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Economic and environmental performance of renewable chemicals and materials

- a survey of the current situation

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1 Introduction

The current use of fossil fuels is unsustainable for several reasons. One is that the combustion of fossil fuels enhances the global warming induced by human activities, leading to a climate change, which will change the living conditions considerably on earth if not curbed in a near future (IPCC, 2007). Another reason why a conversion of the energy system is desirable is the reliance on a finite energy source, often imported from politically instable regions, which is problematic from an energy security point of view.

A transition to a less fossil-fuel dependent society is thus necessary. Mitigation options include amongst others: limiting the excessive use of natural resources and energy; implementing energy efficiency measures; and shifting to the use of renewable energy and materials.

In the renewable energy and material sector, the use of biomass is often highlighted as an industry of significant potential (European Commission, 2011; IPCC, 2011). Biomass can come in many different forms, including products and by-products from forestry, industry, agriculture and society. It is used for numerous purposes - food and feed production, heat and energy and material production such as in the pulp and paper industry, only to give a few examples. The chemistry sector is, however, currently almost completely dependent on fossil raw material.

Still, the use of biomass for energy and material purposes has in recent years become a controversial issue. The two most relevant indirect problems biomass use may entail are competition with food and feed production and land use changes (Di Lucia, 2011). This stresses the importance of the efficient use of biomass. One means to attain effectiveness is through the use of a *biorefinery.* The biorefinery is a multi-input multi-output system working according to the same basic concept as a conventional oil refinery. One central idea is to simultaneously produce high-value low-quantity chemicals and low-value high-quantity bulk chemicals and fuels, which gives the system both economic and environmental viability.

Currently, much research is undertaken in order to develop the production of a number of different chemicals from renewable feedstock. Previous studies (Patel et al., 2006; Hermann et al., 2007; Bozell and Petersen, 2010) have mapped the sector and highlighted some chemicals of significant importance and potential. In Hermann et al. (2007) it is argued that the substitution of fossil chemicals with renewable such could lower the emissions of greenhouse gases from the chemistry sector. Out of the chemicals investigated in these studies, ten have been chosen for further investigation in this report. Updated environmental and economic analyses are conducted based on literature studies of existing life cycle assessments and economic modelling for the economic assessment. One aim of this study is to assess the sustainability of these renewable chemicals, and to discuss their most suitable areas of application. Furthermore, the economic and technical feasibility of the production will be evaluated as well as critical factors affecting the production.

The study thus aims at giving a comprehensive overview of the current situation for renewable chemical production, including the integration of environmental, economic and technical aspects.

1.1 Aim, goal, scope

The aim of the present study is to investigate the environmental, technical and economic performance of a number of renewable chemicals, which could be produced in a biorefinery. The report is a part of a project named Biorefinery Öresund, an Interreg financed research programme. The selection of biochemicals investigated is based on studies such as Werpy and Petersen (2004) and Bozell and Petersen (2010), where a range of chemicals is selected based on economic and environmental potential. The biochemicals chosen in this study include: bioethanol, biobutanol, biosuccinic acid, 3-hydroxypropionaldehyde, hydroxypropionic acid, itaconic acid, furans, levulinic acid, polylactic acid, polyhydroxyalkanoates, 1,3-propanediol and drop-in solutions.

In order to assess the environmental performance of producing and using these chemicals, the environmental effect of their production and use will be compared to that of their fossil counterparts. After this, the environmental benefit of the different renewable chemicals can be compared internally and the benefits can also be related to other possible uses of the renewable resources utilised.

When producing chemicals biochemically, for instance, through fermentation, several parts of the life cycle may be identical (e.g. cultivation), whereas other parts may differ completely (e.g. process). It is useful to identify hot-spots in the raw material production, process, use-phase and end-of-life disposal of the chemicals – both those which all investigated chemicals may have in common, but also those which may significantly influence the environmental performance for some chemicals but are of minor importance for others. The work presented is therefore based on the following research questions:

1. *What is the environmental and economic performance of the renewable chemicals investigated in terms of global warming potential (GWP) and cost per kg? What is the environmental benefit of substituting fossil based chemicals for chemicals based on renewable material?*
2. *Which parts of the life cycle imply the greatest environmental and economic impacts? Are there certain hot spots, which are in common for all chemicals?*
3. *Do the production, use-phase and/or end-of-life disposal give rise to additional environmental effects that should be taken into account in the evaluation?*

2 Methodology

2.1 Environmental assessment

Life cycle assessment, LCA, is a method to evaluate the environmental performance of products or processes. The LCA studies may vary in terms of scope - the time frame and the geographical and technical boundaries are set according to the system boundaries set for the investigation. Guidelines for the procedure are described in an international standard known as ISO 14044 (ISO, 2006). In Figure 2.1 a schematic illustration of the involved stages is given.

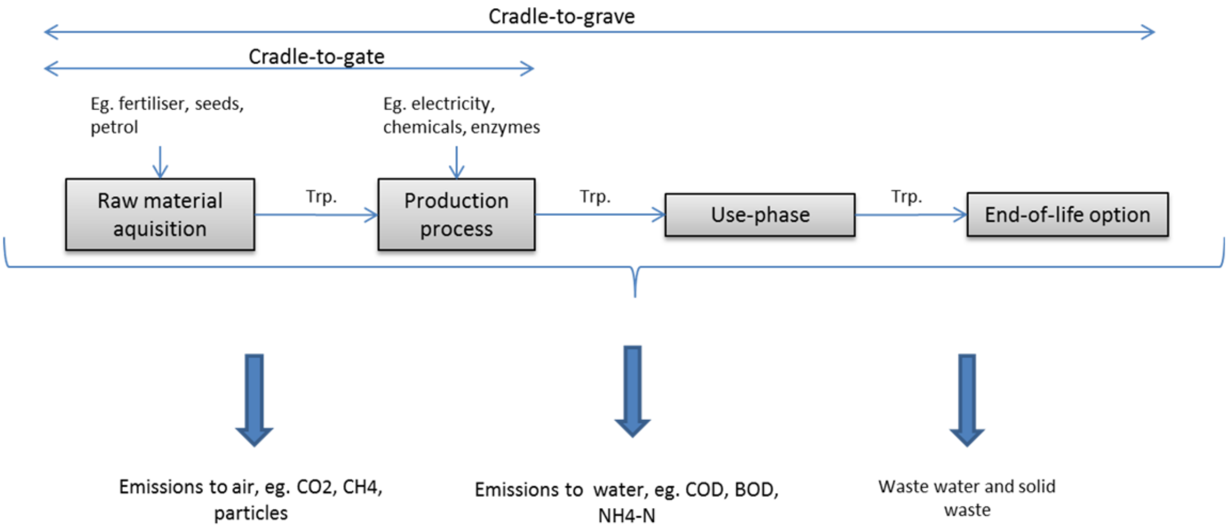

Figure 2.1. Schematic figure of an LCA system.

One example of the system boundaries for a comprehensive cradle-to-gate assessment is given in Figure 2.2 (adapted from Vink et al., 2010) showing the production of the renewable plastic polylactic acid (PLA).

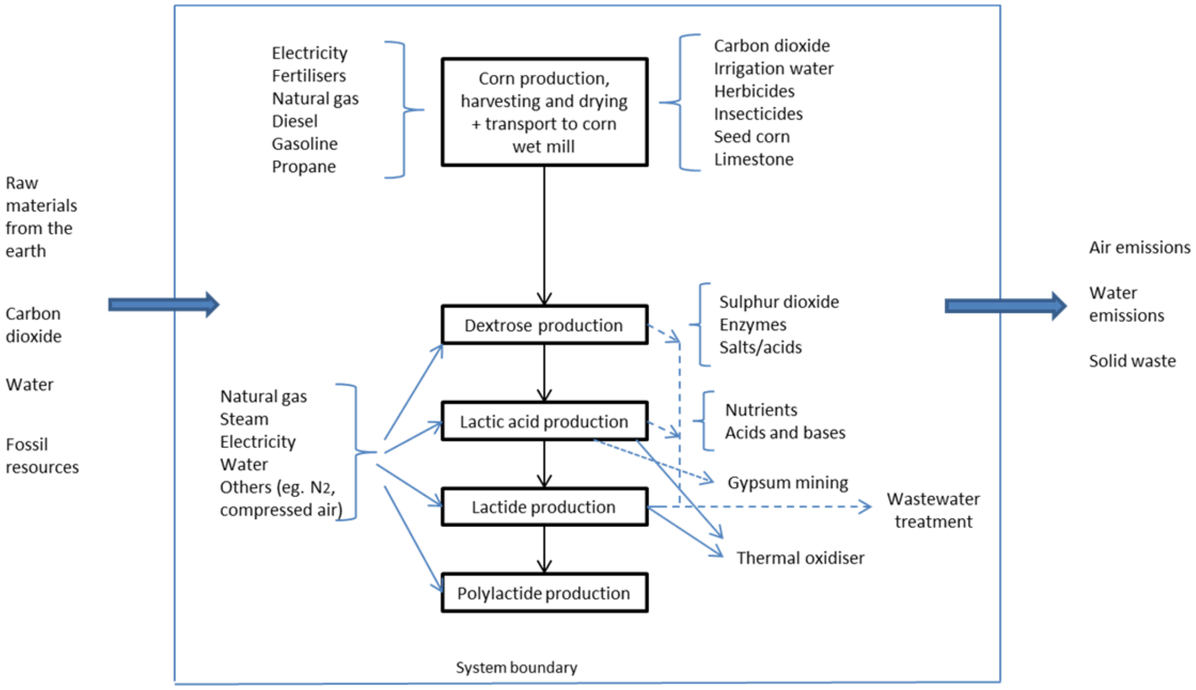

Figure 2.2. Example of a system investigated through LCA. Adapted from Vink et al. (2010).

2.1.1 Methodology

In order to investigate the environmental performance of the renewable chemicals in question, a literature review was performed targeting existing life cycle assessments of the chemicals.

The studied LCAs are often cradle-to-gate investigations, which are of use for comparison of the same chemical. What must be noted, however, is that the sustainability of the chemicals (especially plastics) may improve or be reduced significantly when the whole life cycle, from cradle-to-grave, is taken into account. This may be due to an unsuitable choice of application or end-use. For this reason, a cradle-to-gate study may not be sufficient to assess the environmental performance of chemicals; the use-phase and end-of-life option may need to be considered as well. In the current study, the cradle-to-gate GHG-emissions will be analysed quantitatively using information gathered in the literature review. The significance of the additional effects the use-phase and end-of-life disposal bring about will instead be discussed qualitatively. Also for environmental impacts other than contribution to global warming, the information is rather limited. These other impacts are seldom quantitatively presented in the reviewed LCAs and will therefore not be quantitatively analysed in the current study, they will instead be discussed in a qualitative manner. According to Hermann et al. (2007), the non-renewable energy use is a sufficient measurement of the environmental credibility since many environmental impacts are connected to this activity. It should, nevertheless, be stressed that other impacts (for example, biodiversity and eutrophication) are often of considerable importance for the overall sustainability of the system.

2.1.2 Limitations

Direct comparison of LCAs is often problematic as the scope of the studies varies in a multitude of ways. The LCAs reviewed in this study are not exceptions from this and aspects such as system boundaries, functional unit, feedstock, and electricity mix varies significantly in the investigated reports. The rather arbitrary choice of scope makes numerous results possible, making peer-review and transparency two essential factors for the credibility of the LCA. Life cycle assessment is, nevertheless, the currently most reliable and developed method of calculating environmental performance. When the authors of the LCAs show where system boundaries are set, how calculations are made and make comprehensive sensitivity analyses, interesting notes on the environmental performance of products can often be made.

2.2 Economic assessment

Economic evaluation can be used as a decision-making tool to quantitatively estimate the expected profitability of a process, alongside other criteria. Methods for a full cost assessment are extensive and require detailed information on raw material costs, equipment and location of the site. However, cost estimates should be made throughout the early stages of a project even when comprehensive specifications (or other data) are not available. Most of the products investigated in this report are less mature products, where most are not operating in commercial scale. Thus, the economic comparison is based on estimations and simplified profitability measures.

2.2.1 Methodology

This analysis is as far as possible based on the process economics that would be applicable to the Øresund region but also includes studies from various regions. The production cost for any chemical is composed of the two main categories:

- Capital cost (CapEx)
- Operating costs (OpEx)

The capital costs are mainly attributable to the equipment and facility cost, whereas the operating cost is composed of the costs for raw material, utilities (energy, etc.) and also labour and related services. Table 2.1 summarizes the main considerations used to construct the proposed economic model. In the following section a further discussion of these factors will be made.

Table 2.1 – Summary of the considerations and source of information used in the economic model. k represents the annuity factor i, the capital charge factor (or interest factor) t, the equipment economic lifetime.

Cost	Category	
CapEx	Equipment cost	Matche Inc (www.matche.com), process design software (ASPEN or SuperPro Designer)
	Other capital investment costs	Lang factor 5.0 (typical for fluid processing units)
	Annuity	From equation (2) For the base cases: k= 0.142, based on i=7% and t=10 years
	Equipment scale-up	n=0.6
OpEx	Raw materials	Market quotations, laboratory chemical suppliers
	Utilities	0.1 €/kWh (European Energy Portal)
	Waste handling	2 €/m^3
	Labour	30€/h (Eurostat)
	Supervision cost and indirect OpEx	100% of the direct labour
	Annual maintenance	10% of the annual capital investment cost.
	fixed OpEx	15% of the annual capital investment cost

Capital costs - CapEx

The total capital investment is the one-time expense for the design, construction, and start-up of a new plant. Due to inconsistencies in published reports some of the values have been modified in order to normalize the results in this report. It can also be noted that reports normally do not specify the exact type of equipment used, which introduces a source of uncertainty to the comparisons.

Fixed capital represents the capital necessary for the installed process equipment with all the accessories needed for the process start-up and operation. The foundation of a fixed capital estimate is the equipment cost data. From this information the fixed capital investment can be calculated through the application of multipliers, such as the Lang factor (see Table 2.1. In the early stages of process development, in order to obtain the total investment cost, the equipment cost is multiplied with a factor to cover the costs for all supporting equipment and facilities. Detailed information concerning common factors used can be found in standard process design literature.

To calculate the annual capital cost (depreciation cost) or cost per unit of product, the investment cost can be converted to an equivalent annual cost by multiplying the capital investment with an annuity factor, k (see Equation 1) that is based on the interest rate factor (or desired annual return on investment) and the economic life time of the facility (or depreciation rate). These factors depend on the risk of the project but also on type of financing and competing use of the capital. The interest rate factor is typically around

10% - 15% for the type of processes studied here and the typical equipment (or installation) economic lifetime, t, is 15 up to 30 years.

$$k = \frac{i}{1-(1+i)^{-t}} \text{ (Equation 1)}$$

As expected this range has a major impact on the capital costs, differing a factor 2 between the highest and lowest option. It is notable that published reports often differ widely in the assumptions on annuity rate.

The cost-capacity plot (six-tenths rule) is often applied when the effect of process scale is evaluated (see Equation 2).

$$\text{Cost of equipment B} = \text{Cost of equipment A}\left(\frac{\text{Capacity of equipment B}}{\text{Capacity of equipment A}}\right)^{n} \text{ (Equation 2)}$$

where n may vary between 0.4 and 0.9, depending on the type of the equipment being costed, the operating conditions and the investigated range. However, this short cut should only be used in a limited span of scales.

Operating cost (OpEx)

The operating cost (OpEx) consists of direct, indirect and fixed costs. Direct operating costs includes the cost of raw materials, utilities, waste management and operating labour. Indirect and fixed operating costs can be calculated from direct labour cost and/or annual capital investment cost.

Raw material cost

The cost of the feedstock has a large impact on the production price for both products that are produced in a biorefinery) as well as goods produced from fossil feedstock. In the biorefinery, as will be seen in later sections, 50-90% of total cost emanates from the raw material cost in most cases. The amount of raw material used is obtained from the process mass balances, and the cost of the most common chemicals can be obtained from the suppliers or by consulting trade journals (e.g. European Chemical News or Chemical Marketing Report).

The price of sugar as well as crude oil is critical for determining which route is more economically profitable. As can be seen from Figure 2.3, the price of crude oil has increased significantly in the last decade and maintaining a historical price above $100 per barrel in the whole of 2011. Unsurprisingly, future scenarios indicate that increasing demand in combination with a decrease or stagnation of supplies will lead to a further increase of oil prices. Forecasts for 2020 indicate prices between $120 to $240 per barrel (Benes et al., 2012). However, it should be kept in mind that projections have historically not been correct due to complex interactions of prices, demand, supply and the global economy. It would be easy to conclude that a higher cost of fossil oil coupled to a stable price for sugar would benefit a biorefinery. However, as can be seen in Figure 2.4, historically the cost of sugar has been strongly coupled to the cost of crude oil. Therefore it is not certain that the competitiveness of the biorefineries will increase on short term, even if oil prices soar. It is also interesting to note that other raw materials, such as vegetable oils, wood pulp as well as fertiliser has followed the same general trend in terms of costs, as sugar and crude oil. This of course makes definitive profitability comparisons with oil-based products difficult as this depends on both the cost of the biobased raw material as well as the price of petroleum.

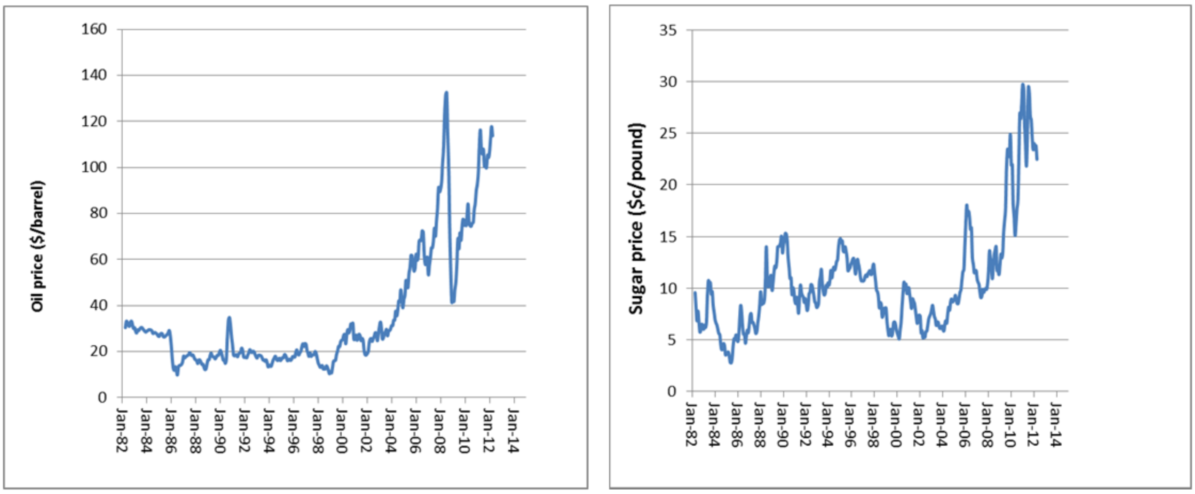

Figure 2.3. A: Historical oil price development between 1982 and 2012. B: Historical sugar price development between 1982 and 2012

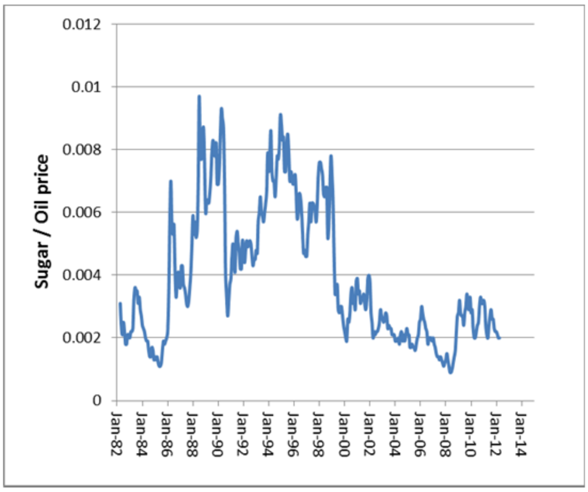

Figure 2.4. Historical relationship between sugar and oil price development between 1982 and 2012

Utility costs

Information on the utilities are often lacking in published studies and normally constitute a minor part of total cost but should be included for fair comparisons. Utility requirements, including the cost of heating and energy for agitation, can be obtained from mass and energy balances and prices can be obtained from suppliers or purchasing agents. In fermentation processes, the dominating energy-consuming operations are mixing, aeration and sterilisation. The energy necessary for mixing can be calculated using rule-of-thumb values, whereas the heat required for sterilisation can be obtained using the heat capacity for water.

Although waste treatment is usually not part of the process design and cost model, waste disposal is an important process cost that should not be disregarded. Typically wastewater treatment costs are 0.5-2 €/m^3 (depending on location), while non-hazardous solid waste disposal has a cost of around 25 €/ton.

Labour

Finally, direct labour costs can be estimated from the process flow sheet based on typical labour needs for each unit operation or by knowledge about labour requirements for the whole process. Labour rates can be obtained from the union contract, from company labour relation supervision or from local statistical institutes (e.g. Eurostat, US Bureau of Labour Statistics). Other operating costs can be calculated from direct labour costs or from annual capital investment. Supervision costs (direct operating costs) and indirect costs (including payroll overhead, quality control, royalties and plant overhead) normally correspond to 80 to 115% of the total direct labour costs. Annual maintenance (direct operating costs) including labour and material adds between 6 to 10% relative to the fixed capital investment. Fixed costs are insensitive to the production scale and include depreciation, taxes, property rents, insurance, etc., corresponding to 12 to 17% of the annual capital investment cost. The direct labour needs were determined through typical labour requirements and in discussion with industry. A value of 30€/h was assumed (based on Eurostat) in order to calculate the cost associated with the direct labour. Labour needs are dependent on the plant scale and the degree of automation. However, for processes within the same capacity range, the labour needs do not increase directly with process volume. Therefore, in this study it was assumed that labour needs did not increase with scale.

Revenue from Co-product credits

The co-product credit has also been determined by the use of the chemical price index. Some of the co-products are inorganic chemicals and the price index used is therefore applicable. However, for the other co-product credits, such as distillers grain, electricity and rapeseed meal, the price index does not give accurate prices in 2010€. The amount of electricity produced has been difficult to deduct, and the chemical price index has therefore been used, despite the ease of finding electricity prices.

2.2.2 Limitations

Evaluation of the costs in the preliminary design phases involves guesses and applications of rules-of thumb, therefore the quality and accuracy of the estimations are dependent on the skill and experience of the engineer as well as the knowledge of the actual project conditions and details. The Association for Advancement of Cost Engineering (AACE) provides a guideline to the level of detail in a cost estimate. AACE defines five estimate classes, from Class 1 (Full-Detail Estimate) to Class 5, which is a conceptual estimate. The accuracy of the estimates ranges from -20% to +100% for Class 5, down to -10% to +15% for the most detailed estimates (Class 1). Regardless of the level of detail and complexity in an economic study and in the underlying project design, a certain degree of uncertainty will always prevail. This makes it is necessary to evaluate the effect of certain modifications to the original project on the total project cost and it should be emphasized that the results obtained should not be regarded as definitive values but as guidelines that can serve as a starting point for other more detailed assessments. Conceptual studies can be used to simply and quickly assess not only if the process is a viable option, but also identify the process bottlenecks. In this way guidance for research and development can be provided to give an understanding of when or under which conditions the process will achieve commercial success.

3 Technical background

Biomass is the world's fourth largest energy source accounting for 10% of the world's primary energy need, following oil (35%), coal (25%), and natural gas (21%) (Demirbas, 2010). In fact, before the Second World War, renewable feedstock was used as standard for the production of many chemicals and materials. However, as the price of oil dropped, these technologies were abandoned for the cheaper petrochemical production. Due to the environmental concerns described in the introduction, the use of organic material for the production may, nevertheless, experience a revival. In principle, all types of biomass, cultivated plants or waste streams, can be converted by different means into chemicals or fuels.

3.1 Biomass feedstock

Presently used substrates are known as first generation feedstock; these consist of relatively easily degradable compounds such as sugars, starches and vegetable oils. They are extracted from substrates such as the grain of corn and wheat or the cane juice of sugarcane. Due to the cost and limited availability of these raw materials, processes using alternative sources, such as wood residues and straw, are being developed. However, as second generation substrates are more difficult to process they are currently not as developed as the first generation options. The main raw materials can more simplistically be divided into its precursors starch, hemicellulose, cellulose, lignin, oil and protein. From these precursors it is possible to produce a wide range of products as depicted in Figure 3.1.

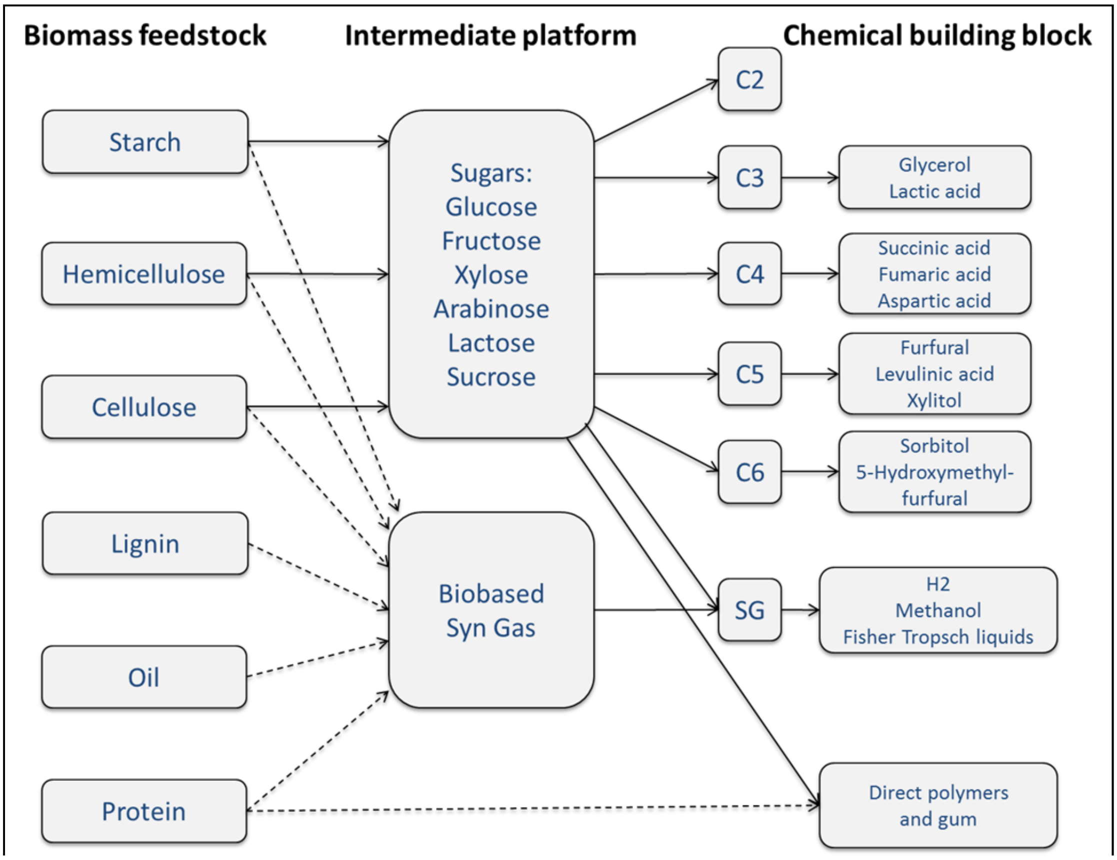

Figure 3.1: Schematic illustration of the breakdown of biomass precursors into intermediate platforms followed by their corresponding sugars (C2-C6) and syngas, as well as examples of the possible chemical building blocks that can be produced from these. Extract of Werpy and Petersen (2004).

The typical raw materials used in biorefineries are sugar, which is used to a great extent in Brazil and the US where also grain of corn is a common substrate. Typical raw materials in European biorefineries are rapeseed and wood (wood pulp is used as an indication of wood prices). The typical costs of these are given in Table 3.1.

Table 3.1: Indicative costs for raw materials used in biorefineries.

Biomass	Price range [€/kg]	Time period	Ref.
Rapeseed oil	0.9 -1.1	Last 5 years	(Index Mundi, 2012)
Wood pulp *	0.4 - 0.73	Last 5 years	(Index Mundi, 2012)
Sugar	0.16 - 0.5	Last 5 years	(Index Mundi, 2012)
Corn (maize, US)	0.1 – 0.26	Last 5 years	(Index Mundi, 2012)
Glycerol (crude)	0.3-0.4	In 2012	(ICIS price report)
Glycerol /refined)	0.5 -0.8	In 2012	(ICIS price report)

3.2 Conversion technologies

The biorefinery systems are currently classified based on raw materials, type of technology, or type of intermediate product. They can be divided into two main classes: those applying the biochemical route and those using the thermochemical route.

3.2.1 Biochemical production

The concept of the biochemical route is to utilize the capacity of microbes to convert biomass into useful molecules through the metabolism of the cell - fermentation. Some microorganisms naturally produce the desired chemical to high yields and concentrations, such as ethanol from baker's yeast. In other cases the biochemical pathways of the cells have been engineered to produce a certain chemical, or accept an unnatural substrate, or to operate at unnatural conditions. Chemicals that can be produced through the biochemical route include: alcohols (ethanol, butanol, 1,3-propanediol; 1,4-butanediol), carboxylic acids (acetic acid, propionic acid, lactic acid, succinic acid) and furans (2,5-furan dicarboxylic acid).

The biochemical production route can be divided into three main process steps: (1) Pre-treatment of raw material, (2) Fermentation, and (3) Product recovery, see Figure 3.2.

Figure 3.2. The main process steps in the production of a biochemical.

Pre-treatment

In cases where a feedstock other than sugar is going to be utilized, for instance starch or cellulose, this has to be converted into fermentable sugars. Conversion of starch into sugars is a well-established technology in the brewing industry and includes dissolving and hydrolysing the starch polymers using enzymes, such as amylases.

Converting cellulosic material into fermentable sugars is more challenging due the physical properties of the feedstock. Bottlenecks include achieving a high concentration of fermentable sugars at a low cost. Acid or base hydrolysis can be used but suffers from causing problems in the subsequent fermentation and recovery steps. Alternatively, enzymatic degradation can be used. However, the cellulose fibers are less accessible to enzymatic degradation than starch and contain other compounds (lignin) that can inhibit the enzymes. Also, to make the cellulose and hemicellulose accessible to the cellulases, the hydrolysis step has to be preceded by physical treatment (e.g. grinding, hot water treatment and steam explosion) (Zheng et al., 2009).

The pre-treatment step is often stated as being critical to the success of using cellulosic materials as feedstocks for biochemical production of chemicals. The cost of the enzymes has been a major bottleneck, but as costs are getting lower and efficiencies higher, this technology is becoming more competitive. Indeed there has been huge progress in the field, and the economy of the enzymatic hydrolysis step has been greatly improved.

Fermentation

In the fermentation a microorganism (yeast or bacteria) converts the sugars into other compounds through the metabolic network of the cell. Most fermentation processes require that air is sparged through the reactor while stirring, and that excess heat is removed from the fermenter (aerobic fermentations). Generally larger equipment gives a lower cost of equipment per produced unit (economy of scale), and therefore the size of the equipment should be as large as possible. However, the process of introducing oxygen and removing heat becomes less effective on larger scale and therefore there is a limit to the size of the equipment that can be used. Normally fermentation vessels larger than 200-300 m^3 are not being used.

For a cost efficient process a number of further parameters interact. The yield (g product/g raw material) influences the cost of the raw material per unit product, the space-time yield (g product/L*h) determines the fermentation equipment cost, and the concentration of product at the end of the fermentation (g/L) determines the equipment and operating cost of recovery (as well as fermentation).

The performance of the producing organism can be improved in different ways, either by optimising the operational conditions (media composition feed rate, temperature, aeration, etc.) or by genetically modifying the organism to enhance the metabolic routes that lead to the product and to stop (knock-out) the routes that interfer with the synthesis of the product.

Product recovery

After (or in rare cases, during) the fermentation step, the desired product needs to be separated from the rest of the components in the broth, mainly water, cells (or parts thereof) and compounds that have been co-produced by the strain (e.g. alcohols or organic acids). Separation of the cells is typically done by filtration (e.g. drum filter) assisted by filtration aids such as flocculation agents. The next main step entails recovering the product from the broth. This is typically done either by distillation (separation based on volatility), crystallisation (separation based on water solubility) or extraction (separation based on distribution between organic and aqueous phase), in which case evaporation is required to concentrate the product. The efficiency, cost and energy use of any of these technologies are strongly dependent on the concentration of the product in the broth. Normally concentration above 100 g/L is required for a cost effective separation. Further considerations include the pH of the fermentation broth. When producing organic acids, at neutral pH these will exist in the deprotonated state (negatively charged). In order to effectively separate them however, they need to be in the protonated (neutral) state. The pH at which this occurs is dependent on the pKa of the compound (for lactic acid pKa=3.9). Some companies have developed fermentations and strains that can be operated already at this low pH which means that the pH does not have to be adjusted in the recovery stage, saving money and avoiding the formation of waste.

Although developing an efficient protocol and strain for producing a chemical is a task that takes skill and time, it has been demonstrated in a number of cases. For instance, several different companies have recently developed cost competitive processes for lactic acid and succinic acid.

3.2.2 Thermochemical production

Using the thermochemical route, synthetic gas or bio-oil is produced through gasification or pyrolysis of biomass, respectively. In syngas production, the biomass feedstock is heated up with a limited amount of oxygen present (BACAS, 2011, Diltz et al., 2011). The synthetic gas consists mainly of H_2 and CO and it is a versatile feedstock, which can be used, both in the chemical industry and for fuel production (Van Dam et al., 2005). Bio-oil is produced by heating up the biomass in absence of oxygen. After clean up, conditioning and stabilisation, the bio-oil can be used in a conventional refinery. Challenges for both technologies include improving the cleaning of the product and developing efficient catalysts for the up-grading processes (BACAS, 2011). A disadvantage of this approach is that large amounts of energy are needed for the production of the syngas (Bludowsky and Agar, 2009).

3.2.3 Combined approaches

In Cherubini and Strømman (2010), the potential maximum production of biofuels and biochemicals from different types of lignocellulosic feedstock is calculated. Three different routes of production are simulated: the biofuel oriented, the chemical oriented and the gasification biorefinery. The results from the calculations show that, for instance, 0.33 kg of bioethanol, 0.06 kg of the platform chemical furfural and 0.17 kg of Fisher Tropsch-diesel can be produced from 1 kg of softwood. The bioethanol is produced from the C6 polysaccharides of the material; the furfural from the C5 polysaccharides and the FT-diesel is obtained through gasification of the lignin part. The mass conversion efficiency of the process is 56%, whereas the carbon and energy conversion efficiencies are 70% and 82%, respectively. Since a significant part of the mass is lost (as renewable CO_2) while a great part of the energy remains in the products, the conversion can be regarded as a means of concentrating the energy in more energy-dense products. Another conclusion from the investigation is that feedstock and products containing larger amounts of oxygen are less appropriate to use, whereas the amount of hydrogen present in the substrates is a limiting factor (Cherubini and Strømman, 2010).

3.2.4 Available information on process performance

Table 3.2 shows available information on process performances.

Table 3.2. Available information on process performances.

	Yield	Concen-tration	Productivity	References
Bioethanol	75 L/ton of sugarcane (direct conversion) 27 L/ton of corn (conversion into sugars with enzymes)	100 g/L (Patel et al., 2006)	Batch process: 1.8-2.5 g/L·h Continuous process with cellrecycle: 30-51 g/ L·h	Kosaric et al., 2012
Biobutanol	25-26 kg/100 kg corn mash	20 g/L (Ramey, 2004)	4.5 g/L·h (Ramey, 2004)	Hahn et al., 2012
Furfural	50% based on pentosan	58 g/L		Hoydonckx et al., 2012 Zeitsch, 2000
HMF	53% based on fructose			Hansen et al., 2009
FDCA	98% based on HMF 25% based on fructose			Gallezot, 2012 Gallezot, 2012
Levulinic acid	60% based on cellulosic material			Gallezot, 2012
Succinic acid	88% based on glucose	80 g/L	1.8 g/L·h	Patel et al., 2006
Lactic acid	85-95% based on the sugars used	160 g/L	5 g/L·h	Chahal and Starr, 2012 Patel et al., 2006
3-HPA	93%	108 g/L	21.6 g/L·h	Krauter et al., 2012
Sorbitol	99.5% based on glucose 95% based on starch.			Gallezot, 2012 Gallezot, 2012
Xylitol	Up to 98% based on xylose	38 g/L		Gallezot, 2012 Bozell and Petersen, 2010

3.3 Chemicals produced in Biorefineries

A large number of chemicals can be produced through the biorefinery. The most important compounds can be categorized as either fuels/platform chemicals or monomers/plastics.

3.3.1 Fuels and platform chemicals

Through further processing of the compounds listed in figure 3.1, all chemicals that are produced from mineral oil in a conventional refinery can be produced in a biorefinery. Chemicals that can serve as a starting point to other chemicals are often called platform chemicals. One such platform chemical is ethanol, which is typically seen as a fuel. Production of this type takes place in Brazil where Braskem produces renewable polyethylene from sugarcane ethanol. Plans are to increase the production to include renewable PP (Braskem, 2012). Renewable chemicals or plastics such as these are known as "drop-in solutions" since they are identical to their fossil alternatives, the only difference being their biomass origin.

An alternative platform is the thermochemical route; one example of this is the gasification of a suitable feedstock (for example wood or plastic waste), to produce syngas which can be further processed to form intermediates such as ethanol, methanol or dimethyl ether (DME), which can thereafter be used for the production of polyolefins (Nouri, 2006). Further, Novomer has developed a technology where CO_2 or CO can be used in combination with conventional feedstocks to produce various chemicals (polyols, polymers, acrylic acid, butanediol and succinic acid), using proprietary catalysts. CO_2 or CO can constitute up to 50% of the feedstock (Novomer, 2010).

Bioethanol

Bioethanol is the most widely used biofuel globally. The production takes place mainly in the US and in Brazil, in 2007 in quantities of 23 and 21 billion litres, respectively (Morschbacker, 2009). Bioethanol is produced primarily from sugarcane in Brazil and from corn in the US and is also a key building block in the chemical industry by dehydration to ethene. Market prices are subject to fluctuations in raw material prices and supply vs demand, but have been varying in the range of 0.45-0.65€/L (EOF – Ethanol, 2011).

Bioethanol is conventionally produced through the fermentation of sugars. However, extensive research and development is conducted focusing on the use of cellulosic material as primary feedstock, known as second-generation bioethanol. Pilot-scale projects have shown promising results and two large-scale production facilities are under construction. In Crescentino, Italy, a factory with a production capacity of 49 million litres per year is under construction, estimated to start operating in the middle of 2012. The facility is run by *Beta Renewables* and wheat straw and Arundo donax (a non-food cellulosic crop) will be used as feedstock (Beta Renewables, 2012). Another large-scale facility (76 million litres/year) is under construction in Kinross, Michigan, US, and it is estimated to start production by the end of 2013. The companies *Mascoma* and *Valero* have started a joint venture to construct and operate the factory. *Mascoma* has developed a process with which the substrate is both hydrolysed and fermented, known as the proprietary consolidated bioprocessing technology platform. With this technology it is possible to use lignocellulosic material as feedstock, in this case hardwood pulpwood (Mascoma, 2011).

Biobutanol

Butanol is an alcohol mainly used as a solvent in paints and surface coatings (Patel et al., 2006), but it can also replace fossil fuels when used as a vehicle fuel (Wu et al., 2007). Butanol is conventionally produced through the Oxo process in which petrochemical propylene is reacted with synthetic gas (Wu et al., 2007). Biobutanol, on the other hand, can be produced through fermentation using anaerobic bacterial strains, the fermentation is known as ABE-fermentation (as by-products include acetone and ethanol). This means of production was applied in large scale until the middle of the 20th century when it was abandoned for the more economic petrochemical production. Butanol has some advantages over ethanol as a fuel; it has higher energy density and can therefore be blended into gasoline to a greater extent than is possible with ethanol. It can be transported in the same pipeline systems as gasoline and when combusted it releases less amounts of volatile organic compounds than both ethanol and gasoline

(Swana et al., 2011). One drawback, however, is that it has a lower octane number than ethanol and gasoline. Also, the high viscosity of butanol can make certain process operations more energy demanding than for other fuels (EPA, 2010). A great barrier for the production of biobutanol is the toxicity of the butanol to the microorganisms that produce it. For this reason, the concentration of butanol in the fermentation broth is kept low which makes the extraction energy intensive and costly (Ezeji et al., 2003). Research efforts are made to develop a bacterial strain that mainly produces biobutanol by "knocking-out" the genes that code for enzymes, which produce ethanol and acetone (European Biofuels Technology Platform, 2011).

Another means of producing biobutanol is through microbial production of isobutyraldehyde using engineered cyanobacteria and CO_2 as feedstock. The isobutyraldehyde can subsequently be converted to isobutanol. In lab-scale, high productivities of isobutyraldehyde have been obtained. The technology is interesting as it is a means of recycling CO_2 without the need to defunctionalise biomass (Atsumi et al., 2009).

The biobutanol production sector is developing rapidly and construction of facilities is planned at various locations in the world. For instance, BP and DuPont have started collaboration and intend to produce biobutanol (Butamax™) using lignocellulosic feedstock in the future. A demonstrational plant is operating in Hull, UK, where first generation feedstock is used (BP and DuPont, 2012). Gevo is another company that develops the commercial production of biobutanol. With Gevo technology, existing bioethanol plants are retrofitted to produce biobutanol – the first example is the conversion of a former bioethanol plant in Luverne, Minnesota, US (Gevo, 2012). As a fuel, the expected market price is low, about 0.5 €/L (Pfromm et al., 2010).

3.3.2 Monomers and plastics

A large portion of the mineral oil used for making chemicals is used for producing plastics and polymeric coatings or fibres. Multifunctional compounds such as succinic acid, lactic acid or 1,3-propanediol, can be used as monomers for polymers. Also compounds containing unsaturations, such as acrylic acid and fumaric acid are used for these means. Bioplastics currently occupy a modest part of the plastics market, 0.4% of the total plastics consumption. The low level of development is one of several reasons why renewable plastics are not economically competitive with their fossil alternatives in most cases. This may, however, change if the price of oil increases and/or if lignocellulosic feedstock can be used. Bioplastics will, moreover, show a greater competitiveness when the industrial biotechnology and the polymer-blend technology develop. The sector is expected to grow significantly as the biobased monomers become cheaper and more available: already a 30% increase per annum is seen (Ravenstijn, 2010).

Biosuccinic acid

Succinic acid is currently used for a wide range of products including pharmaceuticals, coatings, polymers and resins (Cornils and Lappe, 2012). Among the largest emerging applications is for the production of "green" 1,4-butanediol (BDO) (Patel et al., 2006), a chemical widely used in a range of applications including the production of engineering plastics, Lycra (spandex) fibres and solvents. The estimated annual production is around 1.4 million tonnes a year. Combining BDO and biosuccinic acid also opens up the possibility of greener biopolymers, such as polybutylsuccinate (PBS), which is used in biodegradable packaging films and disposable cutlery (ICIS, 2012). Succinic acid is currently only a niche product, with 30,000–40,000 tonnes produced per year and with a historical cost $3-$5 per kilo. However, the production is expected to grow to 180,000 tonnes by 2015 as biobased routes bring costs down to around $1.5 per kilo, transforming biosuccinic acid from a specialty to a commodity chemical.

Succinic acid is petrochemically produced through catalytic hydrogenation of maleic anhydride or maleic acid, but it can also be produced by means of fermentation. In the fermentation, bacterial strains can be used that either specifically produce biosuccinic acid or, for instance, *E.coli* that produce biosuccinic acid as well as other products (Patel et al., 2006).

At least five industrial groups are developing commercial capacity for biosuccinic acid-production - using fermentation of renewable feedstock such as sugars by microorganisms. *Reverdia* (a joint venture between *DSM* and *Roquette*), *Myriant* (US), *BioAmber* (a joint venture with *Mitsubishi*), and *BASF* together with *Purac* are all starting up facilities with a production volume between 10,000 and 25,000 tonnes per year, in 2012 and 2013 (ICIS, 2012). *Reverdia* claims to have developed a superior process based on low pH yeast fermentation that simplifies DSP and generates less waste.

Lactic acid

Polylactic acid (PLA) is currently one of the most widely used bioplastics, mainly used in food, polymer, and industrial applications (Chahal and Starr, 2012). It is biodegradable under industrial composting conditions (NatureWorks, 2012a). In the biobased production of PLA, dextrose is fermented, forming lactic acid. The lactic acid is then converted to lactide, which undergoes a ring-opening polymerisation, producing the final product: PLA (Vink et al., 2007). Lactic acid exists in two stereo-isomers: L(+)- and D(-)-lactic acid. The production of the former isomer is the more mature of the two why PLLA is the most common form of PLA (Groot and Borén, 2010).

Currently, commercial production of biobased PLA takes place in a facility built and operated by the company NatureWorks situated in Blair, Nebraska. The production capacity at the site amounts to 140,000 tonnes of PLA and 180,000 tonnes of lactic acid per year (Vink et al., 2007). Other actors include Purac, that operates a lactic acid plant in Thailand (Groot and Borén, 2010). A plant for producing lactide has been constructed at the same site, this was ready for operation in the second half of 2011. Moreover, plans exist for future PLA production, the facility is expected to start with an initial capacity of 10,000 tons per year but will be capable of expanding to 100,000 tons (Purac, 2010). The price reported for 88% technical grade is around 1.2-1.4€/kg (Sikder et al., 2012). Aside from the mentioned producers further actors, such as *Archer Daniels Midland Company*, are also working towards developing lactic acid based products.

3-hydroxypropionaldehyde - 3-HPA

3-HPA (together with HPA-hydrate and HPA-dimer: ”the HPA system”) is used for food preservation purposes as well as for chemical and polymer production. It can, for instance, be used as a precursor in 1,3-propanediol, acrolein and acrylic acid production. 3-HPA can be produced through fermentation using renewable feedstocks, for instance, glycerol. Six strains of bacteria have been found to convert glycerol to 3-HPA through a one-stage enzymatic catalytic process. High yields of 3-HPA have been reported by the fermentation route compared to the petrochemical production. The toxicity of 3-HPA to the bacteria is, however, a constraint in the production (Vollenweider and Lacroix, 2004) although a recent study by Krauter et al. shows that toxicity can be reduced when using the scavenger carbohydrazide (2012). In the study, *Lactobacillus reuteri* was used for the fermentation of glycerol and the process was optimised, giving exceptionally high volumetric productivities of 3-HPA (26 g/L*h) (Krauter et al., 2012).

Hydroxypropionic acid – 3-HP

By using genetically modified bacterial strains, 3-HP can be produced using either glucose or glycerol as feedstock. Another potential pathway is autotrophical production of 3-HP using CO_2 and water as starting substrates (Jiang et al., 2009).

Polymers of hydroxypropionic acid (3-HP), for instance polyhydroxypropionic acid [P(3-HP)], are interesting as replacements for conventional fossil polymers. Compared to other biopolymers, P(3-HP) has the advantage of lacking a side-chain methyl group, which makes its molecular structure strong. It can replace propylene in the production of various high-volume chemical intermediates such as 1,3-propanediol, 3-hydroxypropionaldehyde and acrylic acid (Jiang et al., 2009). Acrylic acid is a high-volume chemical that feeds into a broad range of products. One of the main applications is in the manufacture of superabsorbent polymers widely used in baby diapers. Acrylic acid is also used in adhesives and coatings. The annual global market volume of acrylic acid is around 4.5 million tons. *Novozymes*, *BASF* and *Cargill* have entered a partnership intending to produce acrylic acid via 3-HP (Novozymes, 2011; BASF, 2012).

Itaconic acid

Polymers based on itaconic acid are suitable for replacement of polymers such as acrylic or methacrylic acid. Other fields of application include the use in adhesives, coatings, thickeners and in synthetic fibres, or it can be used as a co-monomer in resins production (Willke and Vorlop, 2001).

Itaconic acid can be produced through fermentation using, for instance, the fungi *Aspergillus terreus* (Okabe et al., 2009). The metabolic pathway is similar to that of citric acid (Brämer and Steinbüchel, 2004). The potential production is significant (Zwart, 2006) but the technology must develop further as the biochemical production is currently more expensive than the petrochemical production, due to low product yields from the fermentation (final concentration: 90 g/L, yield: 86%). Research to improve this process is undertaken at, for instance, the *Johann Heinrich von Thünen-Institut* in Germany (vTI, 2012). In the production of itaconic acid, xylose, a five-carbon sugar, may be used as feedstock (Zwart, 2006).

1,3-propanediol – PDO

1,3-propanediol (PDO) can be produced through fermentation of either glycerol or glucose, where the latter technology is the one currently used for commercial production. A third production route also exists: fermentation of glucose in a two-stage process with mixed bacterial cultures. This technique is, however, at an earlier stage of research than the other two alternatives (Patel et al., 2006).

In the fermentation producing bio-PDO a bacterial strain specially developed for the production of PDO is used (Kurian et al., 2005; DuPont Tate & Lyle, 2012). Examples of commercially manufactured renewably sourced PDO products are Sorona®, consisting of 37% plant-based material (DuPont, 2012), Susterra® and Zemea® which are completely renewably sourced (DuPont Tate & Lyle, 2012a). Sorona® is a fibre manufactured by DuPont in Kinston, South Carolina, and in Jiangsu, China. It contains terephthalic acid or dimethylterephthalate apart from PDO and is thus a non-biodegradable polyester known as PTT, polytrimethylene terephthalate (Patel et al., 2006). Major areas of application include the use in textiles and carpets (DuPont, 2012) but it can be also be used as a non-biodegradable plastic. Its properties can be compared to those of Nylon 6 (DuPont, 2012) and PET (Kurian, 2005). Zemea® and Susterra®, known as bio-PDO, are produced by DuPont Tate & Lyle in Loudon, Tennessee. For the Susterra® production, corn is used as feedstock and the product is refined to a purity of 99.7%. Means of application of Susterra® include use as anti-freezing and cooling agent and as heat transfer fluid (Miller, 2010), but it is also used for production of polymer resin. Zemea® is mainly used for production of cosmetics, personal care, laundry and cleaning products (DuPont Tate & Lyle, 2012b).

1,3-PDO can also be produced with glycerol as feedstock. Through the fermentation, 3-HPA is formed (described above). 3-HPA is thereafter reduced to 1,3-PDO. High yields have been reported using this route, but so far it has not been used for commercial production (Vollenweider and Lacroix, 2004). Jin et al. (2011) also found that the use of hemicellulosic hydrolysates as co-substrates in the fermentation of glycerol increased the production of 1,3-PDO, compared to the production using solely glycerol as feedstock.

Polyhydroxyalkanoates - PHAs

Out of the polyester group PHAs (polyhydroxyalkanoates), PHB (polyhydroxybutyrate) is the most common form. It is a polymer with properties similar to those of synthetic polymers, for example, polypropylene (Harding et al., 2007). PHB degrades relatively fast; in 200 days 80 % of its original mass is lost (Biocycle, 2012b). PHAs are naturally occurring polymers, used as energy and carbon reserves in granules in plants or bacteria. The polymers are produced by various bacteria under conditions when nutrients are limiting but a carbon source is available (Houmiel et al., 1999; Khanna and Srivastava, 2005). The polymer can be produced by fermentation and subsequent cell disruption, washing and drying (Gerngross, 1999). This technology is described in the LCAs studied later in this report.

The development of PHB production technology has been relatively slow due to difficult and costly production methods and poor mechanical properties of the product. PHB degrades during melting processes and the material is known to be crystalline and brittle. With additives (for instance, plasticisers or nucleating agents) these undesirable effects may, however, be reduced. When used in composites, the mechanical properties can be enhanced by improving the coupling between the polymer and the filler through, for instance, surface treatment of the materials (Pietrini et al., 2007).

PHB is currently produced commercially by Telles at a facility in Clinton, Iowa, where corn is used as feedstock. According to Telles, their product Mirel is biodegradable to a greater extent than other non-starch bioplastics, making home composting possible (Telles, 2012). Also in Brazil, Biocycle are developing the technology of PHB production, where sugarcane is used as feedstock. A 3,000 ton/year production facility is planned to operate soon (Biocycle, 2012a). In Sweden, AnoxKaldnes are performing research on the possibilities of PHA production with waste-water used as feedstock. With this technology, the waste-water treatment plant could be seen as a combined waste facility and plastic production factory (AnoxKaldnes, 2006).

Polyols

Polyols such as mannitol, sorbitol and xylitol can be used for food, pharmaceutical and cosmetic applications (Schiweck et al., 2012) (Schiweck et al., 2012).

Thermoplastic starch and protein

Bioplastics can also be produced without defunctionalising the organic feedstock into sugars suitable for fermentation. Thermoplastic starch is formed when the starch (extracted from, for instance, corn or potato) is heated up and mixed with a plasticising agent, for example, glycerol (Barker and Safford, 2009). Also the protein part of organic feedstock can be used for plastics manufacturing. With certain chemical additives, the molecular structures of the protein are altered, making extrusion and moulding possible. The use of wheat gluten is one example of this technology as is the utilisation of protein derived from blood residues from the meat industry. The production of the latter is described in Bier et al. (2011b), where the patented Novatein thermoplastic protein processing is studied. Thermoplastics have properties similar to low density polyethylene (Bier et al., 2011b) and can be used for applications such as disposable cutlery, packaging, mulch film (for vegetable cultivation) and plastic bags (Barker and Safford, 2009).

Levulinic acid

Levulinic acid (LA) is a chemical with several uses such as anti-freeze agent, solvent, textile-dye and resin (Chang et al., 2007). It can also be used as the precursor for the production of various chemicals such as pyrrolidones, lactones, levulinate (Bozell and Petersen, 2010, Klingler and Ebertz, 2012). Moreover, if reacted with phenol, LA can be used to replace Bisphenol A which is used for the production of epoxy resins, polycarbohydrates and polymers. In lab-scale, levulinic acid has been produced using the cellulosic weed known as water hyacinth as feedstock (Girisuta et al., 2008).

LA is one of the organic acids which are formed from the acid-catalysed hydrolysation of cellulosic plant material (Girisuta et al., 2008). It can be produced in a two-stage continuous process where the biomass feedstock is firstly hydrolysed in a heated reactor containing mineral acid, and hydroxymethyl fufural is produced. This compound is thereafter hydrolysed further, at a lower temperature, forming levulinic acid (Chang et al., 2007). The company *La Calorie* is producing levulinic acid commercially in Caserta, Italy. In the facility, which has the capacity of producing 3,000 tons/year, bagasse from the local tobacco industry and cellulosic paper mill sludge are used as feedstock. The technology employed for the production is developed by the company *Biofine Renewables* (Ritter, 2010). Currently the approximate market price lies in the range of 6.5 – 9.5 €/kg (Rackemann et al., 2011; Patel et al., 2006).

Furans

Furfural is a versatile platform chemical, which is the base for production of many furans (Xing et al., 2011). It is currently used as an extractant for aromatics from lubricating oils, purification solvent for C4 and C5 hydrocarbons, reactive solvent and wetting agent (Hoydonckx et al., 2012). HMF is used as a precursor in the production of special phenolic resins (Lichtenthaler, 2012; Patel et al., 2006) and as a building block for further derivatization such as FDCA, 5-hydroxymethyl-furoic acid, furandialdehyde, 1,6-furandiol, 1,6-furan diamine, tetrahydrofurandimethanol and levulinic acid, typically used as building blocks for bulk polyesters and polyamides (Patel et al., 2006). As for itaconic acid, xylose can be used as feedstock for the production of furfural, furfuryl alcohol and 2-hydroxymethyl tetrahydrofuran (Zwart, 2006). Furfural can also be used directly as a pesticide or as an extractant in the production of, for instance, lubricating oils and diesel fuels. Further feedstock includes pentose-rich waste biomass such as corncobs, cottonseed hull bran and bagasse as well as from birch wood (Patel et al., 2006). Furfural is not produced through fermentation but rather by chemical means. Firstly, the biomass is hydrolysed in aqueous phase using a diluted sulphuric acid. After this, the pentoses are dehydrated to form furfural. The furfural is then separated from the liquid through steam stripping. Relatively low yields are currently obtained (55%) due to difficulties in purifying the furfural from by-products such as alcohols and organic acids (Patel et al., 2006); the estimated market price is around 1€/kg (Yemiş and Mazza, 2012).

4 Environmental impact of biochemicals

The production of renewable chemicals using industrial biotechnology has previously been assessed from an environmental point-of-view. Based on life cycle assessments made with a generic approach, Hermann et al. (2007) found that significant GHG-emission reductions would be possible if certain fossil bulk chemicals were substituted with renewable alternatives. The paper is based on the comprehensive study known as the BREW-report (Patel et al., 2006). Although the aim of the current report is similar to that of the BREW-report the scope differs. Here the goal is to point out parts of the life cycles or processes that may contribute significantly to the environmental performance. This report can also be regarded as an update of the state of the renewable chemical production field or as an "Encyclopaedia" of existing LCAs. The descriptions of the investigated LCAs had to be limited in order to fit the scope and the reader is referred to the complete studies for more comprehensive information. At the end of this section a table can be found, presenting the contribution to global warming for the investigated chemicals.

4.1 Renewable platform chemicals

4.1.1 Bioethanol

As bioethanol is the most developed and most widely used biofuel, comprehensive reviews of LCAs made have already been made. In Von Blottnitz and Curran (2007), 47 reports are reviewed and it is suggested that sugarcane-based ethanol produced in tropical countries should be manufactured (with cautious expansion of the cultivated land); that the use of lignocellulosic feedstock should be investigated further; and that more research is needed to evaluate the use of grasses as feedstock (Von Blottnitz and Curran, 2007).

Owing to a number of preferential conditions, the energy balance for sugarcane ethanol is better than that of corn ethanol - 1:9 compared to 1:1.5 (Morschbacker, 2009)[1]. The advantage is owing to several reasons. Firstly, the growing season in the tropical climate of Brazil is long which makes it possible to harvest four times a year. Moreover, the fermentation of the sugarcane juice takes less time than other types of fermentation and finally, both the by-products from the cultivation and from the distillation can be utilised. The lignocellulosic part of the sugarcane, the bagasse, is used for internal heat and electricity production while the waste product from the distillation, the stillage, is used for fertilisation and irrigation (Morschbacker, 2009). The utilisation of (parts of the) corn stover for internal energy production in the corn ethanol production system could improve the GHG-balance of corn-based ethanol (Kim and Dale, 2005). This is, however, not common practise today.

The environmental performance of bioethanol used as vehicle fuel has, however, been heatedly debated during the last couple of years (see, for instance, Ahlgren and Börjesson (2011) for a comprehensive review of the differing results, or the discussions in Searchinger et al. (2008) and Mathews and Tan (2009)). The issue is complex, and results may vary significantly depending on what type of system is studied. The discussion is important for the renewable chemistry sector also since it is based on the same fundamental question: the validity of claimed environmental superiority. In

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[1] The energy balance for off-shore oil from the Mexican Gulf is 1:10 - 1:25 in the current situation, having decreased from 1:100 in the 1930s (Gately, 2007).

Börjesson (2009), the complexity is illustrated through the example of bioethanol produced from wheat in Sweden. A complete LCA from cradle-to-wheel is made (including cultivation, processing of raw material, and production of bioethanol) showing that the current Swedish wheat ethanol production and use give an 80% reduction of GWP compared to petrol. As comparison, the Brazilian sugarcane ethanol gives an 85% reduction of GWP and the US corn ethanol gives a 25% reduction of GWP. However, a comprehensive sensitive analysis shows that, depending on various factors, the environmental performance may deteriorate (or improve) significantly. Four main factors are identified which influence the result to a great extent: the efficiency of the cultivation and the emissions of nitrous oxide connected to this stage (both from soil and from production of fertiliser); direct land use change (dLUC) - the type of land replaced by the cultivation (organic soil carbon changes); the chosen method for allocation of by-products; and the type of energy source used in the ethanol plant. Depending on different conditions in these areas, the environmental performance ranges from a 97% reduction (a future scenario where system expansion is used to give credit for the by-products draff and straw, N_2O emissions are avoided in the cultivation and the process is streamlined, among other things) and a 350% increase when cultivation takes place on former peat land (Börjesson, 2009).

Also in Kim and Dale (2009), the difference in environmental performance of bioethanol production is investigated. The result varies depending on the location of the production and the farming practice employed. The 40 biorefineries included are all located in the corn belt of the US and, accordingly, the feedstock used is corn. The study is a cradle-to-gate investigation and the functional unit is one kg of biobased product. System boundaries include the cultivation of feedstock, the biorefinery production and the upstream processes and products used. Direct land use changes are included in the study and indirect land use changes are simulated and discussed in a sensitivity analysis. Here, the effect of different tilling-practises is also investigated. System expansion is used to deal with the displacement effect of the by-product DDGS (Distillers' Dried Grain with Solubles). This is assumed to replace corn grain, soybean meal and nitrogen in urea. The result of the study shows that the environmental performance of the bioethanol production varies significantly depending on location and farming practice, the GWP varies between 1.1-2.0 kg CO_2-eq./kg bioethanol. The two sources contributing most to the GWP are N_20 emissions from soil and use of natural gas in the bioethanol production. In order to improve the cultivation system winter cover crops can be grown. This reduces soil N_2O emissions, increases the soil carbon content and, additionally, reduces the leaching of soluble nitrogen to adjacent waters. Furthermore, the planting of cover crops would reduce the risk of decreasing the soil carbon content as a result of removing corn stover for energy production. If corn stover were used for energy production in combination with winter cover crops cultivation and no-tilling practice, the GHG emissions from the system would be reduced by 47-105%. An iLUC effect is also calculated giving an increase in GWP by 7-38% (100 years' time frame for the cultivation) and 48-170% (20 years' time frame) when crops are planted in newly converted ecosystems (Kim and Dale, 2009).

In an older paper by Kim and Dale (2005), life cycle assessments are conducted on the production of bioethanol using corn grain and corn stover as feedstock. The production takes place in Iowa, USA, and the functional unit is defined as "1 ha of arable land for a 40-year period". The focus is thus rather on the cultivation system than on the bioethanol production process. Four cultivation systems are investigated: a corn-soybean rotation without corn stover removal, continuous corn cultivation without removal, continuous corn cultivation with 50% removal and a continuous corn system with 70% removal and winter cover crop cultivation. In the fermentation of corn stover, a lignin-rich residue is obtained which is used for electricity production. In order to avoid the environmental disadvantages of corn stover removal, discussed above, cultivation of winter cover crops is investigated in a scenario of the study. No-tilling practices are assumed and system expansion is applied. The results show that the cultivation of winter cover crops would increase the soil carbon content, even in the case where 70% of the corn stover is removed from the field. The removal of harvest residue and cultivation of cover crops also reduce the nitrogen related burdens from the soil. In terms of GWP, all simulated cropping systems give negative values, i.e. carbon credits, and the system with corn stover removal in combination with winter cover crop cultivation giving the greatest reduction. This is due to the increased soil carbon content given by the cover crop cultivation, and also thanks to greater bioethanol yields per hectare, brought about by better soil properties. However, for contribution to acidification (AP) the corn stover removal scenarios show inferior results than the other two as an effect of the acid treatment of the corn stover for hydrolysation. For eutrophication (EP), the corn-soybean system shows the lowest impact. Sensitivity analyses are made for, among others, the efficiency of the electricity generation of the burning of the residue and of the avoided electricity production system (Kim and Dale, 2005).

A different ethanol production system is investigated in Stichnothe and Azapagic (2009). Here, ethanol is produced in the UK using two different fractions of municipal solid waste (MSW) as feedstock. The ethanol production process differs from the previously described in that the feedstock is gasified before it is bio-catalytically fermented to ethanol. An LCA is made of this process where the assessment includes waste input, start-up fuel, operational materials and process electricity. Butanol and other co-products are generated in the production, and the heat produced in the gasification is used for internal processes, as well as for electricity production. Credits are given for the co-products and the produced electricity. The composition of the feedstock in the two investigated systems differs - *Refuse Derived Fuel (RDF)* consists of plastics and other non-renewable materials to a significant extent (39%) whereas *Biodegradable Municipal Waste (BMW)* almost solely contains biogenic carbon, as the name reveals. This means the LCA-results differ between the two produced fuels: from a GWP perspective, the RDF-ethanol shows a performance (86.5 g CO_2-eq./MJ) similar to that of petrol (84.8 - 94.2 g CO_2-eq./MJ), while BMW-ethanol (6.3 g CO_2-eq./MJ) outperforms them both by far. The GWP reduction when using the BMW-ethanol instead of petrol amounts to 92.5%, which can be compared to sugarcane ethanol (Stichnothe and Azapagic, 2009).

In Mu et al. (2010), a comparison is made of biochemical and thermochemical production of lignocellulosic ethanol in the US. The investigation is based on life cycle assessments of the two routes, where the investigated stages include cultivation and transport of feedstock and ethanol production. For the biochemical route, co-current dilute acid pre-hydrolysis with simultaneous enzymatic saccharification and co-fermentation is employed. The separated lignin fraction is combusted for internal energy demand, and excess electricity produced is sold on the grid and allocated as credits for the avoided use of electricity. Natural gas is used for the production of required process steam. In the thermochemical production, atmospheric-pressure indirectly-heated dual fluidised bed gasification is applied, followed by a Fischer-Tropsch process to generate ethanol. Co-products include mixed alcohols, which are assumed to replace heating oil. The result of the study shows the ethanol yield, energy efficiency and carbon conversion efficiency are greater for the thermochemical route but that the GHG-emissions and fossil fuel consumption are lower for the biochemical route. Both systems are, nevertheless, net carbon sinks. The superior GWP if the biochemical route is due to the valuable electricity production credits given to this system. The results from the study are illustrated in Figure 4.1 below.

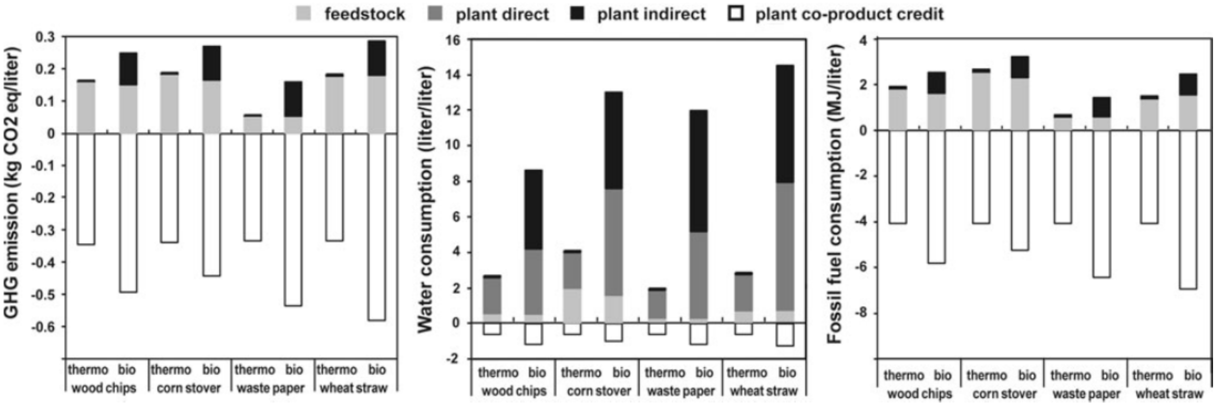

Figure 4.1. Results from the base case scenario (Mu et al., 2010).

As the exact emission factors are rather difficult to read, the results from this study have not been added to the compiling result table at the end of this section. It can, however, be noted that the GWP from these investigated systems are considerably lower than those found for other systems studied. If the mixed alcohols produced as co-products in the thermochemical system where to be separated and used as chemicals, this system would outperform the biochemical in terms of GWP and fossil fuel consumption. This result highlights the fact that a biorefinery approach may increase the environmental performance of a system (Mu at al., 2010).

4.1.2 Biobutanol

One LCA found for biobutanol production is made by Wu et al. (2007). In the study, the cradle-to-grave life cycle performance of corn-based biobutanol is investigated. The study includes the following stages: corn farming, transportation and processing of corn, biobutanol production, biobutanol transportation and distribution, and biobutanol use in gasoline vehicles. Natural gas is used as process fuel and the results are compared to those of bioethanol and gasoline. When energy allocation is applied for the co-products bioethanol and bioacetone, the cradle-to-grave GHG-emissions of biobutanol amount to approximately 2.2 kg CO$_2$-eq./kg biobutanol. The natural gas required for process steam production is identified as a major hot spot in the biobutanol production. If no energy credits are obtained for fossil acetone replacement, these NG induced emissions lead to GHG-emissions (approximately 4.3 kg CO$_2$-eq./kg) three times greater than those of the entire bioethanol production process, and an environmental performance inferior to that of gasoline. For this reason, the behaviour of the market for the co-product bioacetone is of outmost importance for the final environmental performance of biobutanol. The authors fear this market will be saturated rapidly. Moreover, in the biobutanol production, less liquid fuel is produced compared to the bioethanol system and additionally, more input energy is needed in the biobutanol plant (Wu et al., 2007).

A more recent study on biobutanol production is made by Swana et al. (2011). Values for the biobutanol production are taken from the study described above, but the investigation is, however, not an LCA. Instead, the productivities (MJ/L) of bioethanol and biobutanol production are compared. The study is a cradle-to-gate investigation. Two types of biobutanol production are investigated: conventional ABE-fermentation and purification of solely biobutanol, where the co-products bioethanol and bioacetone are regarded as waste. Moreover, production using lignocellulosic feedstock is simulated and compared to the conventional fermentation where corn is used as feedstock. If bioacetone and bioethanol are not purified in the ABE-fermentation, an energy return of 6.5 MJ/L is obtained from biobutanol production from corn-grain. This data on biobutanol is, however, based only on the Wu-case. The energy return from bioethanol production from corn-grain is 0.40 MJ/L. If bioethanol were instead produced from lignocelluloses, the energy return would be 16 MJ/L. The authors assume that the energy return from biobutanol produced from lignocelluloses would be greater still. A simulation shows that through the sustainable removal and harvest of four different energy crops and agricultural residues (corn stover, wheat straw, switchgrass and poplar), approximately 39 billion litres of bioethanol or 31 billion litres of biobutanol could be produced (Swana et al., 2011). What is interesting to note, is the result of superior productivity of biobutanol compared to bioethanol and also the major increase in productivity when lignocellulosic biomass is used.

A more sceptic view of biobutanol production is given in Pfromm et al. (2010). Also in this report, biobutanol production (through fermentation) is compared to bioethanol production. The fuels are compared based on their lower heating value per amount of biomass feedstock. They are, furthermore, compared with regards to their carbon mass balances and the cost of production. Contradictory to the result in Swana et al. (2011), Pfromm et al. (2010) come to the conclusion that the ABE-fermentation results in much lower yields than the conventional bioethanol fermentation. The problem of having to maintain a low concentration of biobutanol in the fermentation broth implies disadvantages such as the need for large fermenters and use significant amounts of electricity to maintain adequate conditions for the extraction of biobutanol. These issues, among others, make the environmental and economic benefits of biobutanol production questionable according to the authors (Pfromm et al., 2010).

4.1.3 Biosuccinic acid

No life cycle assessments have been found for the production of biosuccinic acid or bio-BDO. The lack of data could be due to the fact that commercial production of biosuccinic acid is a relatively new phenomenon. One interesting study has, however, been made on the combined production of biosuccinic acid and bioethanol: Wu et al. (2011) found that the CO_2 emitted in the bioethanol fermentation could be used for subsequent biosuccinic acid production. The process effectively produced both bioethanol and biosuccinic acid in lab-scale. Such an integrated system is a good example of a biorefinery approach, and as both CO_2 is captured and two bio-products are obtained, it is likely that the life cycle performance of the system is advantageous. Further investigations in this area are needed.

4.1.4 3-HPA, Itaconic acid, Furans, Levulinic acid

No LCAs have been found for the production of these platform chemicals. However, according to Zwart (2006), the hydrolysation of five carbon sugars is both less costly and easier, why the possibility to use pentose sugars for the production of itaconic acid and furans is seen as advantageous. Development of a fermentation technology with which both pentoses and hexoses are used would be both environmentally and economically favourable as the biomass would be utilised to a greater extent (Zwart, 2006).

4.1.5 Results, platform chemicals

The results from the literature review are compiled in Table 4.1 below. As can be seen, the GWP-results vary significantly why it is recommended to also read the texts above that describe the reports on which the results are based. In Figure 4.2 the GHG-performance of the investigated platform chemicals are presented.

Table 4.1. Overview of LCAs performed on platform chemicals and fuels.

Author	Cradle-to-?	Func. unit	Substrate	Country	GWP (kg CO_2-eq./kg chemical)	GWP (kg CO_2-eq./GJ)	Hot spots	Other impact categories	Comment
Börjesson (2009)	Wheel	1 GJ of bio-ethanol	Wheat	Sweden	0.5*	19	Efficiency of cultivation, dLUC, allocation of by-products, process energy		GWP varies between 0.11-10* [kg CO_2-eq./kg ethanol] depending on the system.
Kim and Dale (2009)	Gate	1 kg of bio-ethanol	Corn	USA	1.1-2	41-74	N_2O emissions from soil, NG use in bioethanol production		GWP depends on local farming practises: no-tilling practices and winter cover crops reduce GWP
Stichnothe & Azapagic (2009)	Wheel	1kg of ethanol	MSW - RDF	UK	2.3*	85			Gasification + fermentation
Stichnothe & Azapagic (2009)	Wheel	1kg of ethanol	MSW – BMW	UK	**0.17***	6,3			Gasification + fermentation
Wu et al. (2007)	Wheel	1 kg of bio-butanol	Corn	USA	2.2-4.3	66-129	NG for process steam	NREU	GWP depends on the allocation of by-products
Ecoinvent (2010)	Gate	1 kg of fossil butanol			1.8	54		Yes several	
Stichnothe & Azapagic (2009)	Gate	1 kg of petrol			0.57	13			
Stichnothe & Azapagic (2009)	Wheel	1 kg of petrol			3.5	81			

* Based on Pfromm et al. (2010): $LHV_{butanol}$ = 33.4 kJ/g, $LHV_{ethanol}$ = 27 kJ/g, $LHV_{gasoline}$ =43,4 kJ/g.

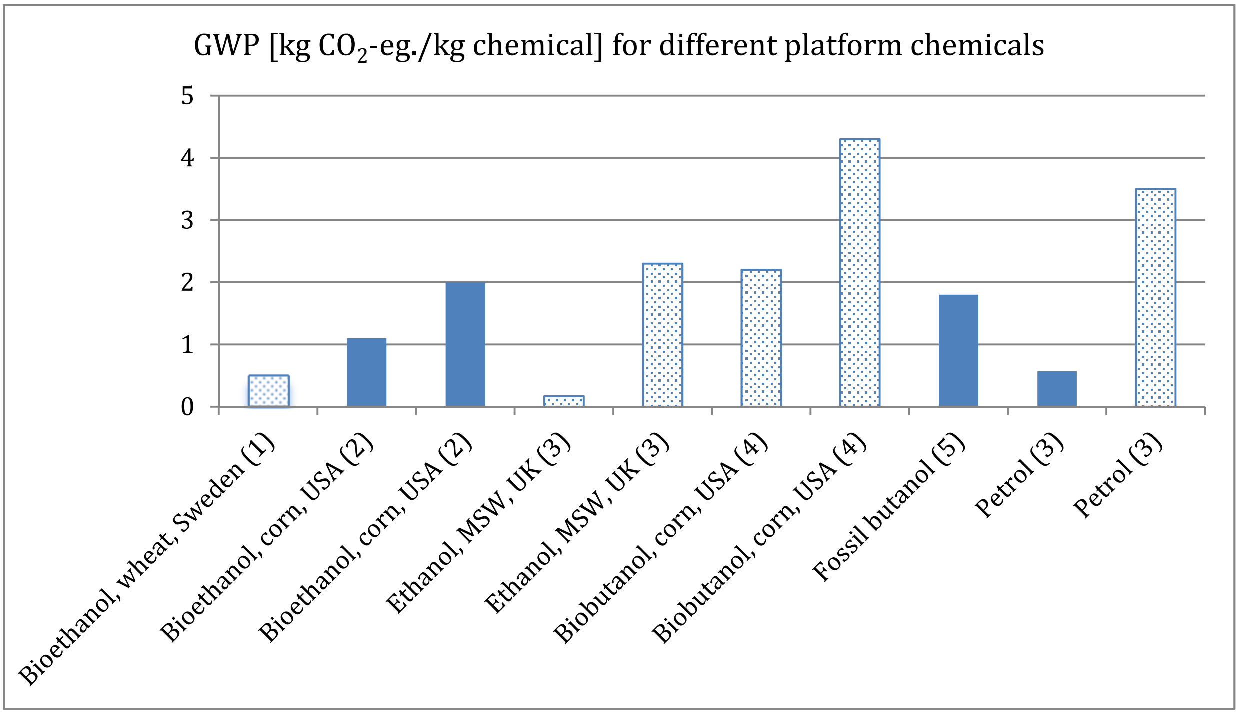

Figure 4.2. GHG-performance of the different investigated platform chemicals. Dotted columns represent cradle-to-wheel studies whereas filled columns represent cradle-to-gate studies. For references in brackets, see footnote[2]

4.2 Renewable plastics

Recently, the German *nova-Institut* conducted a meta-analysis of the environmental performance of the bioplastics PLA and PHA/PHB. Like the current study, the investigation is based on existing LCAs (as well as one specifically made for a certain bioplastic product) and the conclusion drawn is that the bioplastics perform better than their fossil alternatives from a GWP point-of-view (Nova-Institut, 2012).

In Hermann et al. (2010), LCAs of different renewable materials are made and compared to the LCAs of conventional plastics. The functional unit is defined as "1 m^2 of packaging film" and both cradle-to-gate and cradle-to-grave assessments are made. The production takes place in Europe (except for PLA production which takes place in Nedbraska) and system expansion is applied to give credits for avoided electricity and heat production when the production systems provide surplus energy. The survey is divided into studies of both the films used for the outer and for the inner part of the packaging, where requirements are higher for the inner packaging in terms of, for instance, water resistance. The environmental performances of the renewable options are lower than one might have thought, this due to some energy intensive stages of the process as well as a greater material demand to obtain certain functional properties. Also, the lack of experience means the production is not yet streamlined. The GWP-results of the study show that for the inner packs, PLA-based film scores better than the reference fossil material only when wind power credits are bought to compensate for the polymer production. In this category, the greatest GWP-reduction is obtained for a film based on paper and two types of conventional plastics. For outer packs, the renewable options show greater environmental competitiveness. Here, thin film of renewable PE scores better than the reference material in all impacts categories except AP and EP. Also here,

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[2] (1) Börjesson (2009), (2) Kim and Dale (2009), (3) Stichnothe and Azapagic (2009), (4) Wu et al. (2007), (5) Ecoinvent (2010).

the PLA film is attractive compared to the reference material provided that wind power credits are included in the calculation. However, a potential for improvement in the renewable material production exists, and it is thus promising that these already are more or less competitive from an environmental perspective (Hermann, 2010).

In Álvarez-Chávez et al. (2012), the sustainability of commercial and nearly commercial bioplastics is evaluated. The evaluation is based on comprehensive sustainability criteria set up by the *Sustainable Biomaterials Collaborative*, a network of actors working for the sustainable development of bioplastics. The principles of sustainability include among others: "*reduce the amount of material, product and packaging used; eliminate single-use products that can be neither recycled nor composted; avoid fossil fuel-based materials in favour of materials and feedstock derived from renewable feedstock; encourage agricultural systems that are sustainable for farmers, the environment, farm workers and communities*". The investigation is based on a literature review complemented with information from direct contact with manufacturers. The results of the study show that none of the currently available bioplastics are completely sustainable according to the sustainability criteria set up. PLA, PHB and starch-based polymers are preferred over, for instance, nano-composites, cellulose- and lignin-based materials. This is because hazardous chemicals may be used in the manufacturing of the latter whereas environmental concerns of the former materials are rather connected to the possible risks of using GMOs in the cultivation stage (Álvarez-Chávez et al., 2012).

4.2.1 PLA

For the production stage of the PLA resin, LCAs of the processes in the previously mentioned plants in Nebraska and Thailand have been found. Furthermore, there are two additional LCAs investigating a larger part of the life cycle, using inventory data from the production site in Nebraska.

Three LCAs, or "eco-profiles", of the production in Nebraska have been conducted; the first was published in 2003 (Vink et al., 2003). As stages of the production have developed, the eco-profiles have been updated two times, first in 2007 (Vink et al., 2007) and the most recent study was made in 2010 (Vink et al., 2010). Information from the last two LCAs is presented here since it is interesting to see the effect of improvements in the process. All three studies are cradle-to-gate studies including corn production, transportation and processing of the corn in a corn wet mill, fermentation to lactic acid and conversion of lactic acid to polylactide polymer pellets. In the eco-profile from 2007, the lactic acid production is identified as a hot spot where 73% of the fossil energy used is consumed. Results from the study show emissions of 2.0 kg CO_2 eq./kg from the PLA production. However, RECs (Renewable Energy Certificates) from wind power are bought to offset the emissions leading to a reduction of the final emissions to 0.3 kg CO_2 eq./kg PLA (Vink et al., 2007). In the most recent study, the lactic acid production has been improved. Less energy is needed for this stage and the amount of the by-product gypsum produced is reduced. This results in final emissions of 1.3 kg CO_2 eq./kg PLA for the production. In this eco-profile, no wind power credits are bought to offset the emissions from the production (Vink et al., 2010).

The study of the production in Thailand is also a cradle-to-gate investigation, conducted in 2010. The raw material used is sugarcane and the study includes the sugarcane agricultural system, industrial activities related to the auxiliary chemicals used, distribution of raw materials, processing of sugarcane into sugar and the final production of lactic acid, lactides (L and D) and PLA polymers. The data on the lactic acid production is taken from the existing plant in Thailand whereas data regarding the PLA production is estimated based on the design of a planned facility.The LCA shows that the largest improvements, in order to reduce the GWP of PLA production, can be made in the sugarcane milling and in the lactic-acid production. Other hot spots are the production of other chemicals, and the electricity and steam used in the manufacturing of PLA. When all the processes and the carbon sequestration of the renewable feedstock are included in the calculations, the net GHG-emissions are approximately 0.5-0.8 kg/kg PLA. In terms of GWP, PLA scores better than their fossil alternatives, but when it comes to emissions of nutrients to water - the eutrophication potential (EP) - PLA shows a greater impact due to the agricultural practise involved (Groot and Borén, 2010).

In Madival et al. (2009), a cradle-to-grave LCA is conducted with the functional unit “1000 PLA containers with a capacity of fitting 0.4536 kg of strawberries each“. All stages from raw material extraction through disposal are considered. Moreover, the energy recovered from the disposal or the raw material replacement when the plastic is recycled, are also taken into account. The data for PLA resin production is taken from the production in Nebraska. The environmental impact of the PLA container is compared to that of PET and PS showing that the thermoforming of the PLA is less energy demanding than it is for PET and PS. However, due to the underdeveloped infrastructure of the PLA system[3], the environmental performance of PLA is finally of similar magnitude to that of PET and PS. The end-of-life disposal is also identified as a stage of significant importance where a high grade of recycling gives a lower overall GWP. The final GWP calculated in this study is significantly higher than it is in the other cradle-to-gate LCAs described. This implies that the use-phase and end-of-life scenario are of great importance for the environmental performance of PLA (Madival et al., 2009).

Another cradle-to-grave LCA of PLA has been made where the environmental credential of a single-use drinking cup and its lid are investigated. Data for the production stage of the PLA resin is taken from the *Natureworks* production in Nevada. The functional unit is a 16-ounce drinking cup and lid, a unit which has not been possible to recalculate into kg of PLA. For this reason, a comparison with the resulting GWPs of the other studied LCAs is impossible. What can be noted from the study, nevertheless, is that the environmental performance in terms of GWP is superior for the PLA cup compared to that of drinking cups made out of PET and PP. For AP and EP, however, PLA shows a result inferior to that of PP (PE Americas, 2009).

4.2.2 PHA and PHB

In Akiyama et al. (2003), the economic and environmental performance of PHA and PHB produced in the US is compared to that of petroleum-based alternatives. In the case of the PHA production, fermentation is employed and soy-oil is used as substrate. This is compared to the production of PHB, produced through fermentation also but with corn as feedstock. Lab-scale fermentation tests combined with the use of simulation software give an assessment of the cradle-to-gate emissions of commercial production. The study includes the cultivation stage, the fermentation and the downstream processing. The process contributing most to the total GHG-emissions of the production is the steam drying of the polymer in the downstream processing. In the fermentation stage,

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[3] Production of PLA resin, container production, filling and distribution of the fruit take place in different states of the US.

agitation and aeration are identified as hot spots. The results of the study show that the production of PHA from soy-oil is preferential to that of PHB from corn, both considering the environmental and the economic credential. This is due to the higher yield of polymer in the PHA production as well as a lower amount of cumulative energy used per weight of soy-oil in the cultivation stage. The GHG-emissions from the whole process varies from 0.5 kg CO_2-eq./kg PHB to 1.4 kg CO_2-eq./kg PHB (depending on different process and operating conditions), generally being significantly lower for the PHA production. It is quite difficult to distinguish the effect of carbon sequestration used in the calculations. Both PHA and PHB show great reductions in GWP compared to their fossil alternatives (Akiyama et al., 2003).

In a more recent study, Kim and Dale (2008) calculate cradle-to-gate GHG-emissions of the production of PHB at the existing production site in Iowa described previously. The data is thus site-specific, representing a local, relatively efficient system from an environmental point of view. The system boundaries include incineration of corn stover and fermentation residues to generate energy for the process. Moreover, RECs are bought to offset additional need for electricity. GHG-credits are obtained for the renewable feedstock used, the renewable energy used in the corn wet milling and in the PHB plant and for the utilisation of fermentation residues for energy recovery. The cultivation stage is identified as a hot spot in the process, this due to the nitrogen fertiliser used. The final GWP is -2.3 kg CO_2-eq./kg PHB. Although allocation plays a great part for the result, the sensitivity analyses show that PHB still performs better than fossil alternatives. One simulation is made where a composting end-of-life scenario is considered. Even with the emissions of CO_2 that this operation entail, the composting scenario offers a carbon binding effect (of -0.3 kg CO_2-eq./kg) (Kim and Dale, 2008). In this study, the base case is calculated using system expansion giving GHG-credits for the *avoided* emissions of the products the by-products are replacing. This is the reason the GWP obtained is very low compared to the other investigated LCAs.

In Harding et al. (2007), the data is instead taken from laboratory production of PHB, linked to a pilot-scale process. This study is also a cradle-to-gate investigation, with sugarcane used as raw material. The results are compared to those of PP and PE production. Steam, electricity and NG are used for the PHB production. The system boundaries include cultivation, fermentation and substantial downstream processing as well as raw material and agricultural inputs, detergent and enzyme use and waste water treatment. The GHG-credits are accounted for differently in this report compared to in Kim and Dale (2008). Here also, the agricultural by-product, in this case bagasse, is incinerated and used for internal electricity production. However, the GHG-emissions from this combustion are accounted for as net emissions, leading to a higher GWP, whereas in Kim and Dale (2008) this energy production is given GWP-credits. The resulting GWP obtained in the study is 2.0 kg CO_2-eq./kg PHB, significantly higher than the result of Kim and Dale (2008). Hot spots identified in the study include steam and electricity generation. PHB scores better than PP in all impact categories. It scores better that LDPE and HDPE in GWP but much worse (+500%) in EP due to the cultivation of sugarcane. Moreover, large amounts of water are required for PHB production, with a lot of wastewater produced as a consequence (Harding et al., 2007).

A fourth approach to the investigation of the environmental performance of PHB is given in Pietrini et al. (2007). In this cradle-to-grave LCA two PHB-based products are studied

– a computer monitor housing conventionally made out of high impact polystyrene (HIPS) and the internal panels of a car[4] conventionally made out of PP-GF (glass fibre). PHB produced through fermentation of sugarcane and from corn starch are compared. The LCA includes the agricultural step, the sugar production, the fermentation and downstream processing as well as the extrusion, injection moulding, use-phase and final incineration with energy recovery (which gives GHG-credits). Residual biomass, of which more is obtained from sugarcane than from corn cultivation, is used for electricity production, replacing fossil fuels. This gives low impacts for the production stage of PHB (-3.1 kg CO_2/kg for sugarcane and 0 kg/kg for corn). With a cradle-to-grave approach, the PHB-composite shows a better environmental performance than the fossil alternative when used for monitor housing. Also for PHB used in cars, the cradle-to-gate result is preferential, it represents 15-26% of the fossil non-renewable energy use. With the use-phase included, however, the result deteriorates significantly - there is no advantage in the renewable production, not even for the sugarcane based PHB. This since the PHB composite must have a higher density than the fossil alternative in order to obtain equivalent properties, and for this reason the fuel economy is reduced considerably when PHB is used in a car. The waste incineration credit is, furthermore, greater for high impact polystyrene, HIPS, than for PHB (Pietrini et al., 2007).

In Yu and Chen (2008), a different type of production system is studied. PHA can be made from the wastewater (black syrup) produced in the process of lignocellulosic ethanol production. The system is interesting as a clear biorefinery frame of mind is applied, producing food/feed (corn grain), fuel (ethanol) and a chemical (PHA). The study is a cradle-to-gate investigation where the GWP and fossil energy requirement is calculated. It is based on lab-scale results of ethanol production using corn stover as feedstock pretreated by dilute acid prehydrolysis. The system is illustrated in Figure 4.3 below.

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[4] Life-time of 10 years, travelling 150,000 km.

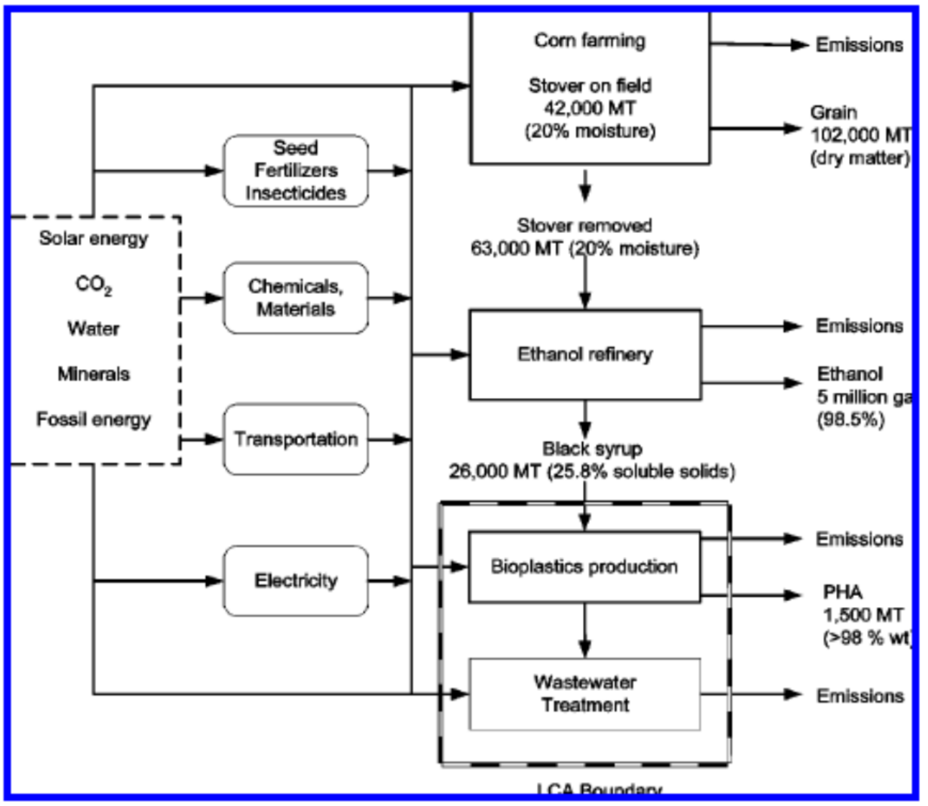

Figure 4.3. Schematic of the biorefinery (Yu and Chen, 2008).

If the black syrup is pretreated under anaerobic conditions, many of the compounds it contains can be converted to PHA. The PHA production process is simulated using special software and it includes seed preparation, black syrup pretreatment, aerobic PHA fermentation and PHA recovery. Both the environmental burden and the carbon sequestration of plant growth are allocated on a weight basis between the corn grain and the corn stover. Only 60% of the stover is collected in order to sustain good farming practices. The GHG-sequestration obtained in the cultivation stage amounts to -5.4 kg CO_2-eq./kg PHA (the black syrup utilisation gives carbon credits of -1.2 kg CO_2-eq./kg raw material). In the subsequent PHA production, the use of ammonia for the fermentation and the aeration of the process are identified as hot spots. Looking at the whole PHA production chain, 62% of the fossil energy is used in the microbial fermentation process. Even though residual biomass is produced and combusted for energy requirements of the process, the need for electricity is assumed to come from combustion of coal, and the gas used is assumed to be natural gas. This is in order for study to be comparable to other studies. The final account of GHG-emissions amounts to 0.5 kg CO_2-eq./kg PHA.

4.2.3 PDO

According to *DuPont Tate & Lyle*, the cradle-to-gate GHG-emissions of their production of bio-PDO in Loudon amount to 2.2 kg CO_2-eq./kg Bio-PDO. This is more than 40% lower than the fossil alternatives (petrochemically produced PDO or propylene glycol) (Miller, 2010). Unfortunately, the LCA on which these results are based is confidential why no further analysis of, for instance, assumptions made or system boundaries chosen can be made. Also for *Sorona*®, an emission factor is given based on results from a confidential LCA. The production gives rise to emissions of 3.8 kg CO_2-eq./kg *Sorona*® according to *DuPont*. This can be compared to emissions of 4.4 kg CO_2-eq./kg for production of PTT through the propylene route, 4.0 kg CO_2-eq./kg for production of PTT through the ethylene oxide route and 9.1 kg CO_2-eq./kg for production of nylon 6 (DuPont, 2012).

In Urban and Bakshi (2009) the cradle-to-gate production of renewable PDO, made using corn feedstock, is compared to the production of fossil PDO. The fossil PDO is produced through catalytically reacting syngas with ethylene oxide. Both types of production take place in the US and the system boundaries for the biochemical production include corn farming, corn wet milling, glucose production and PDO-production. Mass-based allocation is applied since, in this case, mass-based and economic allocations are basically identical and as a system expansion approach is considered too complex. GHG-credits are given when steam from the process can replace natural gas. Both for the biobased route and for the fossil route, transports are neglected since the different processing facilities are assumed to be situated at the same site. Moreover, the production of catalyst for the fossil production is assumed negligible. According to the study, renewable PDO scores better than fossil PDO in terms of GWP (approximately 2.7 kg CO_2-eq./kg compared to approximately 9.4 kg CO_2-eq./kg) but for the EP, water use, land use and soil erosion, the renewable option shows an inferior result. For the projected production of PDO these negative effects will, however, be limited according to the report. (Urban and Bakshi, 2009).

4.2.4 Thermoplastic starch

No life cycle assessments of the production of thermoplastic starch have been found. However, a cradle-to-gate LCA of the previously described blood protein thermoplastic has been conducted. Blood meal is produced by steam drying of blood from the meat industry, and is normally used as a low-value fertiliser. Through addition of sodium sulphite, sodium dodecyl sulphate, urea and plasticiser the thermoplastic is produced, using a technology developed by *Novatein*. The study is described in two separate papers where the first article focuses on the effect of the chosen allocation method and the second paper gives the cradle-to-gate eco-profile of 1 kg of bioplastic hypothetically produced in a facility in New Zealand. The steam drying of the blood and the production of plasticisers are identified as hot spots in the process, and the source of process energy is also recognised as very relevant. Moreover, the choice of allocation method greatly influences the environmental performance - if mass allocation is applied, the investigated thermoplastic shows a GHG performance (13.5 kg CO_2-eq./kg) inferior to those of other renewable plastics. However, the performance improves significantly (-0.2 kg CO_2-eq./kg) if the blood is regarded as a waste product. A comparison with other bioplastics (PLA, PHA and a thermoplastic starch) show that the energy needed for plastic production is in the same order of magnitude for all types (Bier et al., 2012a; Bier et al., 2012b).

4.2.5 Drop-in solutions

In Nouri (2006), the environmental performance of polyolefins (PE and PP) produced through gasification of wood waste in Sweden is investigated. First, a streamlined cradle-to-gate LCA of the process is made in order to evaluate whether or not the system is interesting from an environmental point of view. Process stages include: wood collection, chipping and transport; gasification and methanol synthesis; methanol to olefin process; and polyolefin production. Data is taken from literature and the result is striking: 0.27 kg CO_2-eq./kg polymer is emitted. This is, however, the result of the first screening. To develop the investigation, the LCA is combined with process simulation for the syngas to methanol step by using the modelling software *HYSYS* and industrial data.

The investigation is further extended to include the use of plastic waste as feedstock. Now, however, the results deteriorate: 1.4 kg CO_2-eq./kg for the wood waste and 2.2 kg CO_2-eq./kg for the plastic waste. The hot spot of the system is the gasification unit where the oxygen production is the main emitting process. Sensitivity assessments show that the performance of the plastic waste route can be improved with an improved gasifier and if H_2 is added to the syngas. The addition of H_2 improves the performance of the wood waste system as well. More feedstock is needed for the thermochemical conversion compared to the biochemical one, 9 kg wood waste/kg polymer compared to 2.5 kg corn/kg PLA (Nouri, 2006).

4.2.4 Results, renewable plastics

The results of the literature review are compiled in Table 4.2 below and illustrated in Figure 4.4.

Table 4.2. Summary of LCA studies performed on plastic materials from renewable and conventional resources.

Author	Cradle-to-?	Functional unit	Substrate	Country	GWP (kg CO_2-eq./kg plastic)	Hot spots	Other impact categories	Comment
Vink et al. (2007)	Gate	1 kg of PLA resin	Corn	USA	2	Lactic acid production	NREU, water use	GWP = 0.27 if RECs are included
Vink et al. (2010)	Gate	1 kg of PLA resin	Corn	USA	1.3	Lactic acid production	NREU, LU	Target of reaching 0.8
Groot and Borén (2010)	Gate	1 kg of PLA resin	Sugarcane	Thailand	0.5 – 0.8	Sugarcane milling, lactic acid production	NREU, ADP, LU, AP, POCP, HTP, EP	Bagasse used for steam production. Scores worse in EP.
Madival et al. (2009)	Grave	1000 PLA containers with a capacity of fitting 0.4536 kg of strawberries each	Corn	USA	24	Transport of containers	AP, ODP, EP, respiratory organics and inorganics, ETP	Cradle-to-gate emissions taken from Vink et al. (2010)
Akiyama et al. (2003)	Gate	1 kg of PHB	Corn	USA	0.48 - 1.39	Agitation, aeration, drying	NREU	Scores worse than PHA production from soy-oil.
Kim and Dale (2008)	Gate	1 kg of PHB	Corn	USA	-2.3	Cultivation, N-fertiliser	NREU	GWP-credits for many processes, RECs?
Harding et al. (2007)	Gate	1000 kg of PHB	Sugarcane		1.96	Steam rising, electricity generation	ADP, ODP, HTP, ETP, POCP, AP, EP	
Pietrini et al. (2007)	Grave	PHB monitor housing/ interior parts of a car	Sugarcane		0.23 (0.6 kg/FU) / 23.8 (604.6 kg/FU)*	Use-phase for car interiors	NREU	
Pietrini et al. (2007)	Grave	PHB monitor housing/ interior parts of a car	Corn		3 (7.8 kg/FU) / 26.4 (670.3 kg/FU)*	Use-phase for car interiors	NREU	
Pietrini et al. (2007)	Gate	1 ton of sugar cane PHB/ 1 ton	Sugarcane /corn		-3.1/0*		NREU	Lower quantity of

		of corn PHB						biomass for energy prod. from corn.
Yu and Chen (2008)	Gate	1 kg of PHA resin	Corn stover	USA	0.49	Ammonia use and areation	NREU	Co-produced with lignocellulosic ethanol
DuPont Tate & Lyle (2012b)	Gate	1 kg of Bio-PDO *Susterra®*	Corn	USA	2.16		NREU	Should be compared to Nylon 6?
Urban & Bakshi (2009)	Gate	1 kg of Bio-PDO	Corn	USA	2.8			With mass-based allocation
Bier et al. (2012)	Gate	1 kg of thermoplastic protein	Blood	New Zealand	-0.2 – 13.5	Steam drying of blood, plasticiser production	NREU	Result depends largely on allocation
Nouri (2006)	Gate	1 kg plastic (renewable PE or PP)	Wood waste	Sweden	1.4	Air separation in gasification		Drop-in plastic produced through gasification
LDPE, PlasticsEurope (2005a)	Gate	1 kg of LDPE polymer		Europe	2.1			
LDPE, Footprinted.org (2011a)	Gate	1 kg of LDPE		Canada	2.3			Applies to year 2006.
PP, PlasticsEurope (2005b)	Gate	1 kg of PP		Europe	2.0			
PVC (PlasticsEurope (2006a)	Gate	1 kg of PVC		Europe	1.9			Suspension PVC (accounting for 80% of all PVC)
PS-E (PlasticsEurope, 2006b)	Gate	1 kg of PS		Europe	3.3			
PS-HIPS (Footprinted.org (2011c)	Gate	1 kg of PS-HIPS		Canada	2.2			Applies to year 2006.
PET, Footprinted.org (2011b)	Gate	1 kg of PET		Canada	2.8			Applies to year 2006.
PET, PlasticsEurope (2011)	Gate	1 kg of PET		Europe	2.1			Bottle quality PET

* Calculated average of the four different types of composites studied in the investigation.

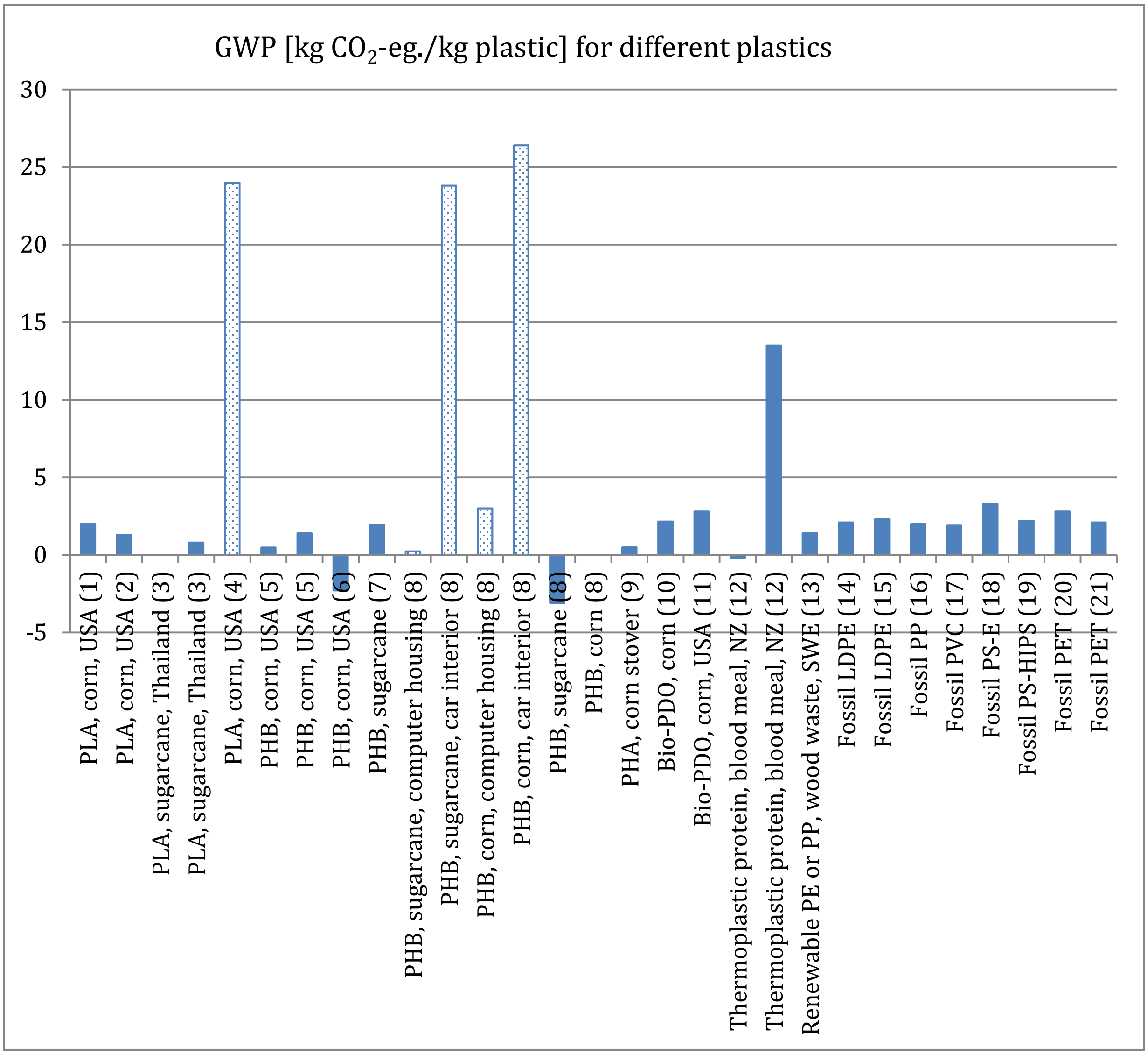

Figure 4.4 GHG-performance of the different investigated plastics. Dotted columns represent cradle-to-grave studies while filled columns represent cradle-to-gate studies. For references in brackets, see footnote [5].

Figure 4.4 illustrates the importance of designing the system so that overall sustainability is obtained. The high values for GWP are due to long transport distances ((4) Madival et al., 2009), unsuitable choice of application in the use-phase ((8) Pietrini et al., 2007) and choice of allocation method ((12) Bier et al., 2012).

4.3 Discussion – environmental performance of biochemical

In this section, the environmental credibility of renewable chemical production will be scrutinised based on the information obtained through the literature review. These findings will be complemented with results from additional studies in order to obtain a more comprehensive, general view of the whole life cycle of biochemicals. The section is divided into subsections where each stage of the life cycle is analysed and hot-spots as well as possible environmental benefits are highlighted. The section ends with a

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[5] (1) Vink et al. (2007), (2) Vink et al. (2010), (3) Groot and Borén (2010), (4) Madival et al. (2009), (5) Akiyama et al. (2003), (6) Kim and Dale (2008), (7) Harding et al. (2007), (8) Pietrini et al. (2007), (9) Yu and Chen (2008), (10) DuPont Tate & Lyle (2012b), (11) Urban and Bakshi (2009), (12) Bier et al. (2012), (13) Nouri (2006), (14) PlasticsEurope (2005a), (15) Footprinted.org (2011a), (16) PlasticsEurope (2005b), (17) PlasticsEurope (2006a), (18) PlasticsEurope (2006b), (19) Footprinted.org (2011c), (20) Footprinted.org (2011b), (21) PlasticsEurope (2011).

discussion of the methodology of LCA and a short reasoning regarding sustainable and effective uses of biomass.

4.3.1 Feedstock and cultivation

The choice and availability of feedstock will have great influence on the environmental performance of the production system under investigation. As described previously, the use of first or second generation feedstock gives rise to different types of impacts: first generation biomass is afflicted with economic and socio-ethical issues (besides the environmental problems related to the cultivation stage), whereas the processing technologies for second generation feedstock are still rather immature. Furthermore, the environmental impact varies among the different types of first and second generation crops. Aspects such as biomass yield, fertilising rate and effect on soil carbon content are important in this context (Tufvesson, 2010).

In the current situation, mainly dedicated, first generation crops are used for the production of renewable chemicals. For this reason, the coming section will focus primarily on issues and possibilities regarding this cultivation and on factors connected to this stage of the life cycle. However, other possible feedstock alternatives will also be briefly discussed.

Hot spots

Important cultivation parameters

From a GWP perspective, certain cultivation parameters are of significant importance for the result. Issues discussed in this study include emissions of N_2O and CO_2 from soil and farming practises as well as the overall efficiency of the cultivation system.

In both Kim and Dale (2009) and in Tufvesson (2010), the effect of biogenic N_2O-emissions from the soil is identified as an important factor. Emissions of CO_2 originating from organically bound soil carbon are also of importance for the GWP. These emissions are, however, discussed in the coming section as they are connected to land use change. The size of the biogenic N_2O-emission depends on, among other factors, temperature, soil moisture and available excess nitrogen in the soil. Thus, an unconsidered N-fertilisation strategy can give rise to these kinds of emissions. Synthetic fertiliser production may also bring about N_2O-emissions (Kim and Dale, 2008), but with catalytic cleaning of the flue gas from the factory, these emissions are reduced. This type of cleaning equipment is installed continuously at production facilities why the problem should diminish. N_2O is, however, a very potent greenhouse gas (approximately 300 times more forceful than CO_2) why the hindering of these emissions is of significant importance. A small amount of CH_4 is also emitted when N-fertiliser is applied. The effect of this is, however, small (Tufvesson, 2010).

Emissions of CO_2 also occur during the cultivation stage. These originate mainly from transport, tractor operations and from the production of fertiliser and seeds (Tufvesson, 2010). In order to reduce the use of fossil fuels on the farm, and thereby the GWP of the cultivation stage, on-farm produced biomass can be used for tractor fuel and nitrogen fertiliser production, among other measures (Ahlgren, 2009).

With the removal and utilisation of agricultural and forestry residues, a reduced soil carbon content can offset the benefit of internal energy production in the case biomass would be the energy source in the base case. If, however, for instance coal is replaced, the removal and use of crop residues can give an overall environmental benefit to the system (Tufvesson, 2010).

The overall efficiency of the cultivation system influences the environmental performance of the renewable chemical produced. A greater harvest will, needless to say, give a larger amount of chemical produced per amount of agricultural input resources. Moreover, plant refinement to produce more of the desired component (for instance starch) would also increase the total product yield and reduce the GWP of the system (Börjesson, 2009). In Akiyama et al. (2003), the importance of the choice of feedstock is illustrated through a comparison of PHA and PHB production using soy-oil and corn, respectively. PHA production is preferential from a GWP perspective because less energy is used in the cultivation stage, compared to corn production (among other reasons). Also in Pietrini et al. (2007), PHB production using corn gives an inferior result compared to PHB production where sugarcane is used as feedstock.

Land use change

Like in all sectors where land is used for production of feedstock or feed (for instance the textile and meat industries), chemical production using crops can give rise to land use changes. A distinction is generally made between direct land use changes, *dLUC*, and indirect land use changes, *iLUC*, and both effects give climate impacts by releasing or binding carbon to the soil, thus giving either negative or positive climate impacts. Direct land use changes occur when one land use practise is replaced by another at one distinct piece of land - a positive effect would be the replacement of annual crops with perennial such and thereby increasing the soil carbon content. Other important benefits this transition entails include: reduced risk of erosion; improved water and nitrogen retention; and reduced need for use of farming equipment, fertilisers and pesticides (Glover et al., 2010). However, the opposite shift from perennial vegetation (in the worst case tropical forests or peat land) to annual crops can lead to large losses of carbon from soil to atmosphere. The same physical effects takes place as a consequence of indirect land use changes, only in this case the former land use is displaced to another location, regionally or even globally. This makes the calculation of iLUC very complex, as it is extremely difficult to estimate where the land use change will occur – one could say the system boundary of the environmental assessment has to be expanded to include the entire global cropland. The inclusion of an iLUC calculation factor in LCAs has therefore been criticised, see for instance Kim and Dale (2009). In this Kim and Dale (2009) it is argued that the current iLUC discussion has fundamental flaws since biofuel production[6] is the only land use activity that is required to take iLUC into consideration. This is a valid argument, and perhaps the iLUC discussion can lead to a more constructive debate of all types of land use and on how we choose to use our arable land currently mostly used for feed production (Hallström et al., 2011).

Not only the GWP is affected by dLUC and iLUC, also the eutrophication potential may increase or decrease, depending on the former land use and what type of energy crop is cultivated. For instance, if willow is cultivated on former grain cultivation land, both the GWP and EP may be reduced; in Börjesson and Tufvesson (2011) even negative results are obtained owing to this type of conversion.

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[6] Biofuel in this case, but the reasoning could just as well be applied to chemical production.

Many of the investigated LCAs include the carbon sequestration of the energy crops cultivated for the production of renewable chemicals. The effect of this cultivation should, however, always be investigated in terms of dLUC in the least (iLUC is very difficult to estimate, but can be discussed qualitatively). dLUC is studied in Börjesson (2009) where the environmental performance of bioethanol depends on what type of land the biomass production occupies. As first generation feedstock are the currently utilised crops for biochemical production, this investigation is of major importance since these are annual crops - the replacement of a perennial crop with, for instance, corn could increase initial GHG-emissions of the system to a not insignificant extent. Brandão and co-workers have investigated this effect for cultivation of energy crops in the UK, where the reference scenario is set to be natural relaxation of the land. The study concludes that the GHG-emissions originating from losses in soil organic carbon contributes to the largest part of the total GWP of the crop production, especially for the cultivation of rapeseed and to a lesser extent for *Miscanthus* (Elephant grass) (Brandão et al., 2011). In Kell (2012), the ability of plants to sequester carbon through growing larger root structures is instead regarded as a potential means to not only mitigate climate change, but also to improve soil properties. It is, nevertheless, stressed that more research is needed in order to develop plant species with suitable properties, and to assess possible adverse effects such a change may have on a system level (Kell, 2012).

It is interesting to note how the perception of LUC has changed over the last few of years. In Van Dam et al. (2005), the production of energy crops on unused arable land is regarded as a positive means to live up to EU-requirements and develop a biobased economy whereas, nowadays, energy crops have obtained an almost black mark.

Additional impact categories

As was briefly discussed earlier in the report, the environmental performance of biobased products may vary depending on which environmental effects are selected as the most relevant. In most of the investigated LCAs, as in this study, primary focus is on emissions of greenhouse gases. An argument for this attention is the pressing nature of the greenhouse effect problematic and the risk of detrimental consequences of the climate change. Controversially, one may argue that prohibitive measures now taken in certain areas (for instance, saving biodiversity) are of limited use if we cannot simultaneously hinder a climate change that could ruin these measures taken to prevent other issues. This, however, is a rather weak argument for ignoring the overall sustainability of the biobased product system under investigation. As is shown in some of the studied LCAs, the cultivation stage of the feedstock for the biobased product generally gives rise to poorer results in impact categories such as eutrophication potential and acidification potential (for instance, Harding et al., 2007; Groot and Borén, 2010; Urban and Bakshi, 2009; PE Americas, 2009; Brandão et al., 2011). The environmental effect can be regarded as pushed from one impact category (GWP) onto others (EP, AP). Also in Álvarez-Chávez et al. (2012), the cultivation is identified as an environmentally complicated stage of the life cycles of PLA, PHB and starch-based polymers. Human toxicity is another impact category included in the study; this may be an issue in the production of, for instance, cellulose- and lignin-based materials (Álvarez-Chávez et al., 2012). Moreover, as certain non-food crops require irrigation, water use may be an impact category of significant importance, especially in areas where water scarcity is an issue of concern.

Competition for biobased feedstock

As will be discussed in the coming section, there is potential for using various alternative sources of biomass for renewable chemical production, one example being the utilisation of organic residues from society, forestry and agriculture. For instance, in Engdahl et al. (2011), this potential (excluding forestry residues) is investigated for a region of Southern Sweden and Eastern Denmark, known as "Öresund region". The conclusion drawn is that a considerable potential for chemical production using these waste streams exists, but that this potential may be limited by competition from other sectors of society. The waste streams are in the current situation mainly used for feed production, which could imply a competition problem (Engdahl et al., 2011).

Possibilities and recommendations

Sustainable cultivation systems

From the discussion in the previous section it is clear that the overall sustainability of the cultivation stage may vary greatly depending on the farming practice applied. In order to reduce both GWP and other potential impact categories, certain measures are suggested in the reviewed LCAs. A strategy with reduced soil tillage (Börjesson, 2009; Ahlgren, 2009), or even a no-tilling system (Kim and Dale, 2009), are proposed as means to hinder emissions of CO_2 due to losses of soil carbon.

In order to avoid negative consequences of an increased utilisation of crop residues (for instance losses of soil carbon content and soil erosion), winter cover crops can be planted. In Kim and Dale (2005), the removal of corn stover for ethanol production in combination with cultivation of winter cover crops is suggested as a means to: increase the bioethanol production; decrease the emissions of N_2O from the soil; increase the soil carbon content; and to increase the yield of the following cash crop (Kim and Dale, 2005). Sustainable cultivation through, for instance, these two measures (no-tilling practices and winter cover-crops cultivation) could improve the environmental impact of this stage of the life cycle considerably - by up to 72% for PHB production where corn is used as feedstock, according to (Kim and Dale, 2008).

Another means to produce energy crops in a sustainable manner is through the use of a judicious crop rotation. For instance, by including a legume in the crop rotation the need for nitrogen fertilisation can be reduced as a result of the biological N_2 fixation of the legume. The effect of including *faba bean* in a crop rotation is investigated in Jensen et al. (2010). It is concluded that the inclusion of the legume supplies nitrogen to the system and also contributes to diversification of the cropping system, making it less susceptible to diseases and pests. However, care must be taken so that a crop with an adequate nitrogen requirement is following the faba bean to reduce the risk of biogenic N_2O emissions from the soil, discussed above (Jensen et al., 2010). In Amon et al. (2007), a sustainable crop rotation is simulated where food, feed and energy crops are produced simultaneously. The focus is on using the energy crops for biogas production, and it is concluded that a significant amount of biogas can be produced while covering the need for food and feed. The final conclusion of the paper is that the maximum yield of biogas not necessarily has to come from the use of one single crop, but could be obtained in a sustainable crop rotation system (Amon et al., 2007). This conclusion can just as well be applied on renewable chemical production where crops are used as feedstock. For another comprehensive review on different aspects of crop rotation schemes, see Zegada-Lizarazu and Monti (2011).

In the case dedicated, lignocellulosic energy crops are used for the production, cultivation may be possible on land not suitable for other crops, such as marginal land. Moreover, as these types of energy crops are often perennial, the cultivation can bring about an additional environmental service through the binding of carbon to the soil, in the case an annual crop is replaced (Tufvesson, 2010).

There is a possibility of domestic use and fair trade biomass export from several developing countries where cultivation conditions are advantageous. As the majority of the poor people in the world live in rural areas, an increased production of feedstock for biofuel/biomaterial production could develop the agricultural sector in these areas and in turn provide an income and possibly a way out of poverty (Börjesson et al., 2009). Caution must, however, be taken so that poor people are not exploited by large-scale actors, so-called "land-grabbing" must be avoided – possibly through sustainability criteria. Cultivation systems should, moreover, be designed so that food and biofuel can be produced simultaneously (Goldmann, 2011). The potential of these kinds of systems, *Integrated Food-Energy Systems,* is also highlighted in a comprehensive study published by the FAO (Bogdanski et al., 2010). Also, the choice of crop should be well-advised in order to obtain possible synergetic benefits such as decreased soil degradation. A successful example of this is demonstrated at the Mampu plantation in the Democratic Republic of Congo. Here, the establishment of a forest of Acacia trees (for charcoal production) is combined with cultivation of cassava, maize and honey. In addition to supplying the farmers with an income from the vending of charcoal, the trees maintain the soil unharmed, enabling continuous cultivation of the food crops required (Bogdanski et al., 2010).

Use of waste

As mentioned previously, there is a potential for using organic residues from society, agriculture and forestry for the production of renewable energy, biofuels and biochemicals. The use of waste and residues is generally regarded as a preferential option as it is less complex from a sustainability point of view – issues such as land use, competition with other sectors, and economic feasibility are easier to deal with compared to when using first generation crops. Already in 1991, the production of second generation ethanol using residues and crops was advocated with hopes for commercial production in ten years' time (Lynd et al., 1991). Currently, it is instead estimated that the production will develop over the coming 10-15 years and increase significantly after this (Cherubini and Strømman, 2010).

However, as with second generation crops, the often high lignin content of many residues currently poses a problem for the biochemical handling of these materials. Considerable research efforts are made, focusing on different means of pretreatment of these more complicated materials. So far, however, only a limited number of LCAs have been published which investigate the environmental impact of these processes. One of these is Mu et al. (2010) where biochemical and thermochemical production of lignocellulosic ethanol are compared. It is concluded that, depending on circumstances and how the system boundaries are set, both alternatives can be the better performing alternative. Both technologies, however, show very favourable GWP performances (Mu et al., 2010).

If the thermochemical route is chosen, less pretreatment is needed in order to utilise these woodier or complicated materials. There are, for instance, examples of plastic waste utilisation in Japan for production of hydrocarbon oil and syngas through pyrolysis and gasification, respectively (UNEP, 2009). Also in Stichnothe and Azapagic (2009) the potential of using waste is illustrated. Bioethanol produced through gasification and fermentation of the biogenic fraction of municipal solid waste shows a promising GHG-reduction potential (Stichnothe and Azapagic, 2009). However, a more comprehensive systems analysis may be required in this case in order to assess the best use of this waste fraction. Biogas production, for instance, may give additional benefits such as the provision of a bio-fertiliser.

In another study, Anex et al. (2010), the possible uses for the lignin-rich residue corn stover, are investigated. It is found that the greatest part of the higher heating value of the feedstock is retained in the product if pyrolysis is applied, see Table 4.3 below. However, it is also concluded that all studied types of processing need to be developed further in order to be implemented on large scale (Anex et al., 2010).

Table 4.3. Processing efficiency of different conversion routes calculated in Anex et al. (2010).

Production process	Processing efficiency (%)*
Pyrolysis - H_2 purchase	77.1
Pyrolysis - H_2 production	76.7
Pyrolysis - H_2 production without char	53.7
Gasification - Low Temperature	42.1
Gasification - High Temperature	52.5
Biochemical - Dilute Acid	44.1

* Product net energy out as percentage of biomass feedstock HHV.

For these described processes, however, published comprehensive LCAs are scarce which makes it difficult to say what production route is to be preferred. This lack of studies is an important issue – inherent in such a problematic is the difficulty to develop the right policies and therefore invest in the most efficient technologies.

In the biodiesel production, glycerol is an abundant by-product with significant potential for use as feedstock in a biorefinery. It is currently inexpensive and readily available, suggesting that its use for renewable chemical production would increase the economic feasibility of projects. One example of a chemical possible to produce using glycerol as substrate is the previously described bio-PDO (Bozell and Petersen, 2010). Moreover, the results of Jin and colleagues (2011) - which show an increased yield when adding hemicellulosic hydrolysates as co-substrates in the fermentation – suggest that further improvements in this production are possible.

Various waste streams from the food production sector can be considered possible as feedstock for chemical production, see for instance, Engdahl et al. (2011). In Bier et al. (2012a) the use of blood meal for production of “Novatein Thermoplastic Protein”, is investigated in further detail, this paper is described previously (Bier et al., 2012a). Sakai et al. (2004) study the possibility of producing PLA out of municipal food waste. The proposed process is slightly more energy intensive than the *NatureWorks* PLA production was at that time, but the authors of the paper argue that this may be compensated by the fact that waste is used as feedstock. Moreover, if non-food parts of the waste stream were combusted to provide steam and electricity for the PLA, the environmental performance of the system would improve (Sakai et al., 2004). Unfortunately, no LCA of the process is made[7] and it is unclear whether the research in this field has continued.

Use of unwanted plant species – synergy effects

The use of water hyacinth as feedstock for levulinic acid production is an excellent example of when synergetic benefits can be obtained through the production of bioproducts. The water hyacinth is one of the most fast growing weeds in the world, and its spreading to unnatural habitats has led to serious problems such as destruction of ecosystems, irrigation problems and increase of mosquitos. The mechanical removing of the plants is costly why the production of a refined product from this material would be very advantageous to obtain economic feasibility for removal projects (Girisuta et al., 2008).

"New" types of raw material

Much research is conducted on the possibilities of producing renewable chemicals by using algal biomass as feedstock and the market for algae-based products is expected to be developed in about ten years (Ravenstijn, 2010). The use of macroalgae as substrate is developed by *Novozymes* and *Sea6 Energy* who have started collaboration where the former supplies enzymes for the process and the latter seaweed cultivation technology. Seaweed is of interest for chemical production since it consists of sugars to a large extent - more than half of the dry weight. Seaweed is a very fast growing plant and it can be harvested several times each year in warm waters with a large supply of sunlight (Novozymes, 2012).

Also the use of microalgae is under investigation. Promising results for PHB production in *P. tricornutum* have been attained in Hempel et al. (2011). In a first analysis of the production, without enzymatic engineering and other modifications, a PHB content of 10.6 % of the dry algal weight was obtained (Hempel et al., 2011).

4.3.2 Process

The choice of production process and efficiency of this is of great importance for the overall environmental performance of the system. As is clear from the previous chapters, one can go about in many different ways in order to produce bulk chemicals and materials with, in many cases, rather similar areas of application. It is thus crucial to firstly determine the desired service (for instance, "coating lasting X years" or "container with a capacity of fitting Y material for Z days/years") and after this consider the most environmentally adequate route to produce this. As comprehensive LCAs are scarce for certain processes, the current study can only point out factors of importance for the environmental performance. Further research is certainly needed on this stage of the life cycle.

Hot spots

Yield

Understandably, a high product yield in a biochemical or thermochemical process will give the system a favourable overall environmental and economic feasibility. For this reason, the conversion of bioethanol plants to biobutanol producing such is questioned in Pfromm et al. (2010). According to the study, approximately 25% of the LHV of

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[7] According to the knowledge of the authors.

bioethanol would be produced in the form of biobutanol if a reactor was converted to ABE fermentation. This since the volumetric productivity is lower and the fermentation time is longer for the ABE-fermentation compared to conventional yeast-based bioethanol fermentation. Moreover, the facility would have to be converted to handle sterile operations and inoculum preparation (Pfromm et al., 2010). Also in Wu et al. (2007), bioethanol production performs superior compared to biobutanol production. Contrary to the results of these papers, Swana et al. suggest a transition from bioethanol production to biobutanol production would increase the productivity (2011). Clearly, more research is needed in order to determine what technology is preferential in the case the same area of application is intended. The conversion of bioethanol plants to biobutanol plants should therefore be carefully reconsidered.

Type of process energy used

The environmental performance of the production system is largely influenced by the type of energy source used in the process. In Börjesson (2009), this parameter is identified as a hot-spot – bioethanol produced with coal as process energy (instead of bioenergy as in the base case) gives a GWP larger than that of petrol. In Kim and Dale (2009), the natural gas used in the bioethanol production plant is recognized as a hot-spot. This is also the case for biobutanol production according to Wu et al. (2007). Here, the use of crop residues for internal energy production is a possible solution. This will be discussed further in the coming section concerning biorefineries. *Natureworks* have previously been purchasing renewable energy certificates to come around the problem of a dirty available electricity mix. Hermann and colleagues point out that this solution is valid in an LCA investigating a product from a company perspective, concerning business relations. However, if the aim of the LCA is to investigate a certain technology, bought RECs will not be relevant for the result of the study (Hermann et al., 2010).

Highly emitting processes

Certain production processes are highlighted as important from a GWP perspective. In the PLA production, for instance, both in Vink et al. (2007, 2010) and Groot and Borén (2010) point out the lactic acid production as a process stage contributing significantly to the GWP. In Groot and Borén (2010), the pretreatment[8] of feedstock is also identified as a hot spot. For PHB production, the steam drying of the polymer and the agitation and aeration of the fermentation process are the major GWP-contributors, according to Akiyama et al. (2003). Also in Yu and Chen (2008), aeration is an important emitting process. Focus should thus be on reducing the impacts these stages give rise to.

Thermochemical vs. biochemical production

In the literature search made for this study, only three life cycle assessment have been found where the GWP of biochemicals produced through gasification is calculated (Nouri, 2006; Stichnothe and Azapagic, 2009; and Mu et al., 2010). However, the result obtained in Nouri (2006) is interesting as it is in the same range or lower compared to other plastics, both renewable and conventional such (Nouri, 2006). Also in Stichnothe and Azapagic (2009), gasified waste performs well in terms of GWP. In Mu et al. (2010), biochemical and thermochemical lignocellulosic ethanol production show similar environmental performances, both acting as carbon sinks from a cradle-to-gate perspective.

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[8] Sugarcane-milling in this case.

The reason so little research has been made in this field is difficult to tell, perhaps problems related to gasification, such as formation of ash and tar, are regarded as difficult to overcome. However, the thermochemical production is developing, alongside the biochemical production. *Cortus*, for instance, has recently succeeded in producing syngas with a very low content of polluting compounds, which makes the whole process more efficient as the need to clean the gas is reduced. Moreover, with this new technology, feedstock of with varying properties (wet, dry etc.) can be used (Chemicalnet, 2011).

Recently, the Danish government decided to end previously large investments in biochemical production of second generation ethanol where straw is used as feedstock (Pröckl, 2012). The decision is based on a study, which has resulted from the *CEESA project*, a research project where a future fossil-free Danish energy system is demonstrated. In this study, emphasis is put on electrifying the energy system, and all biomass is used for gasification (Lund et al, 2011). Whether such a strategy is the most efficient or not is difficult to tell - biochemical production is possibly the most suitable technology for certain applications and thermochemical for others.

Possibilities and recommendations

The biorefinery, an integrated approach

The available non-food biomass can be used for several different purposes, as has been discussed previously. The possibility to use several different technologies (such as fermentation, gasification and CHP production) to produce diverse final products may indeed give rise to competition problems. A possible way to reduce those problems is through the use of a biorefinery. Producing biomass-based products in a biorefinery is a way to efficiently make use of the available organic feedstock. The definition of a biorefinery varies, in the US, a biorefinery could be any facility where one single product is produced from one type of renewable feedstock. The future biorefinery should, however, rather produce a number of different products (for instance food, feed, chemicals and/or energy) from a range of different feedstock (for example waste streams, residues and/or crops). The use of cellulose and lignin-rich residues for the production is seen as an advantage since there is a limited competition for this material. When using this type of material the biorefinery is called a second generation biorefinery. In a future biobased economy, a combination of the biochemical and the thermochemical route could be possible in a biorefinery. Van Dam et al. suggest the C5 and C6 residues from the biochemical route are used for thermochemical production of syngas (2005). A similar approach is given in Cherubini and Strømman (2010). Here, the C6 part of the feedstock is used to produce bioethanol, the C5 to produce furfural and the lignin part is used for production of FT-diesel (Cherubini and Strømman, 2010). Another means of an integrated system is given in Bludowsky and Agar (2009) where the use of residual heat from the biorefinery system is used for a special type of thermochemical conversion - aqueous phase reforming. This type of gasification needs lower temperatures than other “conventional” means of gasification.

In Yu and Chen (2008), a biorefinery is simulated where bioethanol is produced from corn stover whereafter PHA is produced from the black liquor that remains from the bioethanol fermentation. The system is thus producing three different products: corn for food/feed purposes, bioethanol and a bioplastic (Yu and Chen, 2008). These types of solutions would simplify many problems related competition and the study confirms the fact that one means of utilisation of a feedstock not necessarily has to exclude another.

General efficiency measures

Most of the production technologies described in this study are at early stages of development. This suggests that there is a considerable potential for improvement, which will give both increased profitability and improved environmental performance per unit produced. For instance, according to engineering estimates of *NatureWorks* from 2003, the fossil energy use for production of next-generation PLA could be decreased to 90% of the use of the petroleum-based alternatives if the following technological improvements were achieved (Vink et al., 2003):

- crop residues used as the primary feedstock (instead of corn)
- separation of cellulose, hemicellulose and lignin in a biorefinery where the lignin would be combusted or gasified to produce steam (which would be used for the conversion processes)
- optimisation of the lactic acid production
- use of wind-power electricity
- optimisation of the energy efficiency in the lactic acid- and PLA-production plants

4.3.3 Use-phase

In many LCAs of renewable products, the use-phase is not included. This can be due to a lack of data, that multiple options are possible or the assumption that the use-phase of the renewable product is equal to that of the fossil alternative (as in, for instance, Hermann et al. (2007)). For drop-in solutions, this simplification is valid but for biodegradable products the use-phase may either improve or reduce the environmental credential.

Hot spots

Replaceability

In the transition to a more sustainable society, the replacement of fossil products and materials with renewable such is generally regarded as a possible way forward. Often, this conversion gives environmental benefits (at least in terms of GWP) as has been observed in the current study. However, before replacing a conventional material with a renewable such, the whole life cycle of the product should be contemplated. The importance of this pre-consideration is made very clear in Pietrini et al. (2007). The environmental benefit of the production of a renewable plastic (PHB) is completely offset in the use-phase when this material is used for interior finishes of a car. This is due to the higher density of the PHB compared to its fossil alternative, which reduces the fuel-economy considerably and thus also increases the environmental impact. For comparison, a “non-mobile” computer housing is also made out of PHB – for this purpose the use-phase implies no problem, the renewable computer housing performs better than its fossil substitute (Pietrini et al., 2007).

Furthermore, some mechanical properties of the renewable plastics have to be further investigated, for instance their duration if placed close to mechanical or electrical components where heat is generated. According to Pietrini et al. (2007), *“…it is well-known that, during the biodegradation process, the mechanical performances of a polymer decrease dramatically”.* This stands in contrast to results from Auras et al. (2005) which show that virgin PLA, but also PLA mixed with recycled PLA, have mechanical and physical properties similar to those of PET and PS, why PLA functions adequately for packaging purposes (Auras et al., 2005). Also in Van Tuil et al. (2000), it is argued that biobased plastics can obtain the desired mechanical properties through either blending of different polymers or adding of, for instance, plasticisers, fillers or fibrous materials (Van Tuil et al., 2000).

For certain applications, such as the packaging materials described in Hermann et al. (2010) and the shopping bags described in Mattila et al. (2011), other types of renewable materials (for instance, paper) may provide the same service with a lower environmental impact. In the same way, the use of plant materials in biocomposites (described below) gives the opportunity to "supplement" the use of renewable polymers which may reduce the environmental footprint of the product, as is shown in Zini and Scandola (2011). It is thus important to have a holistic view in order to obtain a function in a means as sustainable as possible.

Where produced, where used?

If, due to a currently limited infrastructure for the renewable plastics, the products have to be transported large distances to fulfil their purposes, the environmental benefit may be reduced. This is the case in the previously described LCA by Madival et al. (2009), where PLA resin/containers used for strawberries are transported across the US a number of times for different production stages. This problem should, however, be relatively easy to handle through more measured planning of the logistics (which is needed in the goods-transportation sector in general). Also, with a development of the renewable-plastics sector, more facilities necessary for different processing stages will be built which should simplify logistics.

Possibilities and recommendations

The biochemically produced plastics have different characteristics than the drop-in solutions and fossil plastics why other fields of applications may be suitable, uses where their inherent biodegradability comes of hand instead of being a disadvantage.

Replaceability

Contrary to the example described above, where the use of PHB car interior gave a very negative environmental impact due to the use-phase, the use *biocomposites* can have the opposite effect on the fuel economy of vehicles. For example, as plant fibre have lower density than glass fibre, the use of composites made out of polymers reinforced with plant fibre will give an improved fuel economy compared to glass fibre composites when used in the automotive sector. Other advantages of natural fibre composites include good insulation properties and non-toxicity. However, care must be taken to avoid moist in the production process as components of the cellulose are hydrophilic, which may lead to porous products. Crops that may be suitable to use as reinforcements in biocomposites include, among others, Switchgrass and Indian grass. Moreover, various agricultural and industrial residues can be used such as rice husk, wheat straw, feathers and by-products from the wool industry. When the environmental performance of plant fibre reinforced products have been compared to products where glass fibre is used, the GWP is reduced significantly in the biocomposite cases. A biocomposite where the polymer used is a renewable such, is known as a green composite (Zini and Scandola, 2011).

The replacement of conventional materials with renewable substitutes can also, in certain applications, bring about other types of benefits. One example is the reduced impact on health when chemicals such as styrene and bisphenol A are replaced (Ravenstijn, 2010).

4.3.4 End-of-life

When discussing the final disposal options available for renewable products, a reminder of what is known as the waste hierarchy is in place: "*to reduce, reuse, recycle*" or as Ravenstijn (2010) presents it: "*True waste management begins with limiting waste, that is, reducing the amount of waste generated in the first place, and reusing items and their components to the fullest extent possible".* Both from a natural resource and an energy conservation perspective, having this frame of mind is crucial. There is little possibility of sustainable development if the production of renewable products is not combined with an overall reduction of the amount of products used.

Like for the use-phase, the end-use of the product is excluded in many of the investigated LCAs. This is a problem since the environmental performance of a product may be improved or reduced depending on the final disposal alternative chosen. The difference between, for instance, incineration with energy recovery and landfilling would give very different LCA results for two products with otherwise identical life cycles up to this point. In Mattila et al. (2011), the significance of different assumptions regarding end-uses is made clear. In the paper, the GWP-performances of five different types of shopping bags are investigated from cradle-to-grave, with comprehensive sensitivity analyses made. One robust finding is that the recycled plastic bags outperformed all other bags in a scenario with a low level of waste combustion. In this scenario the biopolymer gives the worst environmental footprint. However, in scenarios with high levels of combustion the situation changes, depending on what fuel being replaced in the heat production. (Mattila et al., 2011).

Hot spots

Uncontrolled emissions of methane and unused potential for energy recovery

If the final disposal of a biodegradable plastic is landfill, its environmental performance can be reduced due to uncontrolled emissions of methane if anaerobic conditions prevail. In a study by Morken and Nyland (2002), this effect proved to have significant importance, making the biodegradable plastic perform worse than its fossil alternative in terms of GWP. Also in Ravenstijn (2010), the unreservedly positive marketing of biodegradability is questioned. The author argues that the uncontrolled biodegradation of bioplastic material is a waste of energy, and moreover, that it, under unfavourable conditions, can bring about methane emissions rather than carbon dioxide and water emissions (Ravenstijn, 2010). According results from experiments carried out by *NatureWorks*, however, their PLA products will not release methane when landfilled (NatureWorks, 2012b). Moreover, the amount of waste disposed of in landfill will hopefully be reduced thanks to preventative measures such as the *Landfill Directive* in the EU (European Council, 1999). The issue is, nevertheless, very important to take into account as methane is a very potent greenhouse gas.

An interesting finding made in Hermann et al. (2010) is that for non-renewable plastics, the best end-of-life option (from a GWP point of view) is incineration with energy recovery whereas for biodegradable plastics, the best option is digestion. Digestion scores higher than composting and slightly higher than incineration for these materials (Hermann, 2010).

Biodegradability

The fact that different types of bioplastics are biodegradable to different extents and degrade at different speeds should be made clear for the customers. PLA, for instance, is marketed as a biocompostable plastic but this applies for industrial composting conditions (NatureWorks, 2012a). Home composting is thus not an option, and new infrastructure for the collection of PLA for centralised industrial composting must be developed in order for the PLA to be truly biodegradable. One may also argue that other disposal options would give greater environmental benefits, see the waste hierarchy described previously. If recycling is not possible, incineration of PLA would give green electricity and heat which is not the case in the composting scenario.

Recyclability

From the reasoning above it is clear that the preferential end-of-life option for many renewable products (as well as conventional) would be recycling. However, the introduction of biomaterials into the existing recycling infrastructure must be made with care in order to obtain a harmonic transition. Moreover, recycling of PLA, for instance, is currently not common practice (Madival et al., 2009; PE Americas, 2009) and the physical and mechanical properties of the material may make the recycling problematic. Results from experiments carried out by Scaffaro et al. show that recycling of PLA (blended with impact modifiers) makes the material stiffer and reduces its deformability, impact resistance and water absorption (2011). On the other hand, Auras et al. (2005) argues that the properties of virgin PLA mixed with recycled PLA are sufficient for packaging applications. 3GT polymers (for instance, Sorona®) are possible to recycle but it is of greater importance that the material is dry, clean and free from other polymers than it is for, for instance, PET (Kurian et al., 2005).

As for the different types of conventional plastics, separation of the renewable plastic from the conventional ones must be made possible in order to avoid contamination of the new, recycled material. Both in the US and in Europe, different labelling exists for different plastics (Barker and Safford, 2009) but it may still be problematic to ask consumers to sort these different fractions. Another approach is to mechanically sort the different plastics after collection. *NatureWorks* have investigated the possibilities to extract PLA from the stream of recycled plastics by means of either *Near-Infrared sorting* or *Black Light Illumination*. With both technologies, promising results have been obtained (NatureWorks, 2012c). Nevertheless, recycling companies in Sweden now warn that the mixing of biodegradable plastic bags into the conventional recycling may lead to considerable problems. The only way to save a recycled plastic batch contaminated with biodegradable plastic is to add large amounts of antioxidants, which is not environmentally sound. With the currently used technology, the biodegradable bags cannot be separated from conventional bags (Karlsson-Ottosson, 2012).

As have been discussed before, these problems do not apply for drop-in solutions since these plastics have the same properties as conventional plastics. They can thus be recycled in the existing infrastructure, which makes the focus more general – how do we increase the overall rate of recycling?

Possibilities and recommendations

Biodegradability

Above, the disadvantages of biodegradability are discussed. Normally this is not done since the concept of biodegradability is regarded as something positive, as a means to handle the great problems of littering and build-up of mountains of waste. One may argue, however, that these problems should be solved on a more personal or infrastructural level rather than the end-of-pipe solution of creating litter that will dissolve. Biodegradability can, nevertheless, be a property of great value for certain areas of application. For instance, seedlings used in reforestation (see Figure 4.5 A) or agricultural mulch film (see Figure 4.5 B) are products where biodegradability may enhance the performance. Removal of conventional mulch film is costly and labour intensive why hopes are high for the introduction of biodegradable such, especially in organic farming. According to estimates made by the biomulch-film producer *Novamont,* 50% of the GHGs emitted when using conventional mulch film can be saved if biodegradable film is used instead. *Novamont* also suggests that their biodegradable plastic *Mater-Bi*® should be used for production of, for instance, food waste bags (Novamont, 2009). This approach has recently been tested in Berlin where biodegradable (but not completely renewable) plastic bags were handed out for the collection of organic household waste. The test proved successful as it both increased the overall amount of waste collected and also decreased the amount of non-biodegradable plastics in the waste stream. The collection procedure was also perceived as less complicated and more hygienic. The bioplastic bags reduced odour, kept away insects and reduced the need to clean the collection bin (European Bioplastics, 2012).

Figure 4.5. A: Seedling used for reforestation (Biocycle, 2012c). B: Agricultural mulch film (Wikipedia, 2012)

Biodegradability could also be of great use for products used in the medical sector. Objects needed for tissue engineering and drug delivery therapy are, indeed, gaining in utility when they can biodegrade into non-toxic compounds inside the body (Aldrich, 2011).

Durability ("Unconventional carbon capture and storage")

Accordingly, biodegradable plastics are of great use for certain applications, whereas durability of the material is key for other uses. One example of this is in the construction sector. Here, drop-in solutions with long life-times are suitable - one could even argue that the use of these could work as a carbon sink. For example, if renewable ethylene is used for the production of PE or PVC and this plastic subsequently is used for the production of piping systems, the carbon up-taken by the plant in the beginning of the life cycle would be stored for as long as the pipes are in the ground. This is an interesting thought, which is applicable for many other products used in the construction sector. The same is indeed true for all renewable plastic objects if they are completely recycled (and not biodegrading). In Vink et al. (2003), the authors assert that the NatureWorks PLA acts as a means of carbon sequestration when it is recycled. As PLA degrades slower than certain other types of biodegradable plastics, this is true to some extent but it is, nevertheless, a rather equivocal claim from a company that produces a plastic marketed as biodegradable. Another example of confusing marketing for carbon sequestration is "*Novomer's technology can make the first carbon negative diaper*" (Mahoney, 2012). The diaper will only store carbon for as long as it is not used and disposed of.

A final interesting example of how the final disposal can give a favourable overall environmental performance of a system, is given in Intini and Kühtz (2011). The study is a life cycle assessment where recycled PET is used for insulation of buildings. The result of the study shows that the use of recycled PET gives a greater environmental performance than the use of virgin PET. The energy pay-back-time for the recycled PET insulation is two years (Intini and Kühtz, 2011). The use of PET bottles made out of renewable polyethylene would most likely give an environmental performance greater still.

4.3.5 LCA as a tool, comparability

Direct comparisons of LCAs to assess environmental credibility can be problematic. Uncertainty regarding data, choices and relations within the system as well as spatial, temporal and technological variability must be acknowledged (Mattila et al., 2011). When conducting an LCA, certain guidelines found in international standards (ISO, 2006) are to be followed but it is, nevertheless, up to the author to decide various features which may influence the result. The literature compilation made in this study confirms this fact – in some cases the results from LCAs made of the same product vary significantly even when similar production systems are analysed.

System boundaries and allocation

The choice of system boundaries is the author choice, and can thus be seen as a rather arbitrarily part of the study. As the effect of this choice can have significant impact on the result, transparency is essential as well as openness about the possibly limited comparability of the study. The choice of allocation (or system expansion) should be made according to the aim of the study. If, for instance, the result of an LCA of a renewable product is to be compared to that of its fossil alternative, the same allocation procedure should be used for the two products.

The environmental impact of the renewable chemical production depends largely on how the system boundaries are set for the production system. One of the most important decisions made here is what time frame to analyse, which has been discussed in the previous sections. It is clear that the result of a study may vary significantly, both to the better and to the worse, if, for instance, a cradle-to-gate LCA is made instead of a cradle-to-grave assessment.

Also the choice of allocation is connected to the system boundaries. According to the ISO-standard of LCA, allocation should be avoided through extension of the system boundaries when possible (ISO, 2006). One example of this is when by-products from the raw material production can be used for the internal energy demand. This is the case at the PLA production site in Thailand where the by-product bagasse is used for steam production for the sugar mill. Surplus steam produced can, moreover, be used for electricity production, which makes this biopolymer production system a net producer of green electricity (Groot and Borén, 2010).

System expansion is, however, applied to different extents in different LCAs. The effect of this is very clear in the comparison of the LCAs of PHB production carried out by Kim and Dale (2008) and Harding et al. (2007). In Harding et al. (2007), the system boundary is rather narrowly set. When bagasse is combusted for energy production, this is not counted as a carbon neutral process but as a net emitting process. This is true in the case the sugarcane is not regrown, but the conventional way of calculating GHG-emissions from crops is to assume carbon neutrality. In Kim and Dale (2008) on the other hand, the system boundaries are instead extended and the renewable process energy produced from by-products is not only regarded as carbon neutral, but carbon credits are also given for the use of these by-products. Another extensive system expansion is made in Vink et al. (2007). Here, renewable energy certificates are bought to offset the fossil energy used in the production of PLA (Vink et al., 2007).

When residues are used for production of biochemical, the allocation procedure can largely influence the environmental performance of the system. The two allocation methods suggested in the ISO-standard, physical and economic allocation, both have their disadvantages: with physical allocation an unreasonably large part of the environmental impact can be allocated to relatively “heavy” by-products whereas values used in the economic allocation are not constant over time. To avoid these issues, system expansion can be applied. This may, however, also be difficult if the residue has many alternative areas of utilisation – separate LCAs for these alternatives will be needed and a comprehensive sensitivity analysis should be made to show the effect of different scenarios. Such an assessment is made in Bier et al. (2011a) where the effect of different allocation methods in the production of a bioplastic from blood meal is comprehensively investigated. The GHG-performance of the product varies significantly depending on the rather complex question of how the blood residue should be valued (Bier et al., 2011a). With mass allocation, the advice to policy makers would be not to encourage the production of the thermoplastic at all while the recommendation would be the opposite if the blood is regarded as a waste stream (when the entire environmental burden is allocated to the produced meat). A similar result is obtained in Törnvall et al. (2009) where fatty epoxides are produced using either rapeseed or a by-product form the pulp industry, tall oil, as feedstock. Due to the fact that the tall oil is considered a by-product, it outperforms the rapeseed product by far from GHG perspective (Törnvall et al., 2009).

Local conditions

The comparability of LCAs can also be complicated by different conditions caused by the geographic variances of the systems. The local energy mix is the parameter, which most prominently influences the result in this sense, both directly (the actual energy source being used for the process) or indirectly (the energy source assumed to be replaced with a system expansion).

This is exemplified in Gerngross (1999) and Gerngross and Slater (2003) where environmental benefit of PHB production by means of fermentation is been questioned. These studies conclude that the environmental benefit of the renewable feedstock is offset by the fossil energy used in the cultivation and production of the renewable polymer (Gerngross, 1999; Gerngross and Slater, 2003). What must once again, however, be held in mind are the local conditions. The result comes from American conditions where both the corn cultivation and the process electricity used imply large amounts of fossil energy. Gross and Kalra respond to the described articles by highlighting the example of Brazilian sugarcane-based PHB production which, in combination with an integrated use of crop residues for internal energy production, would give zero net emissions (Gross and Kalra, 2003). The local electricity mix also proved important in Bier et al. (2011b) where thermoplastic production in New Zealand gives a rather favourable GHG footprint owing partly to the fact that the national electricity mix consists of 65 % hydropower (Bier et al., 2011a). The same is showed in Börjesson (2009) and Mattila et al. (2011) where the GHG performances of bioethanol and plastic bag production, respectively, are largely influenced by the type of process energy used and replaced.

5 Economic assessment of biochemicals

In the following section an overview of available economic assessments of biorefinery systems in literature will be presented followed by findings from the economic model developed by the authors, which will be used to normalise the results and to demonstrate the effects of the key process parameters.

5.1 Overview of economic assessments in literature

The products, with available economic assessments in the literature, have been listed in Table 5.1 together with a description of the biomass used, and the general type of process used.

Table 5.1. Information on bio-derived products used in the economic model.

Product	Biomass	Process	Reference
Ethanol	Corn	Fermentation (Yeast)	Tao and Aden, 2009
Ethanol	Cornstover	Fermentation *(Zymomonasmobilis)*	Tao and Aden, 2009
Ethanol	Woodchip	Thermochemical Gasification	Tao and Aden, 2009
Butanol vs Ethanol	Corn and switchgrass	Fermentation (yeast or *Clostridium acetobutylicum*)	Pfromm et al., 2010
Butanol	Corn	Fermentation *(Clostridium acetobutylicum)*	Tao & Aden, 2009
HMF	Fructose	Biphasic Chemical transformation	Kazi et al., 2011
Furfural	Waste aqueous hemicellulose solution	Thermochemical Biphasic dehydration	Xing et al., 2011
Lactic Acid	Sugarcane juice	Fermentation *(Lactobacillus plantarum)*	Sikder et al., 2012
Succinic Acid	Glycerol	Fermentation	Vlysidis et al., 2011
Levulinic acid (As ethyl levulinate)	Paper sludge, agricultural residue Waste paper	Thermochemical Acid hydrolysis	Kamm et al., 2006
Glycerol	Rapeseed, waste oil	Transesterification	Vlysidis et al., 2011

5.1.1 Bioethanol and Biobutanol

The main source of information for the process economic data for bioethanol and biobutanol is extracted from *“the economics of current and future biofuels”* by Tao and Aden (2009), see Table 5.2. The study compares the process economics of bioethanol produced from corn, corn stover, and wood chips in different types of processes, as well as biobutanol produced from corn. It is a relatively comprehensive study, which considers most of the research done in this field.

Table 5.2. Baseline economic assumptions and results of the process economic studies of bioethanol and biobutanol (Tao & Aden ,2009). The study assumes 170,000 m³ production operating a 350 days per annum. The installation factor was 3 and the economic life time of the equipment was set to 20 years.

	BioEthanol Corn	BioEthanol Corn stover	BioEthanol Wood chips	BioButanol Corn
Process type	Fermentation	Fermentation	Thermo-chemical	Fermentation
Feedstock	Corn	Corn stover	Wood chip	Corn
Feedstock cost (€/kg)	0.13	0.05	0.05	0.13
Total capital investment (10^6€)	116	162	212	243
Total production cost (10^6 €/yr)	101	57	60	208
Raw material (% of op. cost)	63%	56%	45%	57%
Operation (% of op. cost)	20%	16%	18%	27%
Labour (% of op. cost)	1%	2%	2%	1%
Equipment (% of op. cost)	7%	14%	18%	6%
General expenses (% of op. cost)	9%	12%	16%	9%
Total op. cost (€/kg)	0.75	0.43	0.44	1.51
Co-product credit (€/kg product)	0.11	0.02	0.07	0.82
Total production costs (€/kg product)	0.64	0.41	0.37	0.69

From the results in the study it can be seen that the lignocellulosic feedstock, corn stover and wood chips respectively, result in the lowest product price due to lower production costs and high co-product credits. A more detailed analysis of the results further shows that the feedstock costs are the most significant cost factor. Wood chips and corn stover is less than half the price of corn, which in turn result in lower selling prices. It is also seen that operating costs and to a certain extent the equipment costs have a significant impact on the production cost. It is found that the equipment costs are somewhat higher when using cellulosic raw materials due to the more technically challenging pre-treatment. Interestingly, also the credit from the co-products have a major impact on the final production costs, especially so for biobutanol (where acetone and ethanol are co-produced). A graphical illustration of the overall cost distributions for the bioethanol and biobutanol refineries are shown in Figure 5.1.

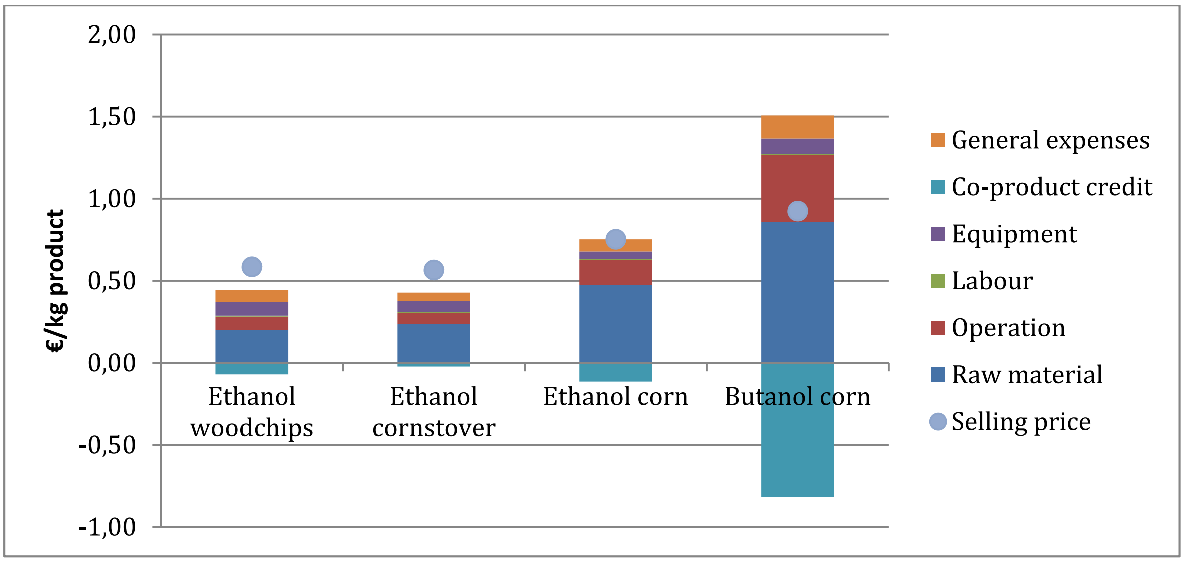

Figure 5.1. Bar graphs of the production costs for ethanol and butanol production from different feedstocks. The expenses are illustrated above the x-axis and the revenues from co-product credits are illustrated below the x-axis. The light blue dots show the selling price based on a 10% return on investment. For biobutanol the selling price is significantly decreased by the co-product credits.

5.1.2 Other biochemicals

Few articles can be found which assess the process economics of the production of chemicals other than the biofuels. Some articles are focused on the economic assessment of integrated biorefineries producing biodiesel with succinic acid, and glycerol as the co-product (Zhang et al., 2003; Haas et al., 2006; Tao and Aden, 2009; Vlysidis et al., 2011). Apart from these there is a lack of studies. For instance, it has not been possible to find articles assessing the process economics of levulinic acid, despite the fact that levulinic acid has been considered one of the top value-added bio-derived chemicals for over a decade (Kamm et al., 2006; Werpy and Petersen, 2004; Bozell and Petersen, 2010). Only one article including the production cost of levulinic acid through the Biofine™ process (Kamm et al., 2006) was found, however the product was the ester of levulinic acid, ethyl levulinate. From the ones found the overall findings are analysed and discussed in the section below.

Furfural

Xing et al. (2011) have studied the chemical production of furfural and carboxylic acids from waste aqueous hemicellulose solutions from pulp and paper and cellulosic ethanol industries. The objective of the study was to optimize the reaction conditions in a continuous flow biphasic reactor. On the basis of this, a conceptual design was developed together with a preliminary economic analysis.

Compared to existing processes the studied process presents a cheap and abundant raw material (waste hemicellulose solution from pulp and paper industry), lower energy intensity and good compatibility with pulp and paper processes.

The raw materials and utilities costs were the most significant cost factors in the total production cost. Still, the cost of xylose is very low because it is extracted from a hemicellulose waste stream from the pulp and paper industry (Xing et al., 2011). The cost of furfural was also significantly lowered by the co-product revenues of acetic acid and formic acid (60% compared to operating costs), see Table 5.3.

Table 5.3. Baseline economic assumptions and main results of the process economic study of furfural (Xing et al., 2011).

Furfural		
Basic economic assumptions (2009$)	Plant capacity:	78 ton/yr
	Operation:	8150 h/yr
	Raw material (xylose) cost:	$130/dry ton
	Installed equipment cost:	$24,550,000
Results	Production cost	$366/ton
	Largest cost components:	Raw material costs (xylose, HCl and THF) and utilities (steam)

THF: Tetrahydrofuran

HMF - Hydroxymethylfurfural

Kazi et al (2011) have performed a techno-economic analysis of dimethylfuran (DMF) and hydroxymethylfurfural (HMF) production from pure fructose in catalytic processes based on published laboratory results.

Raw material costs constituted 52% of total production cost whereas operating cost was 20%. Feedstock availability and price, low yields and high capital costs were seen as the most significant challenges for a commercial implementation of the HMF process. The technologies studied are not well developed but their characteristics are favourable for rapid technological development and cost reduction, see Table 5.4.

Table 5.4. Baseline economic assumptions and results of the process economic study of HMF (Kazi et al. 2011).

HMF		
Basic economic assumptions (2007$)	Performance criteria:	Discounted cash flow method: 10 % internal rate of return (after tax), 100 % equity financed
	Plant capacity:	60,900 ton/yr
	Equipment lifetime:	20 years
	Operation:	350 days/yr
	Fructose cost:	$300/ton
	Installed equipment cost:	$102,370,000
Results	Product cost:	$1.33/L
	Largest cost components:	Fructose cost, by-product prices, catalyst costs and purchased equipment costs.

Lactic acid

Sidker et al. (2012) performed a techno-economic analysis of membrane-integrated bioreactor system for production of lactic acid from sugarcane juice.

The single largest operating costs were yeast extract and raw material costs (85% of total production costs). The fermentation step represented the most of the fixed capital investment. To decrease the raw material consumption it is found that a continuous operation in a membrane integrated bioreactor coupled with microfiltration and nanofiltration could be useful. It should be noted that lactic acid was produced from sugarcane juice (Sidker et al., 2012), a relatively inexpensive raw material, see Table 5.5.

Table 5.5. Baseline economic assumptions and results of the process economic study of lactic acid (Sikder et al. 2012).

Lactic acid		
Basic economic assumptions (2011$)	Performance criteria:	5% interest rate and 15 years payback period
	Plant capacity:	16900 ton/yr
	Equipment lifetime:	15 years
	Operation:	325 days/yr
	Sugarcane cost:	$200/ton
	Installed equipment cost:	$1,910,550
Results	Product cost:	$3.15/kg
	Largest cost components:	Sugarcane juice and yeast extract

Succinic acid and glycerol

A techno-economic analysis of biodiesel biorefineries was performed by Vlysidis et al. (2011). Integrated designs for the co-production of fuels and chemicals were assessed. The concept of integrated biorefineries was explored in a study of the process economics of alternative schemes for the co-production of biodiesel and chemicals. The schemes used in this study were: the co-production of succinic acid and the production of 95% glycerol.

Small capacity biodiesel plants (<$10\cdot10^3$tonne/yr) require additional revenues apart from biodiesel profits, due to the high costs of raw materials. Succinic acid showed the most profitability compared to glycerol due to higher revenues, see Table 5.6.

Table 5.6. Baseline economic assumptions and results of the process economic studies of succinic acid and glycerol (Vlysidis et al., 2011).

Biodiesel with co-production of Succinic acid and Glycerol		
Basic economic assumptions (2007$)	Performance criteria:	Net present value, return on investment, discounted payback period, payback period, and internal rate of return
		7840 ton/yr
	Plant capacity:	20 years
	Equipment lifetime:	330 days/yr (7920 h/yr)
	Days running	€335/ton
	Rapeseed	
	Installed equipment cost	€8,361,100
	Succinic acid	€4,302,200
	Glycerol	
Results	Product cost	
	Biodiesel (succinic acid co-production)	€1.01/L
	Biodiesel (glycerol co-production)	€0.90/L
	Succinic acid	€4311/ton
	Glycerol	€350/ton

Levulinic acid:

In a study by Kamm et al. (2006) *the Biofine™ Process* is assessed for the production of levulinic acid, furfural, and formic acid from lignocellulosic feedstocks (paper sludge). The Biofine™ process consists of a two-stage acid catalysed reaction. In the first plug-flow reactor the feed is dehydrated to HMF. Levulinic acid is then produced in the second back-mix reactor together with formic acid and furfural. The formic acid and furfural is kept in the vapour-phase to ease the separation of these products (Rackemann et al., 2011). The levulinic acid is finally converted to ethyl levulinate (Kamm et al., 2006), see Table 5.7.

Table 5.7. Baseline economic assumptions and results of the process economic studies of levulinic acid (Kamm et al.,2006).

Levulinic acid/Ethyl levulinate		
Basic economic assumptions (2005$)	Plant capacity: Paper sludge: Installed equipment cost:	133,000 ton/yr €40/ton €75,000,000
Results	Product cost	€291/ton
	Cost factor	Raw materials

Xylitol, Sorbitol, 3-HPA, FDCA

No recent process economic articles concerning the production of xylitol, sorbitol, and FDCA are available. In the case of xylitol and sorbitol it is assumed that the lack of recent economic assessments is caused by the fact that these are relatively mature processes. Since the 1950's sorbitol has gained high economic importance and xylitol has been commercially produced since the early 1970s (Schiweck et al. 2012).

For the production of 3-HPA, parallels can be draw to other similar compounds, like lactic acid, where highly efficient processes have been developed. However, the bio-derived production of 3-HPA suffers from product inhibition due to its toxicity, and the large scale commercial production is therefore not yet available. The lack of economic assessments of FDCA, is possibly caused by the currently low yield and the lack of knowledge with respect to industrial processes (Bozell and Petersen, 2010; Werpy and Petersen, 2004).

5.2 Key operating parameters

5.2.1 Raw material cost and process yield

It is clear from the present and other studies that the impact of the raw material cost on the total costs are significant and as can be seen from the results in Table 5.8 both the carbon source (e.g. corn stover or sugar) as well as other raw materials, such as enzymes for cellulose degradation and yeast extract can make up a large portion of the raw material cost. It is therefore logic that the process efficiency or yield in terms of how much of the raw material that is converted to the desired product is of utmost importance. As can be seen in Figure 5.2, improvements in yield can lead to significant savings.

Table 5.8. Summary of total raw material costs for the bio-derived product where the biomass costs showed lower than 90% share of the total raw material costs.

Bio-derived product	Raw materials	Costs [€/kg product]	% of total raw material costs
Bioethanol	Corn stover	0.171	73%
	CSL	0.010	4%
	Cellulase	0.033	14%
	Others	0.019	8%

Furfural	Xylose	0.233	41%
	NaCl	0.029	5%
	Makeup TMF	0.146	26%
	HCl	0.159	28%
Lactic Acid	Sugarcane juice	1.892	41%
	Yeast extract + Nutrients	2.750	59%
Levulinic acid ethyl ester	Paper sludge	0.105	52%
	Sulfuric acid	0.003	1%
	Caustic soda	0.000	<1%
	Ethanol	0.092	46%
	Hydrogen	0.001	<1%
	Others	0.001	<1%

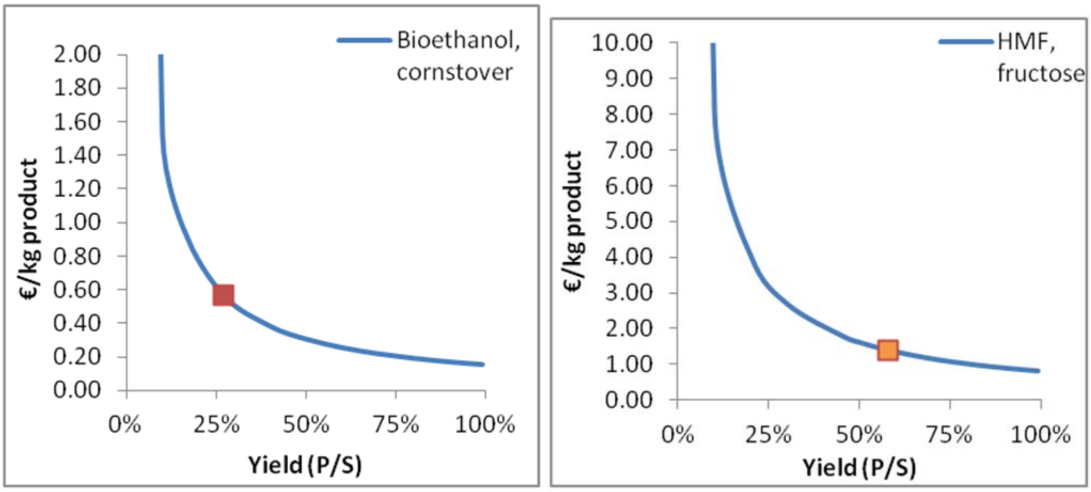

Figure 5.2.The yield with one example from each product segment showing the significance with respect to the selling price. The yield has been taken as the product produced as a function of the basic feedstock used, such as rapeseed for rapeseed oil and glycerol.

5.2.2 Utilities (including process energy)

The typical utilities used in the processes are electricity, steam, water, and gas. Most biorefineries co-produce electricity and heat through the processes and can be used as a means of lowering the product selling price either by selling or using it. The utilities costs was seen to have a moderate effect on the overall process costs, up to ca 25% of total costs, see Table 5.9.

Table 5.9. Summary of type of utility and related costs, where data was available in the reviewed literature.

Bio-derived product	Utilities	Cost of utilities [€/kg product]	% of total production costs	References
Bioethanol from corn	Electricity Natural gas	0.11	15%	(Tao & Aden 2009)
Biobutanol from corn	Electricity Natural gas	0.32	21%	(Tao & Aden 2009)
Succinic acid + Glycerol as co-products in a biodiesel biorefinery	Electricity Steam Water	Succinic acid 0.12 Glycerol 0.06	Succinic acid 9% Glycerol 5%	(Vlysidis et al. 2011)
Furfural	Steam	0.09	27%	(Xing et al. 2011)

Lactic acid	Water Nitrogen gas Electricity Steam	0.02	<1%	(Sikder et al. 2012)

5.2.3 Process concentration

The concentration of the final product in the reactor determines the size of the equipment that is needed – not only for the reaction step itself but also for subsequent down-stream steps. The effect of changing the concentration has been shown in Figure 5.3 based on the economic model. It should be emphasized that the calculations for the effect of the concentration have been simplified and this is only a graphical illustration of the effect of the concentration and not definitive values. The model does for instance not take into account the increased amount of energy needed for the separation or concentration that is normally required. Even so, it is clear that the lower the concentration has a marked effect on the production cost. Concentrations below 50 g/L are only likely to be tolerated for chemicals with a selling price above 5€/kg, and for bulk chemicals a concentration of more than 150 g/L should be the target. At concentrations around 10 g/L, the energy costs alone for stirring and aeration can amount to as much as 1€/kg of product (100h fermentation at an energy input of 1 kW/m^3 for stirring and aeration at a cost of 0.1 €/kWh) and the energy for concentrating the water containing the water is even greater (1.5 €/kg product if 100 kg water per kg product (10g/L) is evaporated (at heat of vaporization of 0.625 kWh/kg water, assuming 75% energy recovery through multistage energy integrated evaporators). These costs are following a similar relationship as that of the equipment cost and will thus act to make the effect even stronger.

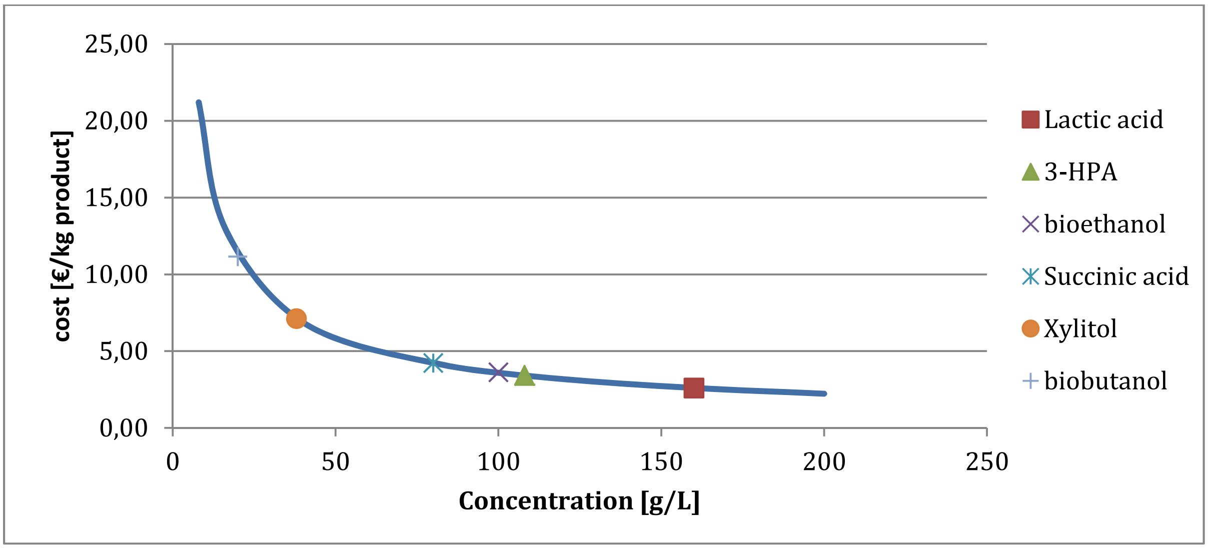

Figure 5.3. The effect of the concentration of the selling price. The given values are taken as an example cases based on lactic acid.

5.2.4 Economy of scale

The cost of process equipment does not increase linearly with scale, but rather becomes cheaper per unit volume on increasing scale (to a certain point). This means that for large plant capacities the product selling price will be lower, see Figure 5.5.

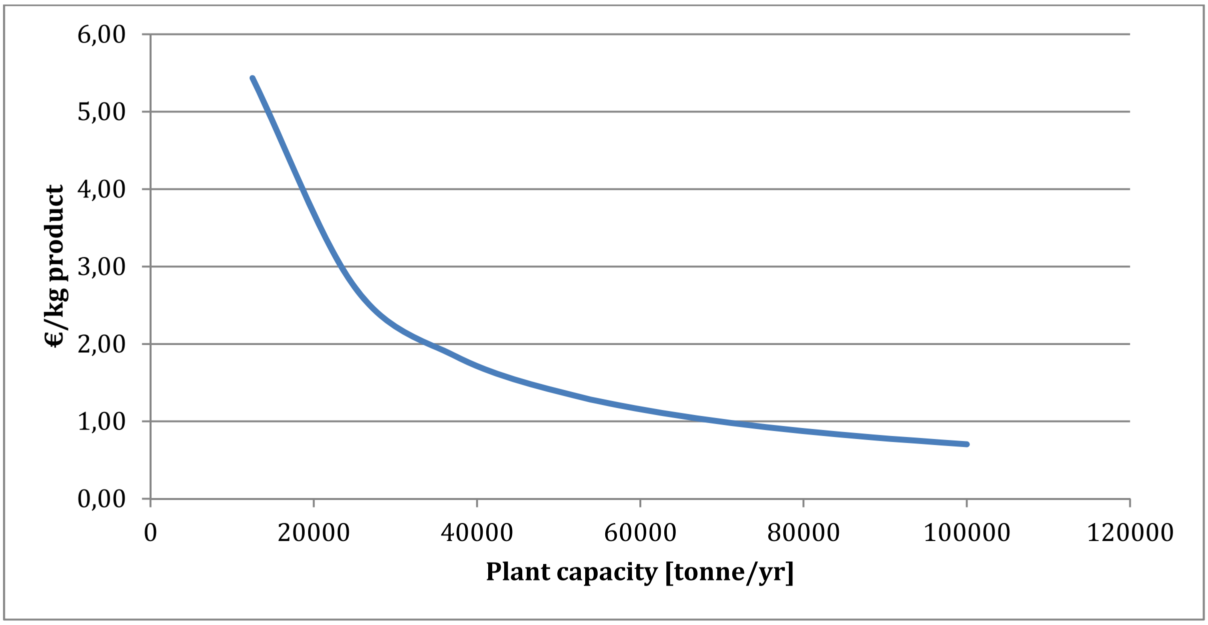

Figure 5.5. The effect of changing the scale of a biorefinery with biodiesel production from rapeseed as a case. Similar trends are observed for the other bio-derived products.

However, the plant also needs to have a secure supply of raw material to match the production capacity. Since biomass often is harvested once every season it is rarely possible to have a constant supply of raw materials. Another issue with a large production facility is that the raw material needs to be sourced from a larger area, thereby increasing the transportation costs. The size of the biorefinery is therefore of great importance; it is already a trend that biorefineries producing low value products, such as ethanol, are placed in places with abundant supply of cheap raw materials (e.g. sugar cane in Brazil or Thailand, or alternatively by a large port), whereas there is a possibility that smaller facilities could be situated where they can be integrated with, for example the waste streams of other biobased industries (e.g. saw mills, food industries, etc.).

6 Concluding remarks

The conclusion that can be drawn from this report is that the raw material production has an important role regarding both the environmental and economical impact of the final product. However, the variations regarding the environmental impact are large and for more detailed information the sustainability of a biobased product the environmental performance needs to be evaluated in every individual case. However, certain environmental hot spots in the life cycle were identified and can be used as guidance for decision-making and future research efforts. These key parameters can be found in the different steps of the life cycle. For the raw material production, which often is the step contributing the most to the overall impact of the chemical these are connected to the cultivation of the raw material. One possibility to the reduce this impact significantly is to use residues from the food or biofuel sector or harvest residues, such as straw for the chemical production.

For the production step the identified hot sports are the yield of the process and the process energy. The yield is directly connected the need of raw material and thereby also the environmental impact from this step. For the production of renewable chemicals it is important to also use renewable energy in the production process.

Also the use phase and the end-of-life treatment can be of significance for the renewable chemicals. Also, in various parts of the life cycle, environmentally preferential routes and options have been identified why the adoption of these should be promoted. Figure 6.1 aims at clarifying the aspects of significant importance.

In the future, as in the renewable energy sector, it is likely that a spectrum of technologies will be used for sustainable chemical and material production. As the technologies are in early stages of development there is a large potential for improvement in many fields and it may be wise to continue research on different techniques, allowing for a parallel development of technologies that may complete each other.

The result also shows that LCA should thus not be regarded as a complete tool for deciding superiority of certain products over others. If this is the purpose, much stricter and more consistent guidelines regarding the methodology are required as well as more developed models in order to avoid uncertainty. LCA should rather be regarded as a tool to highlight environmental hot spots in the investigated processes and as a first step to assess whether environmental superiority over fossil alternatives seems to exist at all.

Raw material cost is critical - the general conclusions from the study are that feedstock costs account for the majority of the total manufacturing costs. For cheaper raw materials the capital investments are generally higher than for e.g. sugar and vegetable oil biorefineries; however the raw material costs still show high significance. Lignocellulosic raw materials show the best potential and are also available in the Öresund region. Corn stover, which is often used as case is not relevant for the Öresund region, however it is assumed that it can be equivalent to e.g. straw, which is already used in the existing biorefinery owned by Inbicon in Denmark. Xylose from wood or recycled paper could also be a cheap source of carbon in the Öresund region.

The effect of economy of scale will have a significant effect on the production cost. High value co-products could be an important way to increase overall profitability for renewable chemicals or chemicals produced in a biorefinery.

The process efficiency in terms of yield of product per substrate and the concentration of product in the fermentation broth are the two most important process parameters.

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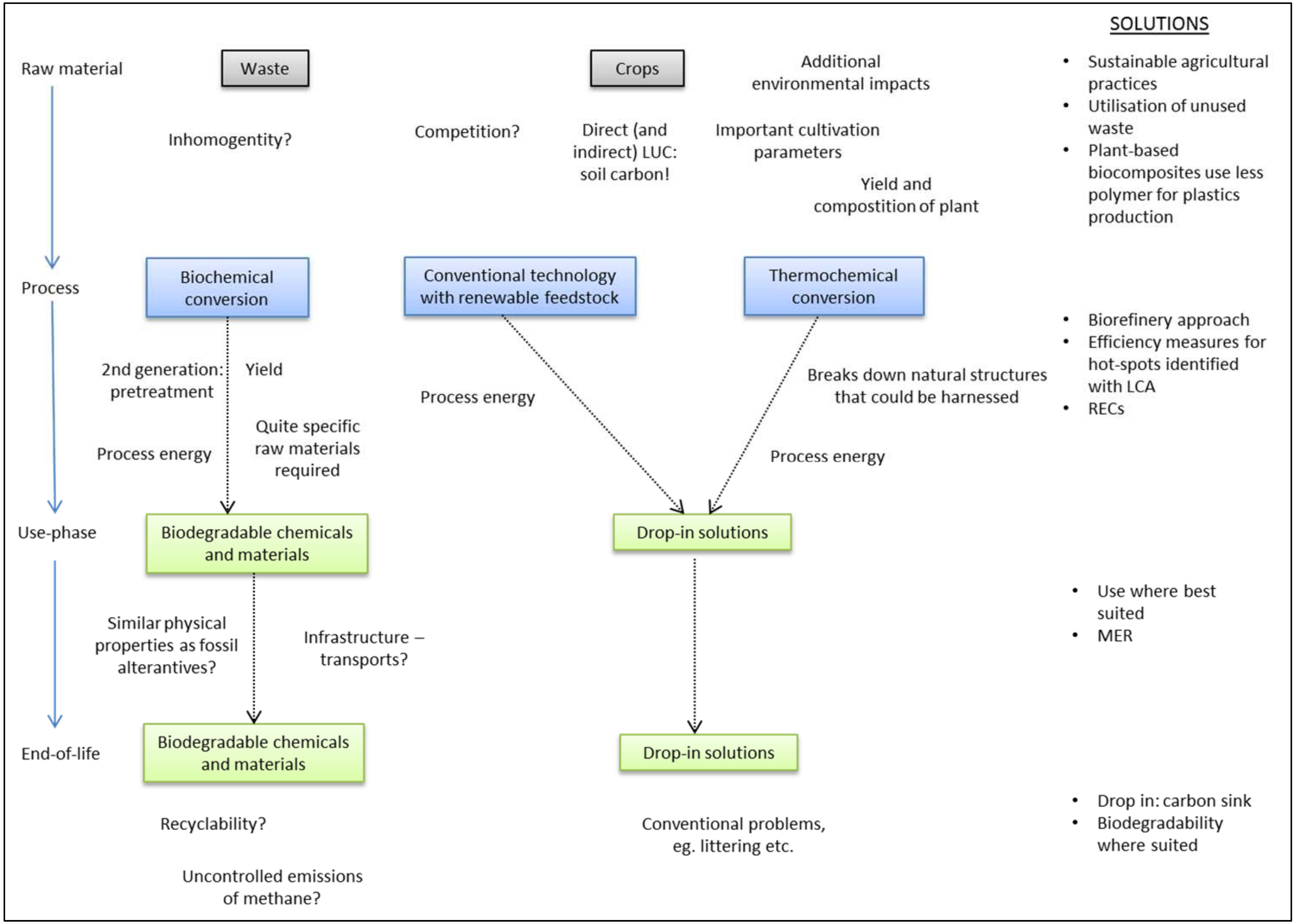

Figure 6.1. The ddddd.

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