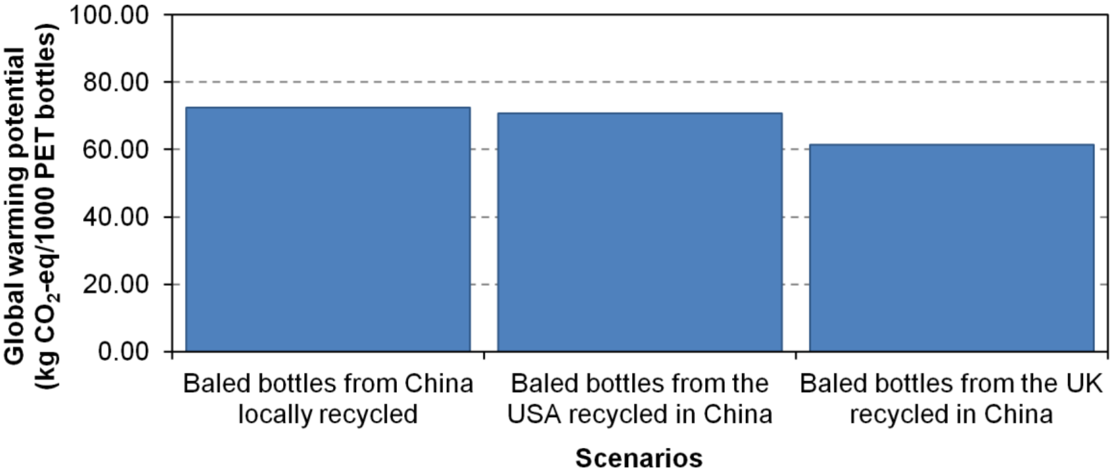


Figure 7.10. Comparison of recycling in China, using local PET bottles from China, or imported PET bales from the USA or the UK.

7.3.3 Multi-Stage Recycling

An interesting analysis can be performed on PET recycling, if hypothetically, the same polymer was recycled several times over. The system boundaries for repeated recycling using the method of system expansion are shown in Figure 7.11. The virgin system is scenario 1a and one cycle of recycling is scenario 1b. For the twice recycled system, initially 442 virgin PET bottles are made, and after recycling these bottles once, an additional 323 bottles can be formed. Finally, recycling those 323 bottles for a second time, a further 236 bottles can be made. At each stage of recycling, there are losses of PET, which means that fewer bottles can be made from the recycled material each time.

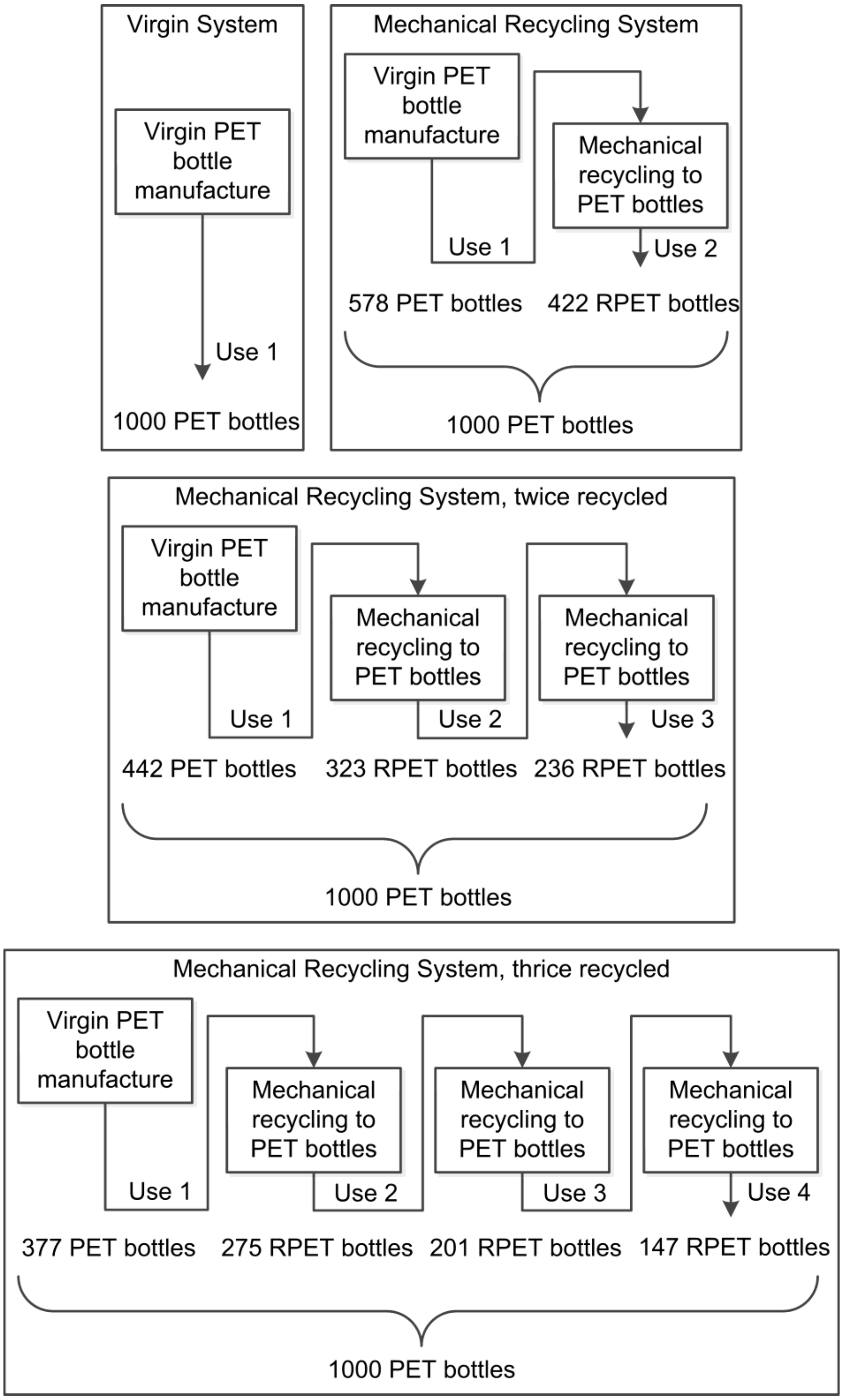


Figure 7.11. System expansion for subsequent recycling cycles of PET bottles.

Each additional cycle in Figure 7.11 produces progressively fewer bottles owing to losses experienced in the sorting and mechanical recycling processes; however, with each additional cycle, fewer initial virgin bottles are required in order for each system to produce 1000 PET bottles in total. Table 7.7 shows the bottles produced from each cycle when recycling the same PET four and five times.

Table 7.7. Bottles produced for recycling PET into bottles four and five times

Cycle	Four cycles	Five cycles
Virgin	340	318
First	249	232
Second	182	170
Third	133	124
Fourth	97	90
Fifth	N/A	66

The global warming potential for each system specified above was quantified and is shown in Figure 7.12. As can be seen, the marginal savings from each additional cycle is reduced, meaning that additional recycling cycles result in diminishing returns. The carbon dioxide emissions associated with virgin PET production decreases with each additional cycle given that more polymer is recycled. Consequently, the carbon emissions associated with recycling are shown to increase. Energy use was found to follow the same pattern.

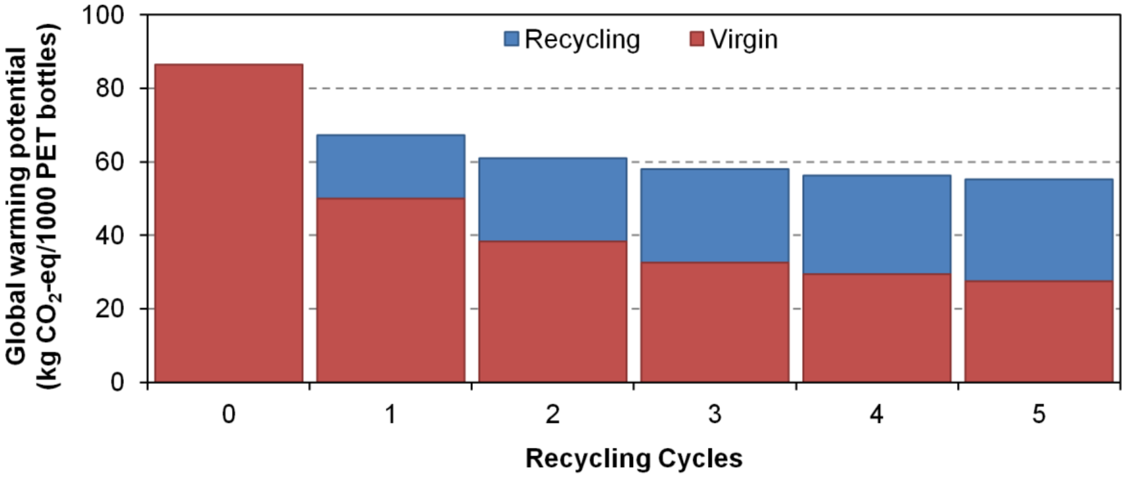


Figure 7.12. Global warming potential with increased number of recycling cycles

In reality, there is a limit to the number of cycles due to polymer degradation and cross-linking. The models used in this analysis do not account for this.

7.3.4 Open Loop Recycling

As explained previously, open loop recycling is prevalent in China. In Figure 7.13, the global warming potential for open loop bottle to fibre mechanical recycling, scenario 3e, is compared to equivalent virgin (scenario 3c) and closed loop recycling (scenario 3d) systems, each producing 1000 PET bottles and 68 polyester t-shirts. It is an interesting result that open loop recycling can reduce the global warming potential more than closed loop recycling when compared with virgin polymer production.

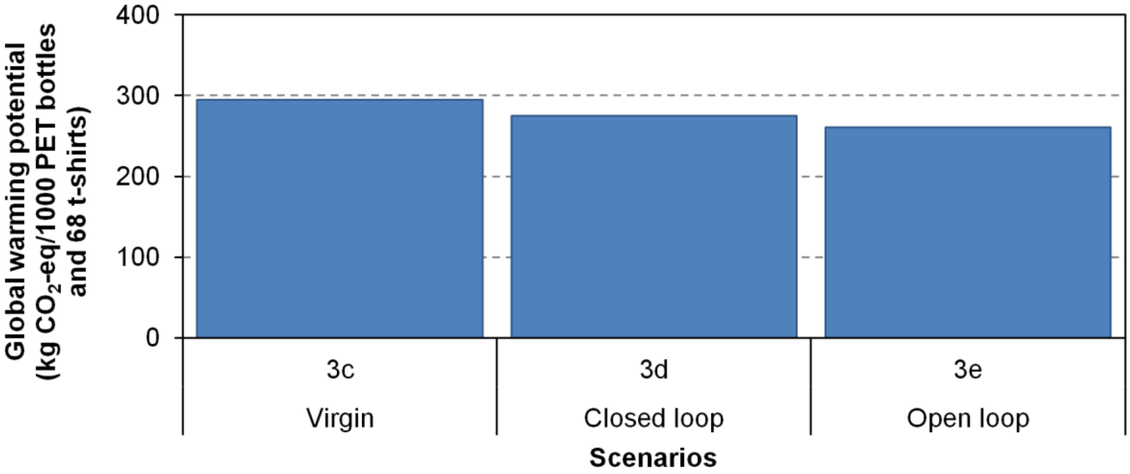


Figure 7.13. Global warming potential for open loop recycling, scenario 3e, in comparison with virgin and closed loop recycling systems, scenario 3c and 3d, respectively.

Figure 7.14 shows the total energy use for scenarios 3c, 3d, and 3e. Again, open loop recycling has the potential for a larger energy saving when compared with the potential energy saving for closed loop recycling.

The reason for the larger savings with this particular case of open loop recycling becomes apparent by inspecting the distribution of energy use among the different processes operations. As can be seen in Figure 7.14, the energy requirement to generate 68 virgin polyester t-shirts is ~61% of the total energy for scenario 3c. This is primarily due to the larger energy requirements for making the polyester fibre product and the larger material losses at each stage of fibre production, *e.g.* in Table 7.4, 12.5% material loss in cutting and makeup. In comparison, the energy required to produce polyester t-shirts from recycled PET is lower. This is because the feedstocks, ethylene glycol and terephthalic acid, used to produce virgin PET are instead displaced by recycled PET. Furthermore, in comparison with closed loop recycling, the total virgin PET losses for open loop recycling are lower. Therefore, by producing the polyester t-shirt from recycled PET, the total energy requirements are reduced to a larger degree when compared with closed loop recycling.

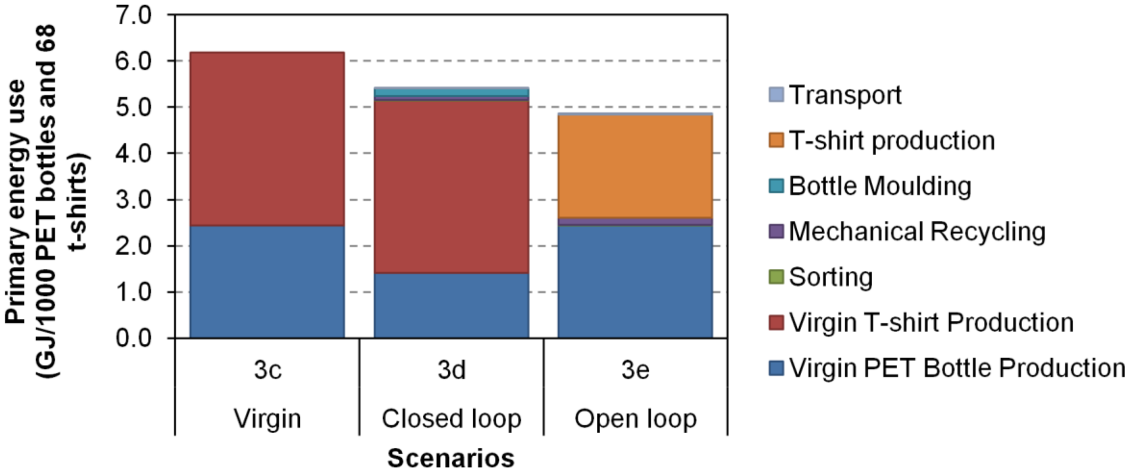


Figure 7.14. Total energy use for open loop recycling, scenario 3e, in comparison with virgin and closed loop recycling systems, scenario 3c and 3d, respectively.

7.3.5 End of Life Scenarios

Finally, polyester waste can end up as landfill or be incinerated with energy recovery. Scenarios 4a and 4b were used to reflect the differences between these two methods. Scenarios 4c and 4d include recycling with each respective end of life method. The global warming potential and total energy use for each scenario is shown in Figure 7.15.

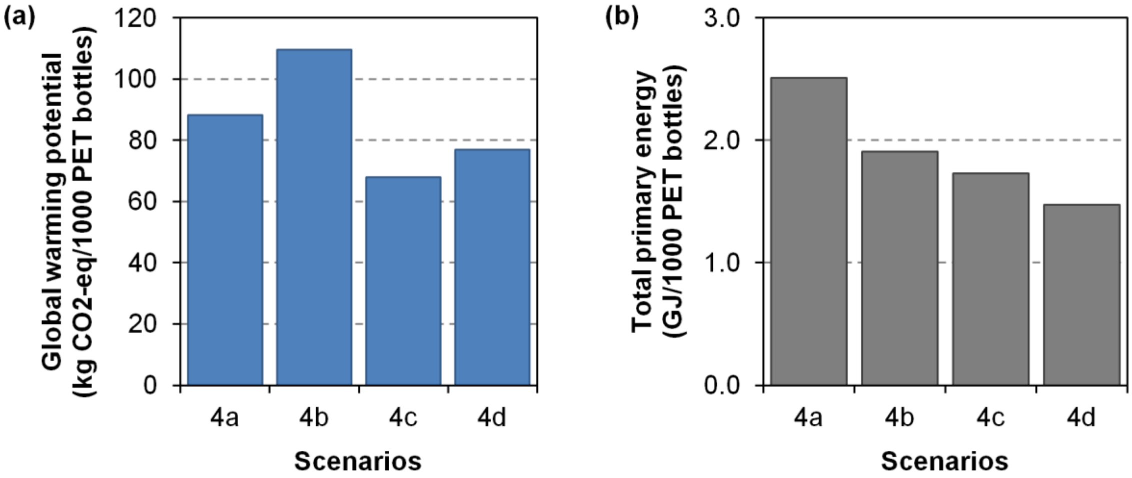


Figure 7.15. For each final end of life scenario, 4a-d, the (a) Global warming potential and (b) total energy use are shown. Scenarios: 4a is landfill only; 4b is incineration only; 4c is recycling with landfill; 4d is recycling with incineration.

An interesting result is that while incineration, scenario 4b, has a 24% larger global warming potential compared to landfill, scenario 4a, the total energy use is 24% lower. This is because combustion of the polymer releases carbon dioxide into the atmosphere; however, with energy recovery, the useful energy released can be used to produce electricity and heat which can be used in other processes. From Figure 7.15, it can be noted that recycling, in all cases, is the preferred. This is because, by recycling, the amount of virgin polymer required is reduced and consequently, the amount of final PET waste is also reduced.

7.4 Discussion

7.4.1 Interpretation

While it has been shown that the global warming potential and energy use are greater for chemical recycling than mechanical recycling, this conclusion disregards the quality of the polymer produced. In practice, owing to polymer degradation and the blending of different polymer colours and specifications, mechanical recycling can cause a low quality of polyester, often with an undesirable grey colour (Bartolome *et al.*, 2012). With chemical recycling, the polymer to be recycled is depolymerised to monomer which can be purified so as to produce a recycled polymer with the same quality as virgin polymer (Shen *et al.*, 2010). When considering polymer quality, recycling polyester with open loop recycling, *i.e.* producing recycled fibre products, there are fewer restrictions. This is because polyester fibres are often blended with other types of fibre and are also dyed, thus obscuring the negative effects of poor polymer quality. Finally, it is important to understand the restrictions for generating food grade products, *e.g.* a drinks container, which are much higher than the restrictions for clothing. Often, in industry, high-quality clear flake is used for closed loop recycling, while low-quality flake is used in open loop recycling (Hopewell *et al.*, 2009).

When considering the transport of intermediate products in each of the recycling chains, transport made a small contribution to the global warming potential and total energy use. This is an important result given the international trade in baled bottles.

Another major benefit of recycling is the reduction of consumer waste. This was most apparent when assessing incineration or landfill. The amount of consumer waste generated, and the percentage reduction from each system by recycling, is shown in Table 7.8. Waste reduction is of importance in order to minimise the quantity of material being sent to landfill. Unlike incineration, landfill makes use of areas of land, which is also an important consideration for sustainability.

Table 7.8. Amount of consumer waste generated

System	PET waste (kg)	Waste reduction (%)
Virgin PET bottles	23.5 (1000 bottles)	0
Closed loop mechanical recycling of PET bottles	13.6 (578 bottles)	42
Closed loop chemical recycling of PET bottles	13.7 (582 bottles)	42
Virgin PET bottles & Virgin polyester t-shirts	35.5 (1000 bottles & 68 t-shirts)	0
Open loop recycling of PET bottles to t-shirts	23.5 (1000 bottles)	34

While the level of detail in the modelling is sufficient to estimate global warming potential and energy use, without further specification of chemicals used in the processes, *e.g.* surfactants in mechanical recycling wash and dyes in fibre production, it is difficult to have a high level of confidence in the results for other environmental impacts. A more detailed model would need to specify these to improve the reliability of the LCA for impacts other than global warming potential and energy use.

7.4.2 Recycling a PET Bottle Derived from Biomass

Combining the savings from recycling with the use of biomass feedstocks an interesting analysis can be made. In Chapter 5, the environmental impacts of producing a PET bottle derived from sugarcane biomass were assessed. In the analysis, the sugarcane bagasse was burnt for electricity generation, while the sugarcane juice was used to produce the *p*-xylene and ethylene feedstock. Closed loop mechanical recycling has been added to this value chain. The following systems were compared:

- Virgin PET bottles in the USA produced from conventionally sourced *p*-xylene and ethylene, defined as scenario 1a above.
- Closed loop mechanical recycling of PET bottles in the USA produced from conventionally sourced *p*-xylene and ethylene, defined as scenario 1b above.

- Scenario 5a, Virgin PET bottles in the USA produced from sugarcane biomass sourced *p*-xylene and ethylene, *i.e.* analysis from Chapter 5.

- Scenario 5b, Closed loop mechanical recycling of PET bottles in the USA produced from sugarcane biomass sourced *p*-xylene and ethylene, *i.e.* analysis from Chapter 5 with closed loop mechanical recycling.

Each system was based on a functional unit of 1000 PET bottles. The global warming potential and energy use of scenarios 1a, 1b, 5a and 5b, are shown in Figures 7.16 and 7.17, respectively. From Figure 7.16, the global warming potential of recycling a bottle derived from sugarcane biomass, scenario 5b, is larger than scenario 5a. While it appears that recycling is counteracting the global warming potential savings of using biomass, this is certainly not the case when considering energy in Figure 7.17. Here, with recycling, the non-renewable and renewable energy uses are both reduced. This means that, by recycling, less biomass feedstock is required in order to produce the same functional unit. Furthermore, as discussed earlier, when considering consumer waste, scenario 5b has 42% less consumer waste than scenario 5a.

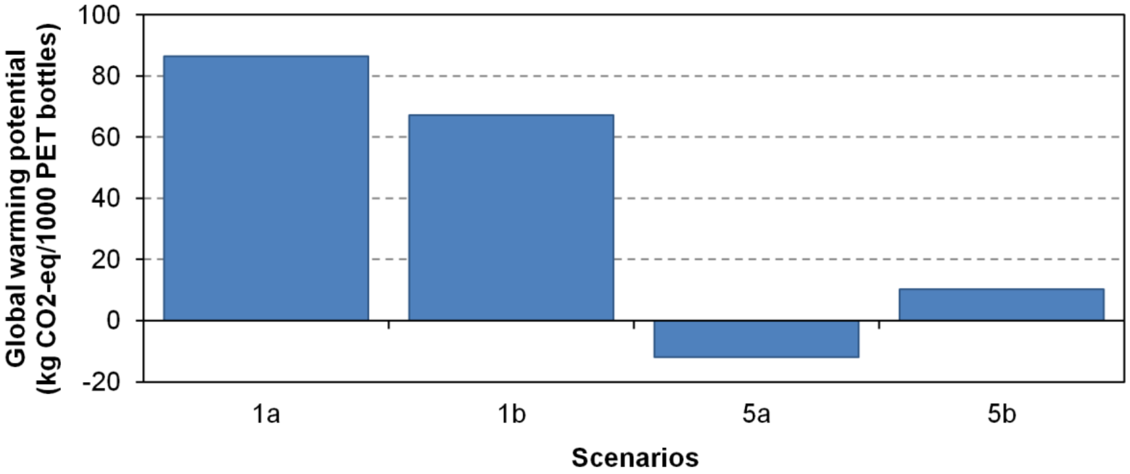


Figure 7.16. Comparing global warming potential for virgin PET sourced from conventional and sugarcane biomass and with the recycling of PET. Scenarios: 1a, Virgin polymer conventional processing; 1b is mechanical closed loop recycling; 5a is virgin PET bottles from sugarcane biomass sourced ethylene and *p*-xylene; 5b is mechanical closed loop recycling of biomass sourced polymer in 5a.

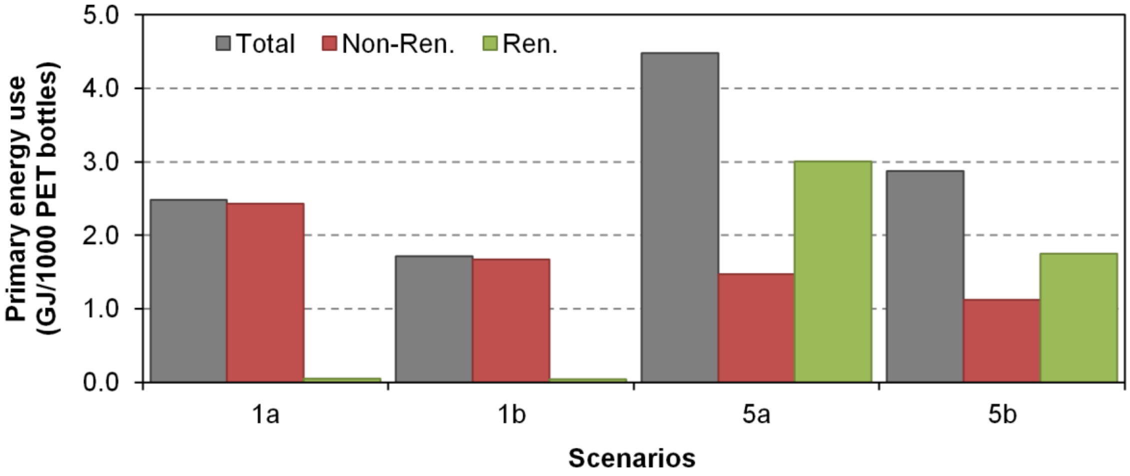


Figure 7.17. Comparing energy use for virgin PET sourced from conventional and sugarcane biomass and with the recycling of PET. Scenarios: 1a, Virgin polymer conventional processing; 1b is mechanical closed loop recycling; 5a is virgin PET bottles from sugarcane biomass sourced ethylene and *p*-xylene; 5b is mechanical closed loop recycling of biomass sourced polymer in 5a.

7.5 Conclusion

In this Chapter, the possible savings to both global warming potential and energy use of recycling PET bottles in closed loop, with mechanical and chemical recycling, and open loop systems has been demonstrated. The open loop recycling system studies had better savings for global warming potential and energy use when compared with closed loop recycling. The transport associated with the international trade of baled bottles, largely imported by China, was shown to have a minimal effect on the possible savings by recycling. Finally, while recycling a PET bottle, produced from biomass-derived raw materials, resulted in lower savings in global warming potential, such a system is still preferable, because of the reduced energy use, both non-renewable and renewable, and reduced waste.

Chapter 8 Conclusions and Further Work

8.1 Conclusions

This Dissertation has investigated the environmental impacts associated with various routes to polyester production and compared them with the environmental impacts of the existing polyester value chain based on raw materials from fossil fuels. This was undertaken in order to assess the sustainability of the possible routes using LCA.

The three main conclusions of this research are:

1. It has been shown that the raw material feedstocks, ethylene and *p*-xylene, for polyester production can be derived from a range of biomass sources and result in savings to the global warming potential and non-renewable energy use.

2. The potential uses of biomass within the polyester value chain, whether as a feedstock for chemicals (ethylene or *p*-xylene) production, or for generating process heat or electricity were compared; the best possible use of biomass within the value chain is by combustion for process heat to reduce the global warming potential and non-renewable energy use.

3. Recycling is beneficial in all cases because it reduces the raw material feedstock requirements and consequently lowers all environmental impacts.

These three conclusions are now discussed in more detail.

In Chapter 4, the environmental impacts of producing a PET bottle using ethylene glycol derived from biomass, both sugarcane and willow, were investigated, and compared to conventional production. For sugarcane, the sugars contained in the juice were fermented to bioethanol and the cellulosic sugarcane bagasse was burnt for electricity generation. It was found that the global warming potential and non-renewable resource use could be reduced with respect to conventional production of PET by 28% and 16% respectively, when bioethanol from the fermentation of sugarcane is converted to ethylene. The main drawback in using sugarcane as a feedstock would be an increase in other environmental impacts, such as acidification and eutrophication potential. This is largely caused by the cultivation of the sugarcane and its requirement for artificial fertilisers. Willow was considered as a source of lignocellulosic biomass. First, its content of cellulose and hemicellulose needs to be converted to sugars, which can then be fermented to ethanol. Willow could also potentially reduce non-renewable resource use by 16%, and did not increase acidification and eutrophication as significantly as sugarcane. From the analysis of a putative supply chain, with PET production located in both the UK and USA, the transport of finished and intermediate products only made a minor contribution to the environmental impacts.

Chapter 5 focused on an alternative route for producing *p*-xylene, the precursor for terephthalic acid. Conventionally *p*-xylene is derived from naphtha; however, new technologies indicate that *p*-xylene could be manufactured from biomass. In the analysis, the relevant parts of willow, sugarcane bagasse and corn stover, would first be deconstructed to sugars. Sugarcane juice, mainly a sucrose solution, could avoid the deconstruction step. The sugar solutions could then be catalytically reformed to *p*-xylene. For the various feedstocks assessed, only willow and sugarcane, both juice and bagasse, could be reliably assessed by avoiding allocation. Producing a PET bottle using *p*-xylene derived from willow could reduce the global warming potential and non-renewable energy use by 32% and 2% respectively. Using sugarcane juice for *p*-xylene production and burning the bagasse to generate electricity resulted in larger savings to global warming potential of 87% and non-renewable energy use of 26%, when compared with conventional bottle production. Again, a disadvantage of using biomass as a raw material was that all other impact categories, most notably, those for eutrophication and acidification, were increased over the conventional raw material.

Chapter 6 compared the potential uses of biomass within the polyester value chain, whether as a feedstock for chemicals (ethylene or *p*-xylene) production, or for generating process heat or electricity. The various cases were assessed in terms of the biomass energy input that would be required in order to reduce the global warming potential and non-renewable energy use in the production of 1 tonne of bottle-grade PET. From the analysis, it was found that the best possible use of biomass within the value chain would be combustion for process heat. This was closely followed by burning biomass to generate electricity. Only in one scenario, ethylene made from ethanol produced by the fermentation of sugars from hydrolysed willow, and for one measure, global warming potential, was producing a chemical from biomass better then combustion for process heating. A sensitivity analysis showed that the results were sensitive to conversion efficiency; however, with a 5% reduction of heat and electricity conversion efficiency, the overall conclusions remain unchanged. This conclusion is also sensitive to the energy sources from which heat and grid electricity are produced. The optimal use of biomass as a chemical feedstock or energy source may therefore shift in the future as conventional energy sources change.

Finally, in Chapter 7, the possible savings, in both global warming potential and energy use, when recycling PET bottles has been demonstrated. This applies both to closed-loop and open-loop systems. The open-loop recycling system had better savings for global warming potential and energy use when compared with closed-loop recycling. The transport associated with the international trade of baled bottles, largely imported by China, was shown to have a minimal effect on the possible savings by recycling. Finally, recycling PET bottles produced from biomass-derived feedstocks resulted in lower savings in global warming potential than producing virgin PET bottles from biomass-derived feedstocks. However, such a recycling system would still be preferable because of the reduced waste and energy use, both non-renewable and renewable.

8.2 Further Work

The studies conducted in this research have yielded suggestions to reduce the environmental impacts of producing polyester; however, an economic feasibility study would be required before such alternatives routes could be adopted by the industry.

Secondly, while preliminary land calculations for the use of biomass have been performed in this Dissertation to provide an element of scale to the reader, the consequential LCA for land use has not been investigated. This is an area for more detailed analysis in future work.

A suitable solution for the issue of allocation for biomass crops in the routes investigated was not found. Sensitivity analysis showed that allocation method could significantly affect the results. Further work developing an understanding of causal relationships between the agricultural inputs and crop outputs would enhance this research in this area. Alternatively, further work expanding the system boundary for other uses of the biomass by-products could be done.

While a detailed analysis has been performed on the polyester value chain and its alternative routes, there are several promising routes still to be investigated, which were described in Chapter 1. These include:

- The catalytic route to glycols from biomass
- The fermentation route to isobutanol and the catalytic post-processing to *p*-xylene

Another useful area of work not covered in this Dissertation would be to develop a comparison of the substitutes for, and alternatives to, PET, *e.g.* glass or aluminium for packaging, cotton for fibres, and PEF and PLA as alternative polymers. As described in Chapter 2, while some comparisons have previously been made, studies have compared different drink container sizes, thereby making unfair comparisons, while others have not specified the functional unit correctly or make assumptions with no practical basis. Given the broad range of products, use patterns, and production requirements, a detailed study on this area would be time consuming, yet valuable to many different industries by illustrating the strengths and weaknesses of each product.

Finally, the simplified models used in Chapters 6 and 7 meant that other environmental impacts beyond global warming potential and non-renewable energy use could not be reliably investigated. With more detailed study, improvements could be made to these models, for example, by including the full range of chemicals used in fibre manufacture or by using a more detailed power plant model.

Nomenclature

Symbol	Description	Units
η	Efficiency	-

Abbreviations

ADP	Abiotic depletion potential	kg Sb-eq (for elements) MJ-eq (for fossil fuels)
AP	Acidification potential	kg SO_2-eq
EP	Eutrophication potential	kg Phosphate-eq
eq	Equivalents	-
FAETP	Freshwater aquatic ecotoxicity potential	kg 1,4-Dichlorobenzene-eq
GWP	Global warming potential	kg CO_2-eq
HTP	Human toxicity potential	kg 1,4-Dichlorobenzene-eq
LCA	Life cycle assessment	-
MAETP	Marine aquatic ecotoxicity potential	kg 1,4-Dichlorobenzene-eq
MVR	Mechanical Vapour Recompression	-
ODP	Ozone depletion potential	kg CFC-11-eq
PEF	Polyethylene furanoate	-
PET	Polyethylene terephthalate	-
PLA	Polylactic acid	-
POCP	Photochemical oxidant creation potential	kg Ethene-eq
PSA	Pressure Swing Adsorption	-
TETP	Terrestrial ecotoxicity potential	kg 1,4-Dichlorobenzene-eq

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Appendix A

This Appendix covers the process modelling for the LCA undertaken in Chapter 4.

A.1 Process Modelling

Detailed process flowsheeting was undertaken for processes to make the following materials: ethylene from bioethanol, ethylene oxide, ethylene glycol and PET polymer. These processes are described in detail in the following sections. All pressures specified are absolute.

A.1.1 Ethylene from Bioethanol

The flow diagram for the conversion of bioethanol to ethylene was assumed to be as shown in Figure A.1, capturing the main features of those described in the literature (Kochar *et al.*, 1981; Morschbacker, 2009). In Figure A.1, stream 1, consisting of 25 × 10^3 kg/h 95 wt% ethanol is combined with an equal mass flowrate of water in stream 2 (Kochar *et al.*, 1981; Morschbacker, 2009). Given that the dehydration of ethanol is endothermic, the additional water, which is later vaporised, acts both as source of sensible heat and reduces the formation of by-products (Kochar *et al.*, 1981; Morschbacker, 2009). The combined stream 3 is heated by interchange with the reaction products in heat exchanger, HX1, to 174°C and subsequently in furnace H1 so that the gaseous mixture of steam and ethanol, stream 5, enters the reactor system at 450°C and 11.4 bar (Kochar *et al.*, 1981). The reactors, R1 to R3, are packed beds containing catalyst based on either alumina or zeolitic materials (Kochar *et al.*, 1981; Morschbacker, 2009). At these conditions, the conversion of ethanol is 99.9 mol% with a molar selectivity of 98.5% to ethylene (Kochar *et al.*, 1981). The by-products are diethyl ether, acetaldehyde, acetic acid, methane, ethane, carbon monoxide and carbon dioxide (Kochar *et al.*, 1981; Morschbacker, 2009). The inter-stage heating, H2 and H3, is provided by a furnace because the reaction is endothermic. The exit flow from the final reactor, stream 6, contains, typically, 21 mol% ethylene, 78 mol% water, and small fractions of the other by-products. After interchange with stream 3 in HX1, the product stream is cooled in condenser C1 against cooling water to a temperature such that most of the water in stream 7 condenses. After removal of the water in knock-out drum F1, the products, stream 9, are compressed to 27 bar and cooled by C2 with cooling water to remove most of the remaining water. Aqueous side-products are also entrained in the water streams 8 and 10; these go to waste water treatment. A potassium bicarbonate scrubber removes carbon dioxide from stream 11. Based on Kothandaraman's (2010) analysis, the energy requirement for regenerating the scrubber solution is ~2.5 MJ/kg CO_2. The drying unit removes the remaining water from stream 13. At this stage, in stream 14, ethane accounts for the remaining impurity in the ethylene flow. The ethylene is purified using a cryogenic C_2-splitter (Morschbacker, 2009). The cooling at C3 is provided by a refrigeration unit, assumed in the present study to use propane as a working fluid operating at a condenser pressure, in the refrigeration cycle, of 11 bar, to allow cooling water to be used to liquefy the propane. Cold recovery with the product stream 17 in heat exchanger HX2 improves the cooling capacity of the refrigerant. The refrigeration cycle operates with an evaporator pressure of 1 bar, thereby providing the required cryogenic temperature of -25°C for the condenser C3. Stream 17 consists of 14.7×10^3 kg/h of ethylene at 99.9 mol% purity. The impure ethane in stream 15 is used in the furnaces H1-H3 to reduce fuel gas requirements. For the process, the furnace heating requirements are 3.9 MJ/kg ethylene, electricity requirements are 0.5 MJ/kg ethylene, and cooling water duty is 3.8 MJ/kg ethylene.

Depending on the reactor configuration and operating conditions, the catalyst regeneration from coking can be minimized to once a year, and potentially once every two years (Morschbacker, 2009). As the life cycle impact allocation of catalyst formation regeneration is spread over more ethylene product, the catalyst's life cycle contribution becomes negligible.

With limited information available on the kinetics of side-reactions; the final reactor exit stream has been approximated to achieve yields of the ethylene product and side products similar to those published by specifying the selectivity to ethylene to be 98.5% (Kochar *et al.*, 1981; Morschbacker, 2009). The high selectivity for ethylene means that enthalpy calculations are dominated by the ethylene reaction and side reactions have little impact on the heat balance over the train of reactors.

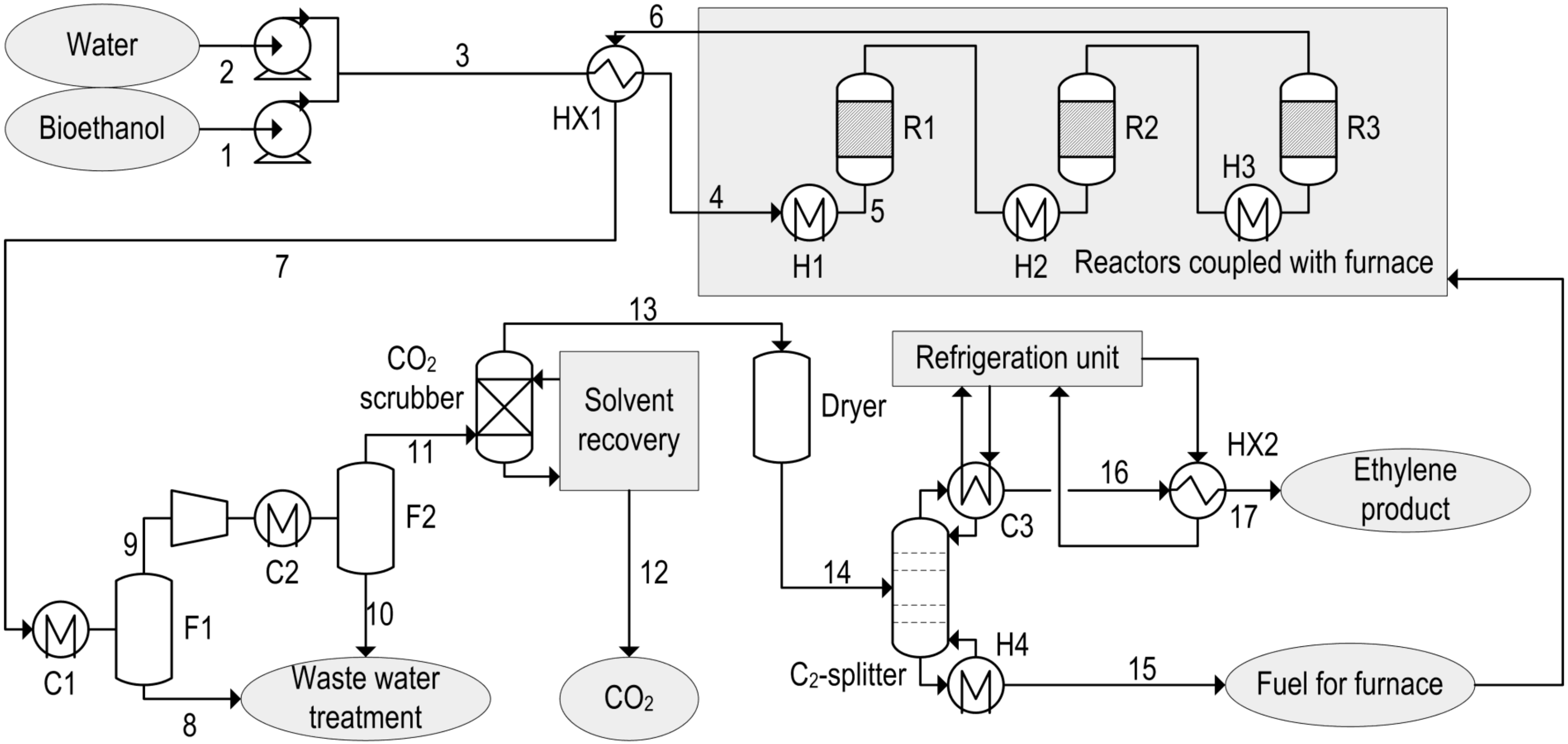


Figure A.1. Process flow diagram for the conversion of bioethanol to ethylene showing principal operations and flows.

A.1.2 Ethylene Oxide

Figure A.2 shows a flow diagram for the oxygen-based, direct oxidation process for the formation of ethylene oxide from ethylene (Dever *et al.*, 1998). Gaseous ethylene, stream 1, is compressed to 20 bar, and combined with a stoichiometic amount of 99.5 mol% pure oxygen, stream 2, at the same pressure. The combined feed of ethylene and oxygen is preheated to 215°C in heat exchanger, HX1, interchanging with the reactor products. The partial oxidation of ethylene to ethylene oxide occurs over a silver-based catalyst in the reactor, R1 (Dever *et al.*, 1998). Combustion to carbon dioxide and water also occurs and the overall reaction can be approximated as (Dever *et al.*, 1998):

$$7C_2H_4 + 6O_2 \longrightarrow 6C_2H_4O + 2CO_2 + 2H_2O$$

At the reaction conditions of 225°C and 20 bar, the conversion of ethylene per pass of the reactor is 10%, and, as shown by the reaction stoichiometry, there is a molar selectivity of 6/7 (85.7%) to ethylene oxide (Dever *et al.*, 1998; Weissermel and Arpe, 2003). The reactor itself consists of a packed-bed through which cooling tubes pass employing boiling water, which generates medium pressure steam at ~16 bar for other unit operations (Dever *et al.*, 1998). The heat integration of streams 3 and 4 in HX1 increases the amount of heat available in the reactor for steam generation by 60%.

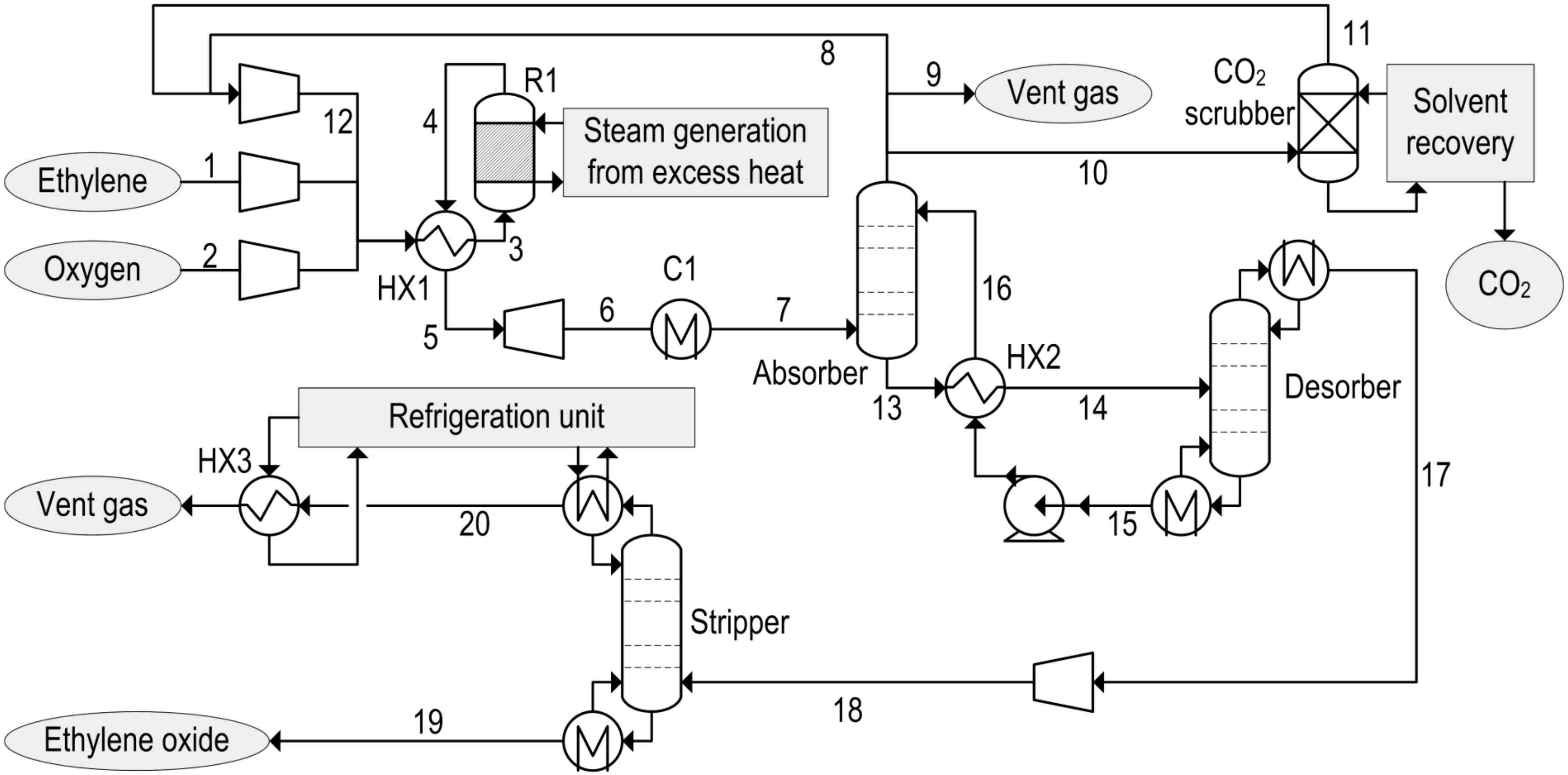


Figure A.2. Annotated process flow diagram of the oxygen-based direct oxidation process of ethylene to ethylene oxide showing principal operations and flows.

Owing to the low conversion per pass, the process operates with a recycle, stream 8 (Dever *et al.*, 1998). Thus, the exit gases from R1, stream 5, are expanded through a turbine to 10 bar to recover energy and cooled to 30°C (stream 7) to ensure that the absorber gives a high recovery of ethylene oxide. In the absorption column, ethylene oxide is scrubbed from the entering gases by counter-current contact with water, with the resulting solution leaving in stream 13. Of the gaseous mixture leaving the top of the absorber, ~84% of the flow, stream 8, is directly recycled, 14%, stream 10, is scrubbed of carbon dioxide with bicarbonate solution prior to recycling (stream 11), and the final 2% is purged to prevent trace argon, present in the oxygen feed, from accumulating (stream 9). The presence of CO_2 in the reactor reduces yields of ethylene oxide (Dever *et al.*, 1998); the process calculations for the carbon dioxide scrubber are similar to those undertaken in the conversion of ethanol to ethylene. Recovered energy from the expansion from 20 bar at the reactor exit to the 10 bar in the scrubber balances ~29% of the total compressor energy requirements.

The solution of ethylene oxide, stream 13, is heated by interchange with stream 15 in HX2, and is then sent to a desorption column, operating at atmospheric pressure. Water, low in ethylene oxide concentration, stream 15, is recycled to the absorber. The heat integration of streams 13 and 15 reduces the heat requirements of the desorber's reboiler by 66%. Stream 17 represents ethylene oxide leaving the desorber and requires further purification in a stripper to reduce its content of CO_2 from 2 mol% to 0.02 mol%. The column is operated at 5 bar and the temperature at the top of the column, 4.9°C, requires a chilled cooling duty. A refrigeration cycle was designed using a similar method as previously discussed. The ethylene oxide of purity 99 mol%, stream 19, can be used directly in the reactors for the production of ethylene glycol. The hydrocarbons in streams 9 and 20 are combusted to generate further process steam. The process generates an excess of useful heat at ~200°C, 9.3 MJ/kg ethylene oxide. By extending the boundaries and integrating with the ethylene glycol process, the issue of allocation for the excess heat is avoided.

Although a more detailed consideration of the reaction mechanisms suggests the selectivity in R1 ought to be no more than 80% for ethylene oxide, the value, assumed above, of 85.7% was retained in the modelling, because selectivities greater than 80% have been exceeded in industrial practice by modifying the catalyst

(Dever *et al.*, 1998; Weissermel and Arpe, 2003). The molar yield of ethylene oxide for the whole process is 72%, which is within the range achieved in industry (Dever *et al.*, 1998).

A.1.3 Ethylene Glycol

The flow diagram assumed for the hydrolysis of ethylene oxide to ethylene glycol is shown in Figure A.3. Streams 1 and 2, consisting respectively of ethylene glycol and water, are brought to 150°C and 35 bar, using pumps and a heater, H1, as shown (Forkner *et al.*, 1998). The feed to R1, stream 3, composed of the feedstock streams 1 and 2 and the recycle, 17, contains water and ethylene oxide at a molar ratio of 22:1. At this ratio, there is nearly complete conversion of ethylene oxide and the selectivity for ethylene glycol is high (Forkner *et al.*, 1998). In R1, the water and ethylene oxide react in the liquid phase, with some higher-order glycols being formed from the self oligomerisation of ethylene glycol (Forkner *et al.*, 1998). Owing to differences in processing within the industry, the range of products formed can vary; here, it was assumed that, typically, the exit from R1 would contain 90 mol% ethylene glycol, 7 mol% diethylene glycol, 2 mol% triethylene glycol and 1 mol% tetraethylene glycol (Forkner *et al.*, 1998). The reactor operates isothermally at 200°C; the enthalpy required to raise the sensible heat of the reactants from 150°C to this temperature is balanced by the exothermicity of the reaction.

The separation involves first removing water in multiple columns E1-E4 (Cocuzza *et al.*, 1975; Forkner *et al.*, 1998). In the configuration shown, Stream 4 containing 3.9 mol% ethylene glycol is flashed into the first column, E1, operating at 8 bar. This tray column is provided with heater H2. The bottoms, stream 5, contain 5.6 mol% ethylene glycol. The top product, stream 6, is water vapour at 170°C, and is used to as a heat source for column E2 by integration in heat exchanger, HX1. By dropping the pressure in column E2 to 5 bar, the reboiler temperature requirement is 156°C, therefore enabling the heat integration. Similarly the pressures in columns E3 and E4 are 2 bar and 0.1 bar, requiring reboiler temperatures of 139°C and 133°C. This allows heat from the vapour leaving column E2, at 152°C, to be split into stream 12 and 13 for use in heat exchangers, HX2 and HX3, to drive the respective columns. The vacuum pressure in column E4 is created by a steam jet ejector on stream 16, to achieve the separation specification of 0.4 mol% (0.1 wt%) water content in stream 18 (Cocuzza *et al.*, 1975). The jet ejector steam requirements were calculated using literature methods (Ketterer and Blatchley, 2007; Perry *et al.*, 2004). The condensed water from streams 7, 9, 14 and 15 are combined and recycled to the reactor.

Stream 18 requires further distillation, in D1 operating at atmospheric pressure, to separate ethylene glycol from diethylene glycol and higher-order glycols. This operation is designed to produce ethylene glycol as the top-product, stream 19, at 99.5 mol% purity for the polymerisation. Distillation column, D2, has been shown in Figure A.3, for further purification of higher order glycols; however for the allocation method chosen, this final separation does not affect the inventory analysis of ethylene glycol, as discussed later.

As mentioned previously, the process integration of ethylene oxide and ethylene glycol means the steam generated from the ethylene oxide reactor and waste gas combustion is sufficient to supply the heating requirements for heaters H1, H2, H3 and the steam jet ejector. Combining both processes, in producing ethylene glycol from ethylene, 1.6 MJ electricity and 10.6 MJ of cooling water duty were required per kg ethylene glycol.

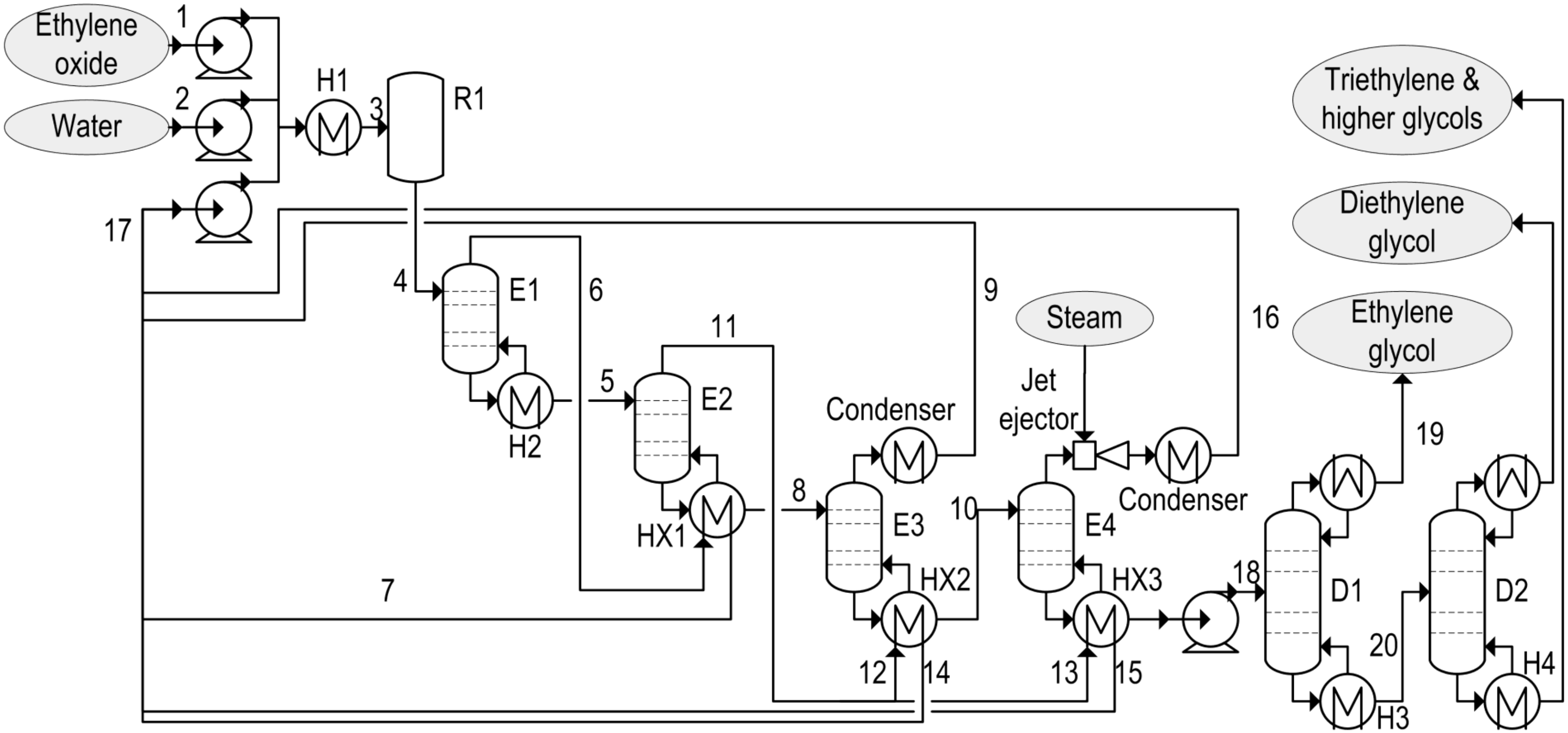
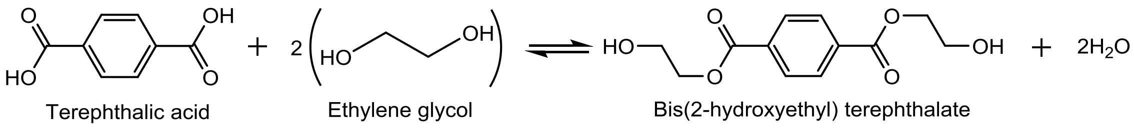


Figure A.3. Annotated process flow diagram of ethylene oxide to ethylene glycol process showing principal operations and flows.

A.1.4 Continuous Polymerisation

The flow diagram for the preparation of the monomer and its subsequent polymerisation is shown in Figure A.4. Ethylene glycol, terephthalic acid and isophthalic acid, streams 11, 2 and 3, are premixed and the resulting slurry, stream 4, is pumped from the pre-mixing vessel to the esterification reactor. The fresh ethylene glycol, stream 1, is added into the process through the hotwells of the spray condensers and mixes with the recycled ethylene glycol (*via* stream 19 and then stream 11) (PCI Xylenes & Polyesters, 2013).

In the feed, stream 4, ethylene glycol is in excess, according to the esterification reaction (Rieckmann and Völker, 2003):



Side reactions lead to the formation of small quantities of diethylene glycol, 1,4-dioxane and acetaldehyde (Rieckmann and Völker, 2003). The transesterification reactions require 0.01-0.03 wt% antimony catalyst, and 1-3 wt% isophthalic acid for bottle grade PET (Rieckmann and Völker, 2003). Here, percentages refer to amounts in the overall incoming feed to the esterification reactor. The esterification reactor operates at 250-265°C and 1.2-1.8 bar. In the model, average temperatures and pressures based on these ranges were used. Conversion of 95% of the terephthalic acid is achieved because the reaction is driven to the product side by the removal of water from the reactor. The reactor is generally a stirred tank, equipped with heating coils and a heating jacket to evaporate the water formed, in association with glycol as the other volatile component (Rieckmann and Völker, 2003). The vapour, stream 7, is sent to a distillation column where ethylene glycol is recovered (stream 9). The ethylene glycol, stream 11, is then recycled as feed. A purge (stream 10) was used to prevent the accumulation of diethylene glycol, dioxane and acetaldehyde in the process. Waste water, stream 8, from the distillation column, containing small quantities of ethylene glycol, dioxane, and acetaldehyde, is sent to waste treatment.

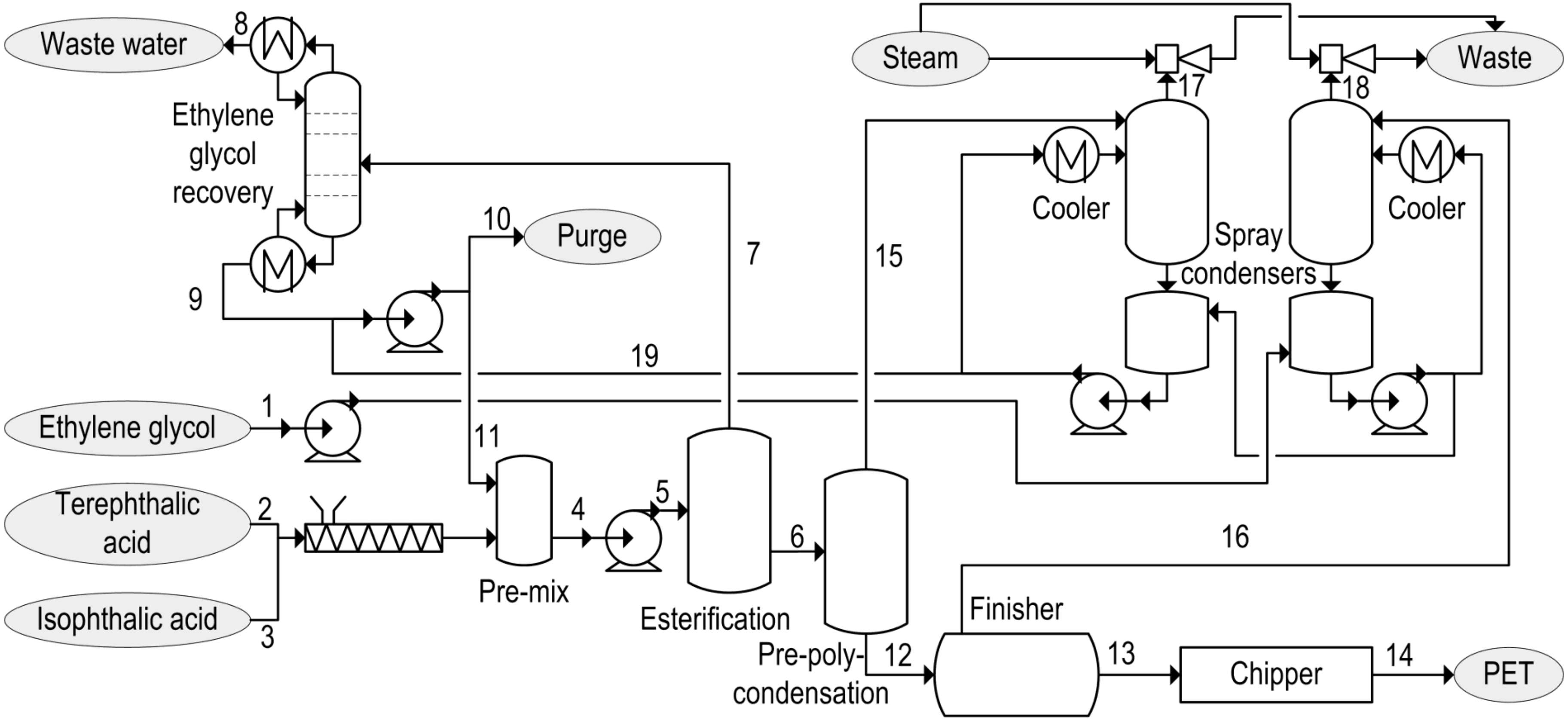
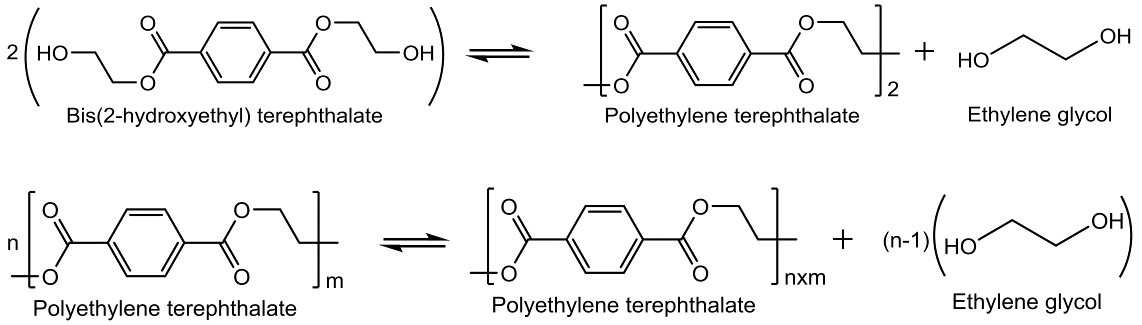


Figure A.4. Process flow diagram of continuous polymerisation process.

The monomer bis(2-hydroxyethyl) terephthalate, contained in stream 6, passes by differential pressure and gravity flow to the pre-polycondensation reactor, where, in the melt-phase, oligomers are formed and subsequently longer chains of polymer (Rieckmann and Völker, 2003):



In the pre-polycondensation reactor, degrees of polymerisation of 25 are typically achieved, corresponding to a number average molecular weight of ~4.9 × 10^3 kg/kmol (Rieckmann and Völker, 2003). The reactor operates at 265-275°C and 0.025-0.030 bar *i.e.* under vacuum. In fact, all reactors involving polymerisation operate under vacuum to exclude oxygen, which causes degradation of the polymer. The slurry passes *via* stream 12 from the pre-polycondensation reactor to the finisher reactor, where, at 275-295°C and 0.0005-0.0015 bar, further polymerisation occurs to degrees of polymerisation of 100, equivalent to a number average molecular weight of 19 × 10^3 kg/kmol (Rieckmann and Völker, 2003). Generally, esterification reaction to monomer continues in the downstream polymerisation reactors until the terephthalic acid is depleted, resulting in ~99% conversion of terephthalic acid into polymer. The final polymer leaving the finisher reactor, stream 13, is cooled, cut into chips and conveyed to storage for the solid state polymerisation (stream 14). The mixing in each of the reactors is provided by impellers or thermal convection. The mixing power was estimated using empirical curves of power number against impeller Reynolds number (Sinnott, 2005).

Steam jet ejectors are provided at the outlet (streams 17 and 18) from the spray condensers, which, are used to remove the ethylene glycol vapour from the pre-polycondensation (stream 15) and finisher reactors (stream 16). Although newer facilities use ethylene glycol ejectors, this LCA focuses on the current PET production technology which use steam ejectors (PCI Xylenes & Polyesters, 2013). The spray condensers cool the vapours, thereby recovering ethylene glycol, which is recycled, stream 19. The water in the overhead streams from the spray condensers contains small quantities of ethylene glycol, and is sent to effluent treatment.

The enthalpies of reaction for the esterification and melt-phase reactions were estimated knowing the enthalpies of combustion for the reactants and products. The enthalpy of reaction was then combined with the sensible and latent heats in order to calculate each reactor's energy requirements.

The utilities requirements for the continuous polymerisation process, on a per kg PET basis, are 2.6 MJ heat provided by heat transfer oil (Dowtherm), 0.07 MJ electricity, and 2.4 MJ of cooling water duty.

A.1.5 Solid State Polymerisation

The polymer chip leaving the continuous polymerisation in Figure A.4 is treated in the solid state polymerisation process to increase the polymer chain length to a number average molecular weight of 25×10^3 kg/kmol (Culbert and Christel, 2003). The flow diagram, shown in Figure A.5, is assumed to be collocated with the continuous polymerisation. The process increases polymer chain length and crystallinity for a higher strength resin, as well as removing impurities, as required for PET bottles (Culbert and Christel, 2003).

In Figure A.5, PET, stream 1, enters a pre-crystalliser followed by a secondary crystalliser, both being air-fluidised beds (Culbert and Christel, 2003). The crystallisers serve to reduce the amount of amorphous polymer (Culbert and Christel, 2003). The main energy requirement is the sensible heat of bringing the polymer to the temperature of 160-180°C in the two beds. Air from the pre-crystalliser, stream 4, is recycled as the exit temperature, ~145°C, is much higher than the fresh air temperature. A proportion of the air is vented to prevent volatile components accumulating in the recycle.

In stream 5, the PET flows into a pre-heater to raise its temperature to 210-220°C. The heating fluid is nitrogen to prevent degradation by any air present at the higher temperature (Culbert and Christel, 2003). The heated PET, stream 7, enters the reactor, also operated with nitrogen. Here, traces of acetaldehyde are removed and the conditions encourage further degrees of polymerisation to the required molecular weight. Towards the bottom of the reactor, the polymer is initially cooled with nitrogen to 175°C. On leaving the reactor, stream 12, the PET chips are further cooled to 60°C in a fluidised bed by air (stream 13). The hot air used in the cooling is sent *via* stream 15 to the pre-crystalliser fluidised bed to reduce the energy requirements.

The nitrogen from the reactor, stream 16, and a fraction of the nitrogen from the pre-heater, stream 10, is sent to treatment prior to recycling (streams 24 and 25). The organic impurities are removed from the nitrogen in a platinum catalyst oxidation bed, only the required amount of oxygen for combustion is added to the system (Culbert and Christel, 2003). Water is removed by stages of condensation (stream 19) and drying (stream 21). A purge, stream 22, prevents the small fraction of carbon dioxide accumulating (Culbert and Christel, 2003).

For the process, heating requirements are 0.039MJ/kg PET, electricity requirements are 0.030 MJ/kg PET, and the cooling water duty is 0.14 MJ/kg PET.

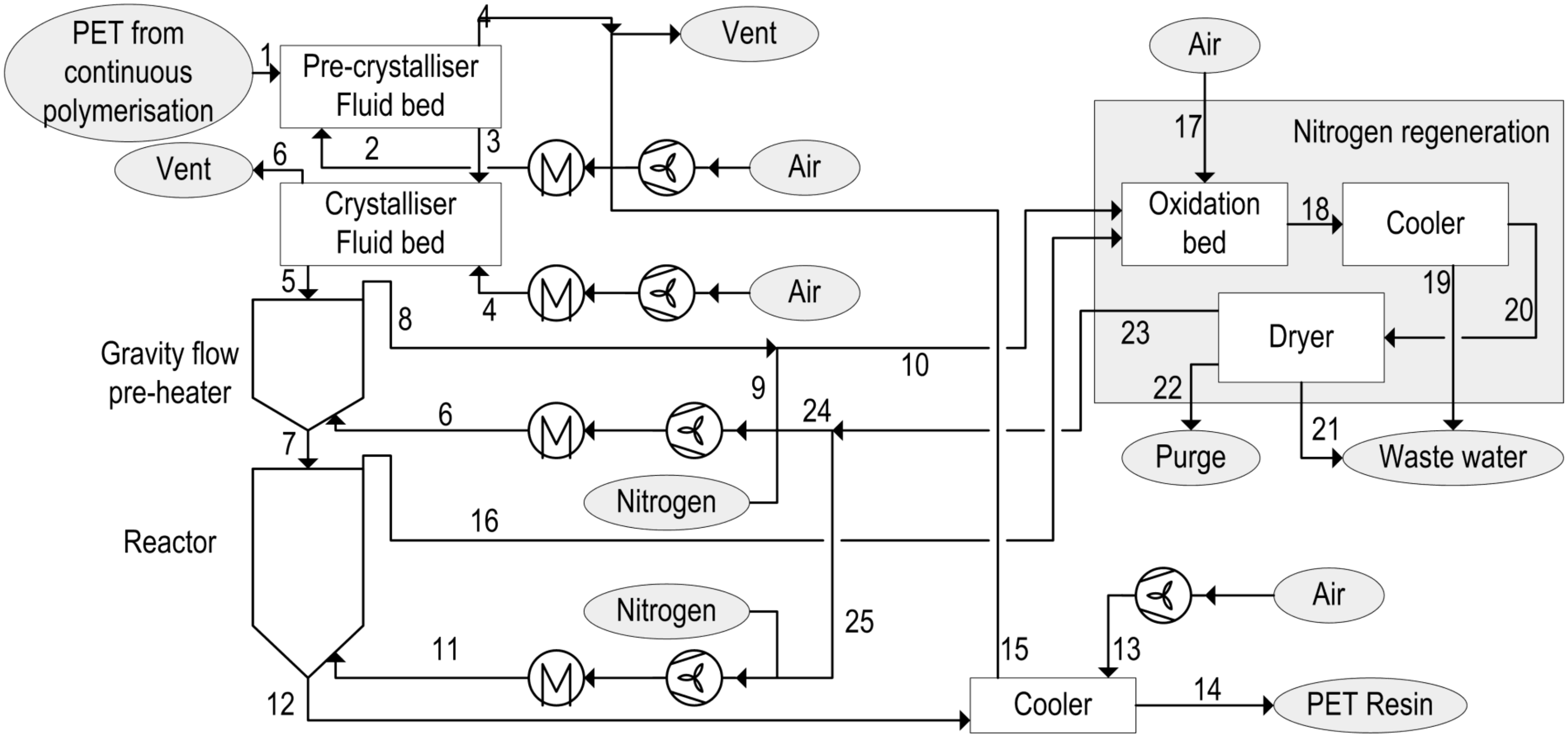


Figure A.5. Process flow diagram of solid state polymerisation process.

Appendix B

This Appendix covers the process modelling and detailed analyses for the LCA undertaken in Chapter 5.

B.1 Process Modelling and Allocation

B.1.1 Conventional *p*-Xylene Processing

Two proprietary designs were analysed for the manufacture of *p*-xylene from naphtha; the first design, from 2008, is currently used by many existing manufacturers in the industry. The second, from 2013, is the most recent including adjustments to heat integration to improve energy savings (PCI Xylenes & Polyesters, 2013). A complete set of flowsheets were provided for the 2008 and 2013 designs (PCI Xylenes & Polyesters, 2013). The flowsheets were used to generate an inventory analysis. Some processes were not included in the flowsheets because they are typically subcontracted. These additional processing areas, such as, hydrogen pressure swing adsorption and sour water stripping have been calculated independently.

A summary of the manufacture of *p*-xylene from naphtha is shown in Figure B.1. The primary feed is full range naphtha; in the hydrotreating process, the feedstock is treated to remove sulphur and olefins to match the specification required by the catalyst in subsequent processes. The result is two streams, light naphtha and heavy naphtha. Heavy naphtha is reformed to increase the octane content, generating reformate, hydrogen and LPG. The reformate is then fractionated: the six processes in blue are highly integrated for energy recovery and have therefore been assessed as one block for the inventory analysis. Xylenes fractionation splits the reformate stream into benzene and toluene, *p*-xylene and *m*-xylene, *o*-xylene, and heavy aromatics. The Parex unit separates *p*-xylene and *m*-xylene, the former is the desired product while the latter is isomerised in the Isomar unit and fed back to xylenes fractionation. The Sulfolane unit uses extractive distillation to increase the purity of benzene and toluene, which are then separated in the benzene-toluene fractionation unit to produce the benzene product. The Tatoray process disproportionates toluene and transalkylates toluene with C9/C10+ aromatics to produce benzene and xylenes, increasing the yield of the desired aromatics.

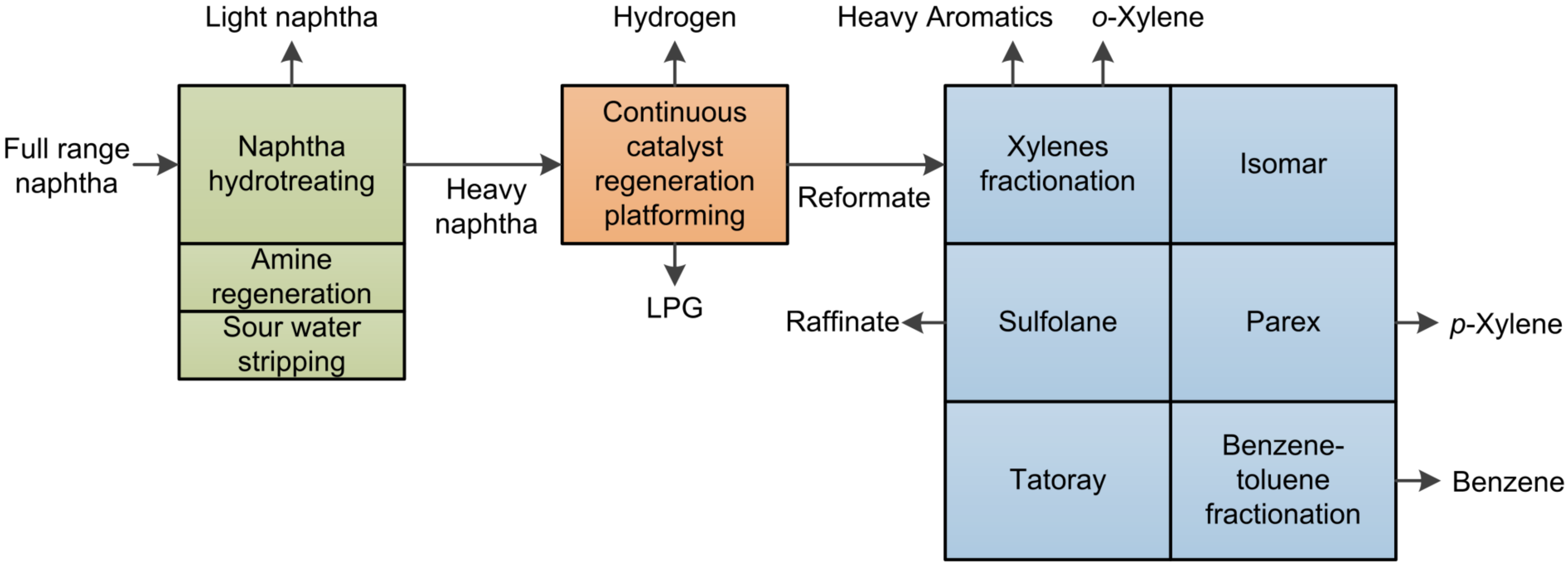


Figure B.1. Block diagram representing principal process areas in *p*-xylene manufacture.

Hydrogen is separated from a mixture of light alkanes produced during reforming using pressure swing adsorption. The energy requirements for hydrogen pressure swing adsorption have been calculated by quantifying the compressor and cooling duties. In this instance, the impure hydrogen stream was assumed to be compressed to ~69 bara at which ~87% of the hydrogen was recovered. The sour water stripping unit, which removes H_2S, was modelled using a distillation column in Unisim. The stripper feed was preheated with the stripper water bottoms reducing the stripper reboiler energy requirements. The stripper column has 8 stages and operates at an average of 2 bara and reflux ratio of 1, in order to maximise hydrogen sulphide removal, but minimise the reboiler duty.

Because the overall process produces several products, and because there is a high level of integration within processes, it is not possible to identify easily the relationships between products and feeds. It was also not possible to redraw or expand the system boundaries for this analysis (the preferred method). Allocation was therefore required. Economic and mass-based allocation methods were used so that the sensitivity to the method of allocation could be investigated. As shown in Figure B.1, the processes were categorised as much as possible before allocation factors were applied to ensure that upstream products (*e.g.* light naphtha, LPG, and hydrogen) were not unfairly allocated emissions from the downstream (blue) processes. While mass allocation is simple, because the mass balances for each process stage are known, economic allocation is more complicated because product values vary with market conditions. In order to account for market fluctuations, an average price for each product over a five year period (2010-2014) was calculated (PCI Xylenes & Polyesters, 2013). Using these averaged prices, the economic value of each product (mass×price) was divided by the process's total value of its *J* products, *i.e.* $\sum_J \text{mass}_j \times \text{price}_j$, to determine the economic allocation fractions.

Sample calculation for mass and economic allocation:

For the 2008 design, the continuous catalyst regeneration platforming process produces 250 t reformate/h, 7.5 t hydrogen/h and 13.6 t LPG/h. Therefore, the mass allocation fraction for reformate is:

$$\frac{250}{250+7.5+13.6}\times 100=92\%$$

The five year average price for reformate, hydrogen and LPG are \$1099/tonne, \$598/tonne and \$646/tonne, respectively (PCI Xylenes & Polyesters, 2013). Therefore, the economic allocation fraction for reformate is:

$$\frac{250\times 1099}{250\times 1099+7.5\times 598+13.6\times 646}\times 100=95\%$$

The allocation factors used for both 2008 and 2013 designs are given in Table B.1. There are only slight differences between the allocation methods; however, the product splits between the 2008 and 2013 designs do vary substantially. These sensitivities were investigated in the results of Chapter 5, as well as a comparison with an existing *p*-xylene dataset from Gabi 6.

Table B.1. Allocation fractions for products from each process stage for both economic and mass-based allocation. The colours in Column 1 refer to Figure B.1.

		Allocation 2008 design		Allocation 2013 design	
Process stage	**Product**	**Mass**	**Economic**	**Mass**	**Economic**
Naphtha hydrotreating (Green)	Light naphtha	18%	18%	36%	36%
	Heavy naphtha	82%	82%	64%	64%
Platforming (Orange)	Reformate	92%	95%	95%	97%
	Hydrogen	2.8%	1.6%	3.6%	2.0%
	LPG	5.0%	3.1%	1.1%	0.7%
Downstream processing (Blue)	Benzene	25%	24%	22%	20%
	p-Xylene	46%	53%	65%	72%
	o-Xylene	11%	11%	N/A	N/A
	Heavy Aromatics	1.0%	0.54%	0.7%	0.4%
	Raffinate	17%	11%	12%	8%

B.1.2 Biomass Composition and Allocation

The types of biomass investigated were corn stover, willow, sugarcane bagasse and sugarcane juice. The composition of each type of biomass, shown in Table B.2, was determined from the literature (Cardona *et al.*, 2010; Davis *et al.*, 2013; Templeton *et al.*, 2010; Walford, 1996). The moisture content shown in Table B.2 refers to the mass fraction of water in the biomass before entering the biomass deconstruction and sugar reforming process. The water content at the time of harvesting and pre-processing is important when considering allocation; this is discussed later in this Section.

Table B.2. Composition of each type of biomass, in wt% on a dry basis, and moisture content.

Component	Corn stover	Willow	Sugarcane bagasse	Sugarcane juice
Glucan	35	43	38	0.0
Xylan	19	15	21	0.0
Lignin	16	26	24	0.0
Ash	4.9	2.0	3.8	4.0
Acetate	1.8	3.0	3.2	1.0
Protein	3.1	0.0	0.5	1.5
Extractives	15	0.0	5.6	0.0
Arabinan	2.4	1.5	1.8	0.0
Galactan	1.4	2.5	0.8	0.0
Mannan	0.6	3.0	0.0	0.0
Sucrose	0.8	0.0	0.7	85
Glucose	0.0	0.0	0.0	2.3
Fructose	0.0	0.0	0.0	2.3
Oligosaccharides	0.0	0.0	0.0	0.3
Polysaccharides	0.0	0.0	0.0	0.5
Salts	0.0	0.0	0.0	2.6
Others	0.0	4.5	0.0	0.6
Moisture content	20	35	48	80

Existing datasets for the production of sugarcane, corn and willow have been used in this study.(Ecoinvent Centre, 2010; PE International, 2013; Stephenson *et al.*, 2010) It was found that the sugarcane and corn datasets did not account for the biogenic carbon absorbed in the sugarcane bagasse and corn stover. As stated Chapter 4, the willow dataset also did not quantify the biogenic carbon absorbed. Given that the boundary, in this case, has been drawn to produce a PET bottle, not accounting for the disposal, these datasets were modified to account for the carbon contained in the biomass. If the bottles were subsequently burnt on disposal, this quantity of carbon would be re-released to the atmosphere.

The simplest method to determine the CO_2 absorbed by biomass is to perform a carbon balance on the feedstock. Photosynthesis fixes carbon dioxide from the atmosphere into sugars in plants, *e.g.*:

$$6CO_2 + 6H_2O \longrightarrow C_6H_{12}O_6 + 6O_2$$

Overall, one can assume that every mole of carbon in the plant is derived, originally, from 1 mole of CO_2 from the atmosphere. This method of calculation does not account for soil carbon changes. The formation of soil carbon is a complex problem and there is insufficient literature to enable a rigorous calculation of how it changes. In order to accurately quantify the carbon content in each type of biomass, it is important to quantify the amount of biomass harvested and the initial moisture content. In the case of a corn plant, the mass ratio of corn cob to corn stover is typically 1:1 (Luo *et al.*, 2009b). However, to limit soil erosion and maintain land fertility, only ~60% of the corn stover should be harvested (Luo *et al.*, 2009b; Spatari *et al.*, 2005). Thus, per kilogram of corn harvested, only 0.6 kg of stover can be collected. The 0.6 kg corn stover harvested has an initial moisture content of ~30 wt% and dries in the field to reach the 20 wt% reported in Table B.2 (Davis *et al.*, 2013; US Environmental Protection Agency, 2007). In the case of willow, the moisture content was assumed to remain unchanged between the point at which it was harvested and its receipt at the biomass decomposition facility. In the case of sugarcane, sugarcane juice is first extracted. Typically, per kilogram of sugarcane, 0.28 kg of sugarcane bagasse with a moisture content 48 wt% is produced at a manufacturing plant producing sugarcane juice.(Cardona *et al.*, 2010) The moisture content was assumed to remain unchanged, because juice extraction would take place immediately before the biomass deconstruction process. The mass of sugarcane juice is therefore 0.72 kg. The initial content of water in sugarcane juice is about 77 wt%: additional wash water is added in the extraction to maximise the sucrose extraction, thus sugarcane juice has a final water content of 80 wt% (Pérez, 1997). Again, as explained for corn stover, it is important to use the initial moisture content for an accurate representation of the crop carbon yield for the carbon content calculation. The leaves and agricultural residues of the sugarcane plant are typically burnt to facilitate easier harvesting, therefore for this analysis, the carbon content of sugarcane leaves and cuttings return to the carbon cycle and do not require calculation (Cardona *et al.*, 2010). Therefore, one kg of sugarcane results in 0.72 kg of juice with an initial moisture content of 77 wt% and 0.28 kg of bagasse with an initial moisture content of 48 wt%.

Using the composition from Table B.2, and the initial moisture content for corn stover and sugarcane juice, the carbon content and hence the carbon dioxide absorbed can be calculated for each type of biomass as shown in Table B.3. The value for sugarcane juice is much lower because of the high content of water.

Table B.3. Summary of moisture content and CO_2 absorbed at the point of harvesting, on wet basis, for each type of biomass

Biomass type	Moisture content (wt%)	kg CO_2 absorbed per kg wet biomass
Corn stover	30	1.0
Willow	35	1.1
Sugarcane bagasse	48	0.86
Sugarcane juice	77	0.33

The corn, willow and sugarcane datasets can now be adjusted to include the corrected CO_2 absorbed for the quantity of crop harvested. The corn dataset is for the functional unit of 1 kg corn, to this 0.6 kg of corn stover has been added and the additional amount of CO_2 absorbed. However, the biomass energy content of the corn stover needs to be included. This is easily corrected given that the dry energy content of corn stover is ~17.6 MJ/kg and the initial moisture content is 30 wt%; therefore, the corn stover energy content is 17.6×(1-0.30)=12.3 MJ/kg corn stover (Pordesimo *et al.*, 2005; US Environmental Protection Agency, 2007). Other parameters within the corn dataset, (*e.g.* fertilizers, water) do not need to be adjusted because the corn stover is a by-product. The willow and sugarcane dataset are for the functional unit of 1 kg willow and 1 kg of sugarcane respectively, requiring no further adjustments.

Because the sugarcane bagasse and corn stover are now identified as valuable outputs from the agricultural system, allocation for these by-products must be considered. It was not possible to change the system boundaries given the inherent integration of crop (corn and sugarcane juice) growth and agricultural waste (corn stover and sugarcane bagasse). Furthermore, given the lack of information within the datasets used, it was not possible to identify relationships between inputs and outputs of the agricultural processes. Allocation of the burdens for the by-products was therefore considered. For economic allocation, the price of corn was taken as \$244/t and of sugarcane \$199/t, averaged over a five year period (2010-2014) (CME Group, 2014; UDOP, 2014). The price of recoverable sugars from sugarcane (ATR) is an industry standard used in Brazil to determine the price for sugarcane and this value was assumed to be indicative of the price of sugarcane juice. An economic value for corn stover and sugarcane bagasse is not readily available; therefore, the value of these materials was determined using their energy equivalent price in coal, given that one use of this biomass is in co-fired biomass-coal power stations. The energy contents of corn stover and sugarcane bagasse, on a dry basis, are 17.6 MJ/kg and 19.25 MJ/kg, with initial moisture contents of 30 wt% and 48 wt%, respectively (Cardona *et al.*, 2010; Pordesimo *et al.*, 2005; US Environmental Protection Agency, 2007). On average, coal has an energy content of 24 MJ and an average price (between 2010-2014) of \$96/t (World Bank, 2014). The equivalent corn stover and sugarcane bagasse economic value on this basis are \$49/t and \$40/t, respectively.

Sample calculation for corn stover price: As calculated previously, by accounting for the moisture content, the corn stover energy content is 12.3 MJ/kg. The coal energy equivalent price for corn stover is therefore: $96 \times \frac{12.3}{24} = \$49/\text{tonne}$.

Finally, it is important to realise that the moisture content of corn, corn stover, sugarcane juice and sugarcane bagasse plays a significant role in allocation by mass. Another method of allocation is to consider the carbon content. Given the secondary function of these crops is reducing greenhouse gas emissions when used as a biofuel or in deriving a biochemical, this type of allocation may become of increased importance. Carbon allocation fractions were therefore determined using the carbon balance described previously. The CO_2 absorbed by corn was found to be

1.33 kg CO_2 per kg corn (Ecoinvent Centre, 2010; PE International, 2013). Table B.4 summarises the allocation fractions using all three methods.

Sample calculation of carbon allocation method for corn stover:

For each kg of corn, 0.6 kg of corn stover is harvested. The biogenic CO_2 contained in corn and corn stover are 1.33 kg CO_2/kg corn and 1 kg CO_2/kg corn stover (wet), respectively. The carbon allocation fraction is therefore: $\frac{1\times 0.6}{1.33\times 1+1\times 0.6}\times 100=31\%$.

Table B.4. Allocation fractions for agricultural co-products.

		Allocation factor		
Crop	**Product**	**Mass**	**Economic**	**Carbon**
Corn	Corn	63%	89%	69%
	Corn stover	38%	11%	31%
Sugarcane	Juice	72%	93%	50%
	Bagasse	28%	7%	50%

B.1.3 Biomass Deconstruction and Treatment

The calculations for this process are based on a process design undertaken by the National Renewable Energy Laboratory's (NREL) (Davis *et al.*, 2013; Humbird *et al.*, 2011). Modifications to the design, described in this Section, were made to enable an analysis using a wider range of biomass compositions and to produce sugars at a higher concentration than that envisaged in the original study. Furthermore, the downstream fermentation and purification operations from the NREL studies are not included because the solution of sugars produced is not fermented but instead catalytically reformed in the hydrodeoxygenation and acid condensation process discussed later.

Figure B.2 shows the process for the deconstruction of cellulose and hemicellulose components in the biomass. The scale of operation is 104 t/h of cellulosic biomass, with moisture content as shown in Table B.2 for sugarcane bagasse, corn stover and willow, entering at stream 1. There is ~0.3% loss of biomass material in the milling process (Davis *et al.*, 2013). The milling energy requirement was estimated from the literature at 0.36 MJ/kg dry biomass; this was based on the average for hammer and disk milling, which was also within the range of other estimates (Schell and Harwood, 1994; Zhu and Pan, 2010). The biomass is first soaked in a deacetylation tank, at 20 wt% solids fraction in dilute sodium hydroxide solution, with a NaOH loading of 17 g/kg dry biomass (streams 2 and 3), heated by steam (stream 4) to 80°C (Davis *et al.*, 2013). The drained fluid in stream 5, black liquor, removes, on average, 22.5% of biomass material, all water extractives, 75% of ash, 20% of lignin, 2% of xylan, 50% of sucrose, and 88% of acetate, and is sent to waste water treatment (Davis *et al.*, 2013). The washed biomass is passed *via* stream 6 to a pre-steamer and a series of horizontal reactors for acid treatment at a solids loading of 30 wt% (Davis *et al.*, 2013). Sulphuric acid, stream 7, is added to the biomass along with steam (stream 8 and 10) to reach 100°C (Davis *et al.*, 2013). At these conditions, hydrolysis reactions occur, converting, among other reactions, 90% of xylan to xylose (Davis *et al.*, 2013).

The partially-hydrolysed biomass enters a blowdown flash tank (stream 11), controlled at 100°C. A proportion of more volatile components, ~60% of the furfural and hydroxymethylfurfural, and 28% of the acetic acid are flashed off with 22% of the water content. The vapour tops are condensed and sent to waste water treatment (stream 12). The 60% removal of furfural is significantly larger than the 30% predicted in NREL’s model (Davis *et al.*, 2013). The flash calculations were performed for furfural and acetic acid in water with Unisim R400 using the UNIQUAC fluid package. Unisim R400 did not have the binary coefficients needed to calculate interaction parameters for hydroxymethylfurfural. Instead a 60% removal was assumed due to the similarities in the structure to furfural. This assumption is unlikely to affect the end result given that there is < 0.1 wt% of hydroxymethylfurfural in the total stream composition.

In the waste water treatment unit, streams 5 and 12 are sent first to anaerobic treatment to produce biogas fuel (stream 14) followed by aerobic digestion. The waste sludge contains biomass cells (stream 15), which are dewatered and then sent to the combustor to recover energy. The anaerobic fermenters remove 89% of the chemical oxygen demand (COD), of which, 85% is converted to biogas (51% methane and 49% carbon dioxide) and 5% to biomass (Davis *et al.*, 2013). Methane is produced at 228 g/kg COD removed (Davis *et al.*, 2013). Aerobic fermenters remove 96% of the remaining COD (Davis *et al.*, 2013). The water is sent to reverse osmosis to produce brine, containing mainly sodium nitrate, which is further concentrated and assumed waste (Davis *et al.*, 2013). The treated water is recycled to the process.

The partially-hydrolysed biomass (stream 13) enters ammonia conditioning. Sulphuric and acetic acid are neutralised with ammonia in stoichiometric quantities prior to enzyme hydrolysis. The slurry is diluted and cooled with water, stream 17, to a solids loading of 20 wt%. Further cooling is required for stream 18 to reach the desired temperature of 48°C (Davis *et al.*, 2013). In enzyme hydrolysis, the NREL design suggested that a loading of 10 g cellulase protein/kg cellulose is possible while maintaining 90% conversion of glucan to glucose (Davis *et al.*, 2013). To produce the cellulase enzyme, the calculations from the NREL reports were used and scaled to the required enzyme loading (Davis *et al.*, 2013; Humbird *et al.*, 2011).

At this point, stream 20a, consists predominantly of sugars, lignin, and water. The sugars solution requires further purification, by filtration, and concentration, by evaporation, to be suitable for hydrodeoxygenation and acid condensation. If the biomass source were sugarcane juice, the hydrolysis could be avoided and so this feedstock would enter the process at stream 20b. Filtration removes impurities, such as lignin, ash, enzyme, and cellulose. The filter cake, stream 23, is combusted to produce energy.

Both types of sugar solutions after filtration, stream 22, typically contain 14-18 wt% sugars. Mechanical vapour recompression (MVR) evaporation concentrates the sugars in solution to ~57 wt% since a concentration towards the upper range of 50-60 wt% is desirable for the hydrodeoxygenation process (Blank *et al.*, 2014). The MVR evaporator reduces the steam requirements significantly while increasing electricity usage for the compression requirement. The water removed by the evaporator, stream 27, is recycled into the process. The evaporator design from the NREL report was for a sugar concentration of 46 wt% (Davis *et al.*, 2013). In order to increase the sugar concentration from 46 wt% to 57 wt%, a Unisim model was created to quantify the energy requirements. The model used both sucrose and glucose in water solution with the UNIQUAC fluid package. The energy requirements calculated from the model for a 46 wt% solution agreed within 5% to those from the NREL report. The model was then optimised for a solution at 57 wt%, stream 26, as required downstream.

The combustor is primarily used to recover energy from unconverted biomass, *e.g.* lignin in the filter cake, and from the biogas produced by waste water treatment. The model for the combustor assumes complete combustion in air. A proportion of the combustor fuel is wet solids and must first be dried, which reduces the total heat released from the combustible materials. As with the NREL design, all heat produced from combustion is used to generate superheated steam at 454°C and 62 bara (Davis *et al.*, 2013; Humbird *et al.*, 2011). The superheated stream enters a series of turbines to generate electricity. It was assumed that side streams of steam at 13 bara for high pressure steam and 4.5 bara for low pressure steam can be bled from appropriate stages in these turbines.

The biomass deconstruction and the hydrodeoxygenation and acid condensation processes are integrated for improved energy recovery. Steam, electricity and combustible waste gases are exchanged between these processes. Owing to the integration, and to avoid complicated allocation procedures for the inventory analysis, the system boundary was extended to include the hydrodeoxygenation and acid condensation processes along with the biomass deconstruction process.

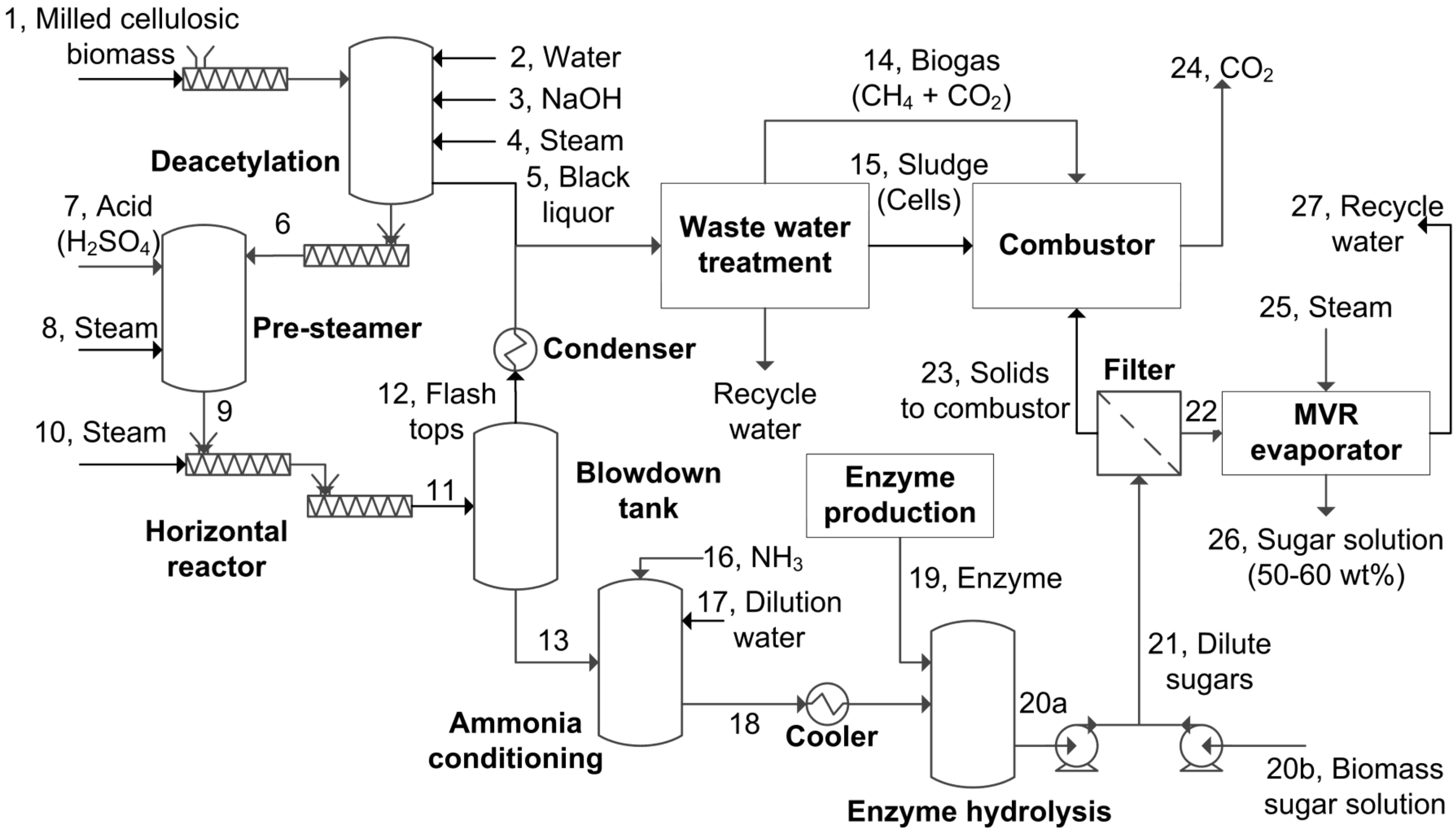


Figure B.2. Process flow diagram for the deconstruction of cellulosic biomass followed by the filtration and evaporator stages to produce a concentrated solution of sugars.

B.1.4 Sugar Reforming: Hydrodeoxygenation and Acid Condensation

Figure B.3 is an example of a hydrodeoxygenation and acid condensation process flow diagram (Blank *et al.*, 2014; Blommel and Cortright, 2008; Cortright, 2009). The concentrated ~57 wt% sugar solution from the biomass deconstruction enters this process at stream 1 and is combined with hydrogen gas, stream 2, in the hydrodeoxygenation reactor. The hydrodeoxygenation was modelled based on details in examples 31-33 of US Patent Application 2014/0051872 (Blank *et al.*, 2014). The hydrodeoxygenation reactor is a trickle bed reactor employing the sugar solution, hydrogen gas, and a solid catalyst (2 wt% palladium, 2 wt% molybdenum, and 0.5 wt% tin supported on tungstated zirconia) (Blank *et al.*, 2014). The reactor operates at 125 bara and the exothermic hydrodeoxygenation reactions give a temperature gradient from 168 to 276°C (between liquid inlet and outlet). Hydrogen gas is added to the reactor at 2.5 moles H_2 per mole of carbon (Blank *et al.*, 2014). An average product breakdown for the reactor and operating conditions is listed in Table B.5 (Blank *et al.*, 2014). Although the examples from the patent application used 60 wt% corn syrup feedstock, similar hydrodeoxygenation compositions have been shown for a variety of oxygenated hydrocarbon sugars, such as glucose, sucrose, or xylose solutions (Blank *et al.*, 2014; Blommel and Cortright, 2008; Cortright and Blommel, 2014).

Table B.5. Average product breakdown of hydrodeoxygenation with corn syrup used in this study.

Hydrodeoxygenation product	**Wt%**
CO_2 and trace CO	0.9
Alkanes	8.4
Alcohols	22.0
Ketones and aldehydes	1.1
Cyclic ethers	21.5
Cyclic ketones	0.8
Diols	6.2
Acids	1.7
Other di-oxygenates	0.4
Unreacted sugars	37.2

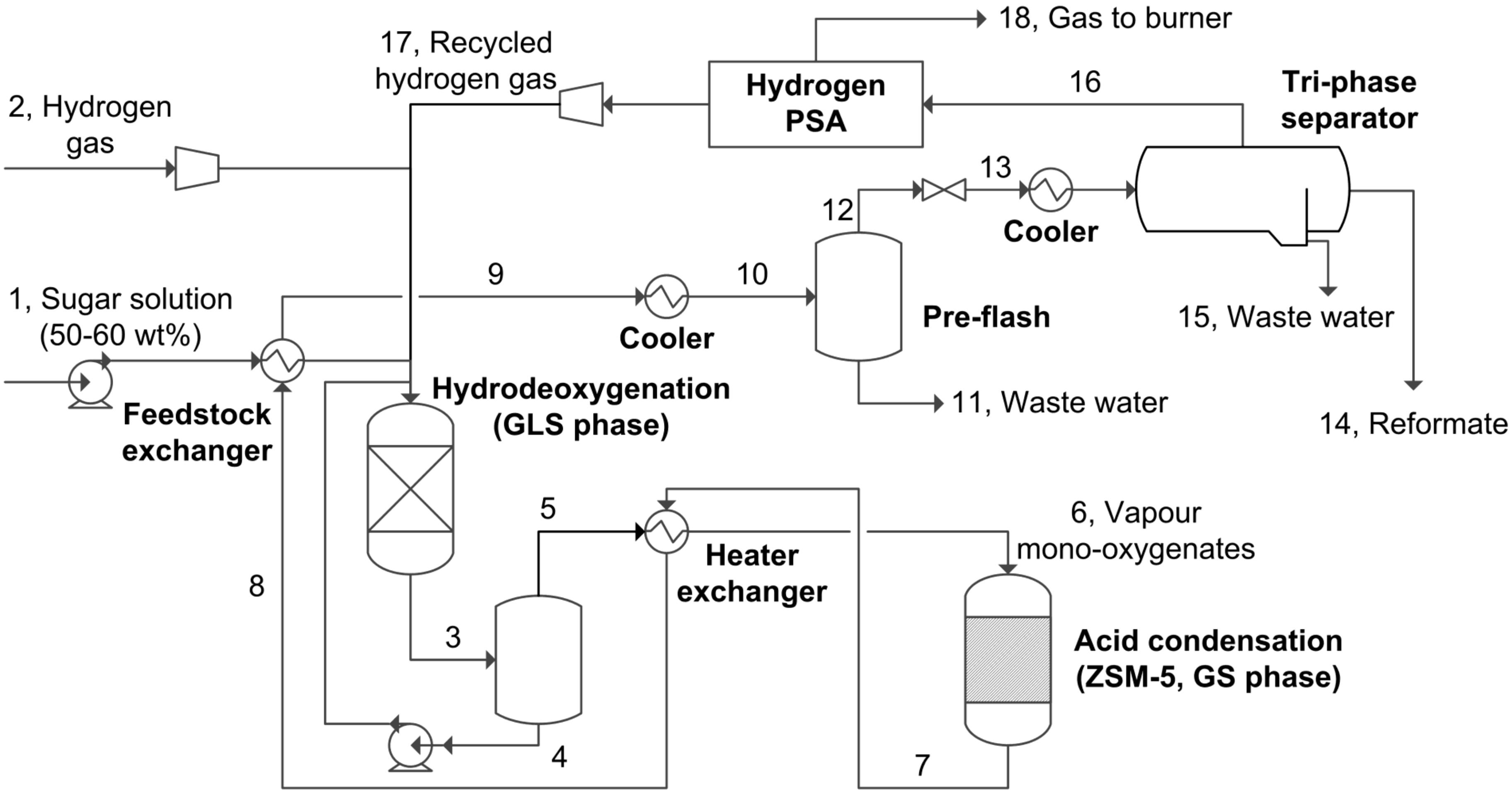


Figure B.3. Process flow diagram of hydrodexoygenation and acid condensation of a concentrated sugars solution to a reformate stream

A wide range of reactions are possible forming a range of different mono-oxygenate products, listed in Table B.5. According to Table B.5, the product from the hydrodeoxygenation reactor, stream 3, contains 37.2 wt% unreacted sugars, which remain in the aqueous phase after a flash separator and are recycled back to the reactor as stream 4. Stream 5 consists mostly of mono-oxygenates, which are sent to a heater to increase the temperature to 350°C for the acid condensation reactor (Blank *et al.*, 2014; Cortright and Blommel, 2014). The acid condensation catalyst is a nickel-modified ZSM-5 (Blank *et al.*, 2014; Blommel and Cortright, 2008; Cortright and Blommel, 2014). A series of reactions occur in acid condensation including: the dehydration of oxygenates to alkenes, oligomerisation of alkenes, cracking, cyclisation and dehydrogenation of larger alkenes to form aromatics, alkane isomerisation, and hydrogen transfer to form alkanes. An average acid condensation product breakdown is shown in Table B.6 (Blank *et al.*, 2014; Blommel and Cortright, 2008; Cortright and Blommel, 2014; Cortright, 2009). Depending on the catalysts and operating conditions, there is 15-45% conversion to CO_2 by the water gas shift reaction; a 30% conversion to CO_2 was assumed in the present Dissertation (Blommel and Cortright, 2008; Cortright and Blommel, 2014). Detailed reaction information is unavailable in the open literature, other than the product compositions shown here. The acid condensation reactor is cooled by generating high pressure steam which is sent to the biomass deconstruction process to reduce steam requirements and avoid allocation by extending the system boundary as discussed previously.

Using the composition from Table B.6, the amount of hydrogen, carbon dioxide and water formed can be calculated for the acid condensation reactor outlet, stream 7. A sample calculation for both reactors can be found at the end of this section. The downstream energy recovery and separation train was modelled in Unisim using the composition of stream 7. Stream 7 requires cooling to 163°C, heat recovery can be used to reduce the heater exchanger, feedstock exchanger and cooler duties in Figure B.3. Stream 10 contains 53 wt% water, and enters an initial flash at 30 bara, removing 75% of the water as waste water (stream 11). Product stream 12 is sent to a three phase separator at 5 bara and 30°C to produce a reformate product stream 14, residual waste water stream 15, and gaseous stream 16. Of the gaseous stream, which contains 70 mol% hydrogen mixed with light hydrocarbons, 87% of the hydrogen is recovered using pressure swing adsorption. The recovered hydrogen, stream 17, is recycled to the hydrodeoxygenation reactor. The remaining gas, stream 18, contains volatile organic hydrocarbons which are sent to the combustor for energy recovery in the biomass decomposition process, discussed previously. Although not investigated for this study, it may be economically favourable to recover some of the lighter fractions as a side product.

Table B.6. Average product breakdown of acid condensation reactor

Acid condensation products		
Carbon number	**Type**	**Wt%**
C4	Paraffins	8.0
C5	Paraffins	11.0
C6	Paraffins	9.5
C7	Paraffins	2.5
C8	Paraffins	1.0
C9	Paraffins	0.5
C5	Olefins	1.0
C6	Naphthenes	2.5
C7	Naphthenes	2.0
C8	Naphthenes	1.0
C6	Aromatics	2.0
C7	Aromatics	9.0
C8	Aromatics	19.0
C9	Aromatics	18.0
C10	Aromatics	7.0
C11	Aromatics	3.0
C12	Aromatics	2.0
C13	Aromatics	1.0
C14	Aromatics	0.5

Sample calculation for reactors:

This sample calculation uses a concentrated sugars solution produced from sugarcane bagasse. The sugars solution, 52117 kg/h, contains 31 wt% glucose, 22 wt% xylose, 4 wt% other sugars, 40 wt% water, and 3 wt% other impurities. The molar mass of glucose is 180 kg/kmol and xylose is 150 kg/kmol. The number of moles of carbon in the solution are:

$$52117 \times \left(\frac{0.31 \times 6}{180} + \frac{0.22 \times 5}{150} + \frac{0.04 \times 6}{180} \right) = 999 \text{ kmol/h}$$

A simple conversion model was used in order to model both reactors. Firstly, as described earlier, 30% of the moles of carbon entering the reactor system is converted to CO_2. The water gas shift reaction for the formation of CO_2 is:

$$CH_2O + H_2O \longrightarrow CO_2 + 2H_2$$

The remaining 70% of the carbon is converted to the range of hydrocarbon products shown in Table B.6. The generic reaction for production of hydrocarbons is:

$$CH_2O + H_2 \longrightarrow CH_2 + H_2O$$

Based on the stoichiometry and the conversions above, the balances for the overall reaction can be done:

- Amount of carbon dioxide produced $= 999 \times 0.3 = 300 \text{ kmol/h}$
- Net consumption of hydrogen $= 999 \times 0.7 - 999 \times 0.3 \times 2 = 100 \text{ kmol/h}$
- Net production of water $= 999 \times 0.7 - 999 \times 0.3 = 400 \text{ kmol/h}$

For the products shown in Table B.6, a sample calculation for the amount of butane (C4) and pentane (C5) is shown:

- Amount of butane (C4), 8% yield, produced $= \dfrac{999 \times 0.7 \times 0.08}{4} = 14 \text{ kmol/h}$
- Amount of pentane (C5), 11% yield, produced $= \dfrac{999 \times 0.7 \times 0.11}{5} = 15 \text{ kmol/h}$

B.1.5 Conventional *p*-Xylene Downstream Separation

Reformate from the hydrodeoxygenation and acid condensation process was compared with reformate from the conventional process in Table B.7. It was found that the compositions of the differently-sourced reformate streams were comparable. Furthermore, given the differences in reformate composition between the 2008 and 2013 processes, the set of blue coloured processes depicted in Figure B.1 is likely to be flexible enough to accommodate the biomass-sourced reformate.

Table B.7. Comparison of reformate composition from conventional and biomass processes.

Component		**Wt % of component**		
Carbon number	**Type**	**Biomass sourced**	**Conventionally sourced 2008**	**Conventionally sourced 2013**
C4	Paraffin	1.0	0.6	0.6
C5	Paraffin	3.7	3.0	1.8
C6	Paraffin	6.8	10.0	3.1
C7	Paraffin	2.7	2.0	5.2
C8	Paraffin	1.3	0.1	0.3
C9	Paraffin	0.7	0.0	0.0
C5	Olefin	0.3	0.0	0.1
C6	Naphthene	2.2	0.2	0.0
C7	Naphthene	2.4	0.1	0.2
C8	Naphthene	1.3	0.0	0.0
C6	Aromatic	1.5	9.3	1.0
C7	Aromatic	9.9	22.0	37.0
C8	Aromatic	23.9	25.5	36.8
C9	Aromatic	23.5	17.0	12.8
C10	Aromatic	9.4	10.1	1.0
C11+	Aromatic	8.8	0.1	0.1

B.2 Total Impact Assessment

Table B.8. Total impact assessment for the final scenarios assessed

		Scenarios				
Environmental impact	**Units**	**Conven. 2013 mod.**	**Willow reformate**	**Sc. juice + bagasse reformate**	**Sc. juice reformate + sc. bagasse electricity**	**100% sc. biomass bottle**
Global Warming Potential (100 years)	kg CO_2-Equiv.	0.087	0.059	0.056	0.011	-0.012
Eutrophication Potential	g Phosphate-Equiv.	0.041	0.22	0.16	0.12	0.14
Abiotic Depletion of Elements	10^{-7} kg Sb-Equiv.	1.1	1.6	1.8	1.7	1.8
Acidification Potential	g SO_2-Equiv.	0.28	0.42	0.49	0.54	0.61
Ozone Layer Depletion Potential (Steady-state)	10^{-9} kg CFC R11-Equiv.	1.2	1.2	1.9	2.3	2.7
Photochem. Ozone Creation Potential	g Ethene-Equiv.	0.029	0.022	0.27	0.43	0.54
Human Toxicity Potential	g DCB-Equiv.	22	17	98	144	181
Freshwater Aquatic Ecotoxicity Potential	g DCB-Equiv.	3.9	3.6	10	14	17
Marine Aquatic Ecotoxicity Potential	kg DCB-Equiv.	12	13	18	12	15
Terrestric Ecotoxicity Potential	g DCB-Equiv.	0.20	0.23	3.6	5.6	7.1