



Universiteit
Leiden
The Netherlands

Biomass refining for sustainable development : analysis and directions

Luo, L.

Citation

Luo, L. (2010, May 11). *Biomass refining for sustainable development : analysis and directions*. Retrieved from <https://hdl.handle.net/1887/15394>

Version: Not Applicable (or Unknown)

License: [Licence agreement concerning inclusion of doctoral thesis in the Institutional Repository of the University of Leiden](#)

Downloaded from: <https://hdl.handle.net/1887/15394>

Note: To cite this publication please use the final published version (if applicable).

**Biomass Refining for Sustainable Development:
Analysis and Directions**



Lin Luo

Biomass Refining for Sustainable Development: Analysis and Directions

© 2010 by Lin Luo

Biomass Refining for Sustainable Development: Analysis and Directions

PhD Thesis University of Leiden, The Netherlands

Printed by Ipskamp Drukkers BV

ISBN 978-90-9025188-2

Biomass Refining for Sustainable Development: Analysis and Directions

Proefschrift

ter verkrijging van
de graad van Doctor aan de Universiteit Leiden,
op gezag van de Rector Magnificus prof. mr. P.F. van der Heijden,
volgens besluit van het College voor Promoties
te verdedigen op dinsdag 11 mei 2010
klokke 15.00 uur

door

Lin Luo

geboren op 15 august 1978
te Beijing, China

Promotiecommissie:

Promotor:

Prof. dr. S.M. Verduyn Lunel

Universiteit Leiden

Co-promotor:

Dr. E. van der Voet

Universiteit Leiden

Overige leden:

Dr. G. Huppes

Universiteit Leiden

Prof. dr. H.A. Udo de Haes

Universiteit Leiden

Prof. dr. H.J.M. de Groot

Universiteit Leiden

Prof. dr. ir. L.A.M. van der Wielen

Technische Universiteit Delft

Prof. dr. A.P.C. Faaij

Universiteit Utrecht

Dr. H. von Blottnitz

University of Cape Town, South Africa

This work has been made possible by the financial support from the Netherlands Ministry of Economic Affairs and the B-Basic partner organizations (www.b-basic.nl) through B-Basic, a public-private NWO-ACTS programme (ACTS = Advanced Chemical Technologies for Sustainability).

To my parents

Contents

Chapter 1	General Introduction	11
1.1	The need for sustainable energy sources	12
1.2	Bioethanol as a renewable energy source	13
1.3	Environmental and energy performance of ethanol from lignocelluloses	15
1.4	Critical issues in LCA on biofuels	16
1.5	Biorefining and its development	18
1.6	Research questions and thesis outline	20
Chapter 2	Allocation Issues in LCA Methodology: A Case Study of Corn Stover-Based Fuel Ethanol	23
2.1	Introduction	27
2.2	Methodology	28
2.2.1	Functional units and alternatives	29
2.2.2	System boundaries	29
2.2.3	Data sources and software	29
2.2.4	Key assumptions	31
2.2.5	Allocation methodology	31
2.2.6	Impact assessment and interpretation	34
2.3	Results and discussion	34
2.3.1	LCA results	34
2.3.2	Contribution analysis	38
2.4	Conclusions	39
2.5	Recommendations and perspectives	41
Chapter 3	Life Cycle Assessment and Life Cycle Costing of Bioethanol from Sugarcane in Brazil	43
3.1	Introduction	45
3.2	Methodology	46
3.2.1	Functional units and alternatives	47
3.2.2	System boundaries	47
3.2.3	Data sources and software	50
3.2.4	Key assumptions	50
3.2.5	Allocation methodology	50
3.2.6	Impact assessment	51
3.2.7	Life cycle costing (LCC)	51

3.3	Results and discussion	51
3.3.1	LCA	51
3.3.2	LCC	54
3.4	Conclusions and recommendations	55
 Chapter 4 Life Cycle Assessment of Switchgrass-Derived Ethanol as Transport Fuel		57
4.1	Introduction	59
4.2	Methodology	60
4.2.1	Functional units and alternatives	60
4.2.2	System boundaries	60
4.2.3	Life cycle inventory: data sources and software	64
4.2.4	Life cycle inventory: allocation	64
4.2.5	Life cycle impact assessment	65
4.2.6	Interpretation	65
4.3	Results and discussion	65
4.3.1	LCA results	65
4.3.2	Sensitivity analysis	68
4.4	Conclusions and recommendations	71
 Chapter 5 An Energy Analysis of Ethanol from Cellulosic Feedstock – Corn Stover		73
5.1	Introduction	75
5.2	Methodology	76
5.2.1	System boundaries and allocation	76
5.2.2	Data sources	78
5.2.3	Energy analysis	78
5.3	Results and discussion	78
5.3.1	Results of energy use	78
5.3.2	Survey of energy inputs	83
5.4	Conclusions and recommendations	87
 Chapter 6 Energy and Environmental Performance of Bioethanol from Different Lignocelluloses		89
6.1	Introduction	91
6.2	Life cycle assessment (LCA)	93
6.2.1	Methodology	93

6.2.2	Results comparisons and discussion	97
6.3	Energy considerations	103
6.3.1	Methodology	103
6.3.2	Results comparisons and discussion	104
6.4	Conclusions and recommendations	107
Chapter 7 Biorefining of Lignocellulosic Feedstocks: Technical, Economic and Environmental Considerations		111
7.1	Introduction	113
7.2	Description of the design	114
7.2.1	Product selection criteria.....	114
7.2.2	Selection of products	115
7.2.3	Design of the biorefinery	116
7.2.4	Market analysis	121
7.3	System analysis	122
7.3.1	Economic analysis.....	122
7.3.2	Environmental impact assessment	124
7.3.3	Comparison of eco-efficiency	124
7.4	Results	125
7.4.1	Economic analysis.....	125
7.4.2	Environmental impact assessment	128
7.4.3	Comparison of eco-efficiency	129
7.5	Discussion	131
7.6	Conclusions	133
Chapter 8 General Discussion, Conclusions and Recommendations ...		135
8.1	General discussion	136
8.2	Conclusions	140
8.2.1	LCA	140
8.2.2	LCC	142
8.2.3	Energy analysis	142
8.2.4	Biorefinery design and system analysis	143
8.3	Recommendations	144
8.3.1	Methodological issues	144
8.3.2	Perspectives and outlook	145

Summary	149
Samenvatting	155
References	163
List of Publications	175
Curriculum Vitae	177

Chapter 1

General Introduction

Sustainable development is “the development that meets the needs of the present without compromising the ability of future generations to meet their needs”.

— “Our common future”, the world Commission on Environment and Development (Brundtland Commission), 1987.

This is one of the quotations that often echo in my mind. The first half of this quote reminds me of the question someone raised at a conference in 2006, ‘While nations are busy with setting goals to use biofuels in Europe, has anyone thought of the people dying from hunger in Africa? When the European Commission set the target of 5% biofuels in the transport sector by 2010, why don’t we just drive 5% less?’ The truth is, with the current paradigm, it is difficult to change the life pattern in the developed world – no one would drive significantly less and people living in poverty will not get any more food if biofuels are not produced. In my opinion, the question is not whether we should use biomass but how to use it in a sustainable way, which is directly related to the second half of the quote – “without compromising the ability of future generations to meet their needs”. While we are reaping the benefits of earlier decisions to extract and exploit fossil fuels, we must immediately begin to make long-term strategies towards a future based on scarcity. This requires sustainable assessment of the new paradigm to achieve maximum benefits.

1.1 The Need for Sustainable Energy Sources

The world population is expected to reach approximately nine billion by the year of 2050 (UNPD, 2006). In the same time, economic development is also expected to increase substantially. Especially developing nations, like China and India, are entering their most energy-intensive phase of economic growth as they industrialize, build infrastructure and increase their use of transportation (Shell Report, 2008). These trends imply that demand for energy, food and other natural resources will increase substantially over the next decade and probably century (UN 2005). Thus one important challenge faced by mankind in this century is to meet the increasing energy demand.

Currently about 80% of the world energy demand is supplied by fossil resources (crude oil, natural gas and coal). Oil refining started with straightforward distillation, but has now been developed into a mature industry, where distillation is combined with sophisticated reaction engineering to develop complex material and energy networks making use of every ounce from a barrel of oil (Realff and Abbas, 2004). Likewise, the technologies for production and utilization of natural gas and coal are well developed.

However, the extensive exploitation of these fossil resources raises a number of worldwide concerns.

First of all, fossil resources, especially crude oil, are limited and scarcity problems are expected in the near future. In the coming decades, extraction of these resources will become increasingly difficult and costly (OECD/IEA, 2007; OECD/IEA, 2008). Secondly, the available reserves are unequally distributed around the globe (IEA, 2006). Therefore, a substantial part of energy demand from many nations will be largely dependent on import of resources. Furthermore, the combustion of fossil fuels is by far the largest contributor to the increasing atmospheric concentration of greenhouse gas (GHG) (IPCC, 2007). Carbon dioxide (CO₂) has risen 36% compared to pre-industrial times and is set to rise rapidly as world economic development accelerates (Shell Report, 2008). GHG emissions at or above current rates will cause further global warming and induce climate changes and increases in sea level (IPCC, 2007).

The increasing world energy demand, depletion and unequal distribution of fossil resources, and the dangers caused by climate change, urge many countries to formulate policies for a more sustainable energy supply. For instance, the European Commission decided in 2007 that a 20% target for the overall share of energy from renewable sources and a 10% target for energy from renewable sources in transport by 2020 would be appropriate and achievable objectives (Renewable Energy Road Map, 2007).

At least for the foreseeable future, low-carbon fuels in liquid form are required to be used in existing internal combustion engines in transportation. Biofuels are potential low-carbon energy sources, and they can provide energy for the transport sector. With the available conversion technologies they may substantially contribute to the renewable energy targets in the near future.

1.2 Bioethanol as a Renewable Energy Source

Liquid biofuels can offer portable energy sources adequate for the type of transport that societies now expect. With 90% contribution in the year 2005, bioethanol is now the most important biofuel worldwide. The production of ethanol by means of biological conversion has been applied by mankind since early time of history. However, the utilization of ethanol as a liquid fuel dates back only to the nineteenth to early twentieth century. In the early phases of automotive industry, ethanol was one of the fuel options for internal combustion engines. However, fuel ethanol was disregarded for several decades until the great depression in 1930's. With increasing oil prices ethanol was again back on stage till the fuel prices fell back to a low and stable level. Nevertheless, the

current worldwide interest in bioethanol is not only due to economic reasons. Ethanol from biomass, with its bio-renewable nature, optimized process technology and potential of greenhouse gas (GHG) mitigation already proved itself as an attractive alternative fuel.

Biomass, storing solar energy via photosynthesis, is available worldwide for further processing to food, animal feed, fuels, chemicals and materials. Most of the current practice only concerns first-generation ethanol from conventional energy crops like corn, wheat, sorghum, potato, sugarcane, sugar beet, cassava etc. This involves the conversion of such conventional starch or sugar crops into ethanol by fermentation followed by distillation (WWI, 2006). Ethanol can be blended with conventional gasoline, typically 5-20% by volume, for use in existing vehicles with no engine modifications; or blended with gasoline, 85-100%, for use in vehicles with specifically modified engines (Homewood, 1993; Keller, 1984). The most important producers of bioethanol are Brazil and the United States, each of which accounts for 45% of the total worldwide bioethanol production in the year 2005 (WWI, 2006). Sugarcane and corn are the main feedstocks in Brazil and the U.S., respectively.

Criticism has been expressed on the first-generation bioethanol with regard to land use requirement and competition with food and nature. It is clear now that land and water use requirements are such that energy from the first-generation crops cannot provide more than a few percent of the worldwide demand. This then has become an incentive for the technology innovation for the second-generation ethanol from lignocelluloses. This refers to not only cellulosic crops, such as switchgrass or certain types of wood, but also residues from agriculture and the food industry, such as corn stover or straw. EC Directive 2009 addressed the importance of commercializing second-generation biofuels (Directive 2009/28/EC, 2009). The United States, as one of the leading nations in promoting biofuels, proposed that cellulosic ethanol must achieve 44% of the total biofuel production by 2020 (DOE/EIA-0383, 2008). The potential contribution of lignocellulose crops and residues to ethanol production is high due to their great tolerance of relatively extreme soil and climate condition, which means larger areas are available for growing this type of crops.

Second-generation ethanol production aims at hydrolysis and subsequent fermentation of lignocellulosic biomass. A side benefit of this technique is the co-generation of heat and power by combustion of lignin residues and wastes. This technology is currently under development in many countries – Brazil (sugarcane bagasse); U.S. (corn stover);

Europe (wheat straw), and various ethanol refineries using this type of feedstocks are under construction.

1.3 Environmental and Energy Performance of Ethanol from Lignocelluloses

A large number of studies were conducted on the environmental impact of bioethanol from conventional crops, focusing particularly on two main aims – net energy and GHG emissions (Beer and Grant, 2007; Curran, 2007; Gnansounou et al., 2008; Halleux et al., 2008; Hu et al., 2004a; Hu et al., 2004b; Kim and Dale, 2005a; Kim and Dale, 2005b; Kim and Dale, 2006a; Leng et al., 2008; Liska et al., 2009; Macedo et al., 2008; Nguyen and Gheewala, 2008; Ometto et al., 2009; Zah et al., 2007). With respect to these two aims the use of bioethanol is not unchallenged. However, different assumptions, methodologies and system boundaries make these studies difficult to compare. Farrell et al. (2006) aligned methods and assumptions in six selected studies mostly focusing on energy balances related to corn-based ethanol ((de Oliveira et al., 2005; Groboski, 2002; Patzek, 2004; Pimentel and Patzek, 2005; Shapouri and McAloon, 2002; Wang, 2001), and removed differences in the underlying data. They indicate that calculations of the net energy value (NEV) are highly sensitive to assumptions about both system boundaries and key parameter values and, as to content, conclude that large-scale use of fuel ethanol certainly requires more sustainable practices in agriculture and advanced technologies, shifting from corn to cellulosic ethanol production. Moreover, a review study (von Blottnitz and Curran, 2007) draws on 47 published assessments that compare bioethanol systems to conventional fuel on a life cycle basis and suggests considering hydrolyzing and fermenting lignocellulosic residues to ethanol.

The focus of the studies performed on ethanol from lignocelluloses is therefore two folded – the life cycle environmental performance (focusing mostly on GHG emissions and fossil energy use) and the energy performance. With regards to the first aim numerous LCA studies were conducted on ethanol from lignocelluloses such as corn stover (Kim et al., 2009; Luo et al., 2009a; Searcy and Flynn, 2008; Sheehan et al., 2004; Spatari et al., 2005), switchgrass (Kim et al., 2009; Wu et al., 2006a), Miscanthus and willow (Styles and Jones, 2008), sugarcane bagasse (Botha and von Blottnitz, 2006; Luo et al., 2009b), cereal straw (Gabrielle and Gagnaire, 2008), woodchip and wood wastes (Beer and Grant, 2007; Fu et al., 2003; Kemppainen and Schonnard, 2005), flax shives (González García et al., 2009a) and hemp hurds (González García et al., 2009b). All these studies, to different extent, show environmental benefits especially in terms of fossil resource depletion and GHG emissions.

In the field of energy analysis, studies have been published for bioethanol from corn stover (Lavigne and Powers, 2007; Luo et al., 2009c), switchgrass (Farrell et al., 2006; Pimentel and Patzek, 2005; Wang, 2001, Wu et al., 2006a) and woodchip (Cardona Alzate and Sánchez Toro, 2006; Pimental and Patzek, 2005). Most of these studies yield a positive NEV, which indicates that lignocelluloses are more favourable feedstocks than conventional crops like corn grain. However, Pimentel and Patzek (2005) exceptionally reported negative NEV from switchgrass- and wood-ethanol systems concluding cellulosic ethanol processes are more energy intensive than ethanol from corn grain. The main reason of these different outcomes seems to be the differences in models used – the inclusion or exclusion of co-product energy credits.

These studies on both LCA and energy analysis of second-generation bioethanol raise a number of further questions. First of all, there is insufficient consistency regarding the definition of system boundaries. For instance, an ethanol refining system may be incomplete by not including the environmental impact from the production of cellulase enzyme which is used to degrade cellulosic feedstocks; moreover, co-products are often neglected, such as stover in the case of ethanol production from corn. Secondly, in different studies allocation methods are rendered differently or unclearly stated. The inconsistency in the definition of system boundaries and allocation methodology made most of the studies incomparable.

1.4 Critical Issues in LCA on Biofuels

Allocation has always been one of the most critical issues in studies of LCA on biofuels. In a multi-product system all the inputs and outputs shall be allocated on each product. The ISO 14040-44 series (2006) recommend avoiding allocation whenever possible by dividing the unit process to be allocated into sub-processes and expanding the product system to include the additional functions related to the co-products; Where allocation cannot be avoided, the inputs and outputs of the system should be partitioned between its different products in the way that reflects the underlying physical relationship between them; when physical relationship alone cannot be established, the inputs should be allocated between the products in a way that reflects other relationship between them, for instance, the economic value of the products. In the Handbook on life cycle assessment (Guinée et al., 2002) the preference differs from ISO – allocation based on the proceeds of products is prioritized, being the only method generally applicable. ISO 14044 (2006) also suggests that whenever several alternative allocation procedures seem applicable, a sensitivity analysis shall be conducted to illustrate the consequences of the departure from the selected approach.

In many LCA studies on biofuels, the mass of the output products is chosen as a basis for allocation, others use energy content in line with EC Directive 2009 (Directive 2009/28/EC, 2009) or economic value. Another widely used method is based on the replacement options of co-products, in which energy and environmental credits are assumed equal to the one required to produce a substitute for the co-products. In some studies expanding the product system to include additional functions is applied (Kim and Dale, 2002; Luo et al., 2009). In most studies a mix of methods is applied, and no discussion is provided for example as regarding the reason for the selection of allocation procedure. In fact, it is important to recognize that the approach to allocation in any particular LCA is a function of the goal and scope definition, and no single allocation method can be appointed as the most appropriate one for all biofuel processes by just not being applicable. For instance, in the case of allocation between ethanol and co-generated electricity mass allocation cannot be applied. Furthermore, a high sensitivity to allocation method has been reported for LCA outcomes when evaluating carbon intensity and fossil energy consumption for bioethanol pathways (Beer and Grant, 2007; Curran, 2007; Kim and Dale, 2002; Luo et al., 2009a; Malça and Freire, 2006). This makes the choice for allocation both important and difficult to standardise. In order to develop LCA methodology as a better decision-making tool, consistency in the application of allocation methods, one choice plus a sensitivity analysis for other choices, is of crucial importance.

Life cycle impact assessment (LCIA) is another critical issue. Most literature on LCA of biofuels only focuses on two impact categories – fossil resource use and global warming. Only a few studies evaluate a wider range of environmental impacts also including ozone layer depletion, photochemical oxidation, acidification, eutrophication, human and ecological toxicity, smog formation etc. (Botha and von Blottnitz, 2006; Curran, 2007; Fu et al., 2003; Halleux et al., 2008; Kemppainen and Shonnard, 2005; Kim and Dale, 2006a; Kim and Dale, 2009; Ometto et al., 2009), however, come up with divergent conclusions, possibly due to the different approaches in scoping. These LCA studies typically report that bioethanol results in reductions in fossil resource use and global warming; however, impacts on acidification, eutrophication, human and ecological toxicity, occurring mainly during the growing and processing of biomass, are more often reported unfavourable for fuel ethanol. Therefore, concluding bioethanol is more environmentally friendly than gasoline with the omission of other impacts is impossible.

LCA as it stands now cannot capture all relevant discussions on biofuel assessment, and land use change (direct: LUC, indirect: ILUC) is one that remains uncovered. The basic

reason is that LCA uses a linear type of modelling, which is not able to reflect non-linearity which abounds in real life. Land use change has clear non-linear characteristics – using more land for one purpose (i.e. biofuel production) by necessity decreases the availability of land for others (i.e. growth of food crops and nature). This discussion becomes more complicated as different impact categories are not independent. For instance, land use change has an impact on global warming, as it can be accompanied by sometimes large changes in GHG emissions from soils, though mainly through transitions effects not easily covered in LCA. As Fargione et al. argue (2008). Searchinger et al. (2008) show that including GHG emissions from LUC and ILUC may change a net GHG benefit into a net cost.

One possible solution for this issue is to shift from attributional to consequential LCA, in which consequences are specified at the functional unit level. On such subjects, like for land use change, there is yet no consensus on how to include this consistently in an LCA. The general idea is to specify what land use changes occur exactly where in the world as the result of changing the land area required to produce the functional unit. Nevertheless, Anex and Lifset (2009) indicate that consequential LCA is still in its earliest stages of development, and a great deal is still unknown about how to perform a reliable consequential LCA. Reckoning adequately with land use requires comprehensive modelling, which may be connected to LCA but requires substantially additional efforts. Estimation of these changes requires the use of economic models, such as the Global Trade Analysis Project (GTAP) global computable general equilibrium model, combined with empirical data on agricultural prices induced deforestation and agricultural supply and demand functions.

1.5 Biorefining and Its Development

Ethanol production is now often regarded as a single-output system, though electricity is often co-produced. However, mostly the electricity generated in such a system is used internally, thus results in no or a little surplus. Moreover, electricity will not contribute substantially to the overall proceeds. Therefore, optimization of a single-output is always limited, especially in terms of profitability. High-value co-products are required to maximize the values derived from biomass. Brazilian ethanol industries have already demonstrated the success of a multi-output production – converting sugarcane into ethanol and sugar in the same plant.

Similar to oil refinery, a system called ‘biorefinery’ has been proposed to produce useful chemicals and fuels from biomass. According to the National Renewable Energy Laboratory (NREL), a biorefinery is a facility that integrates biomass conversion

processes and equipment to produce fuels, power, and chemicals from biomass. It stands ready for the transformation with recovery of sugars being combined with a variety of new fermentation and thermo-chemical processes. By producing multiple products and integrating residues treatment, biorefineries can increase the value derived from biomass feedstocks. Therefore a biorefinery system seems often to have both environmental and economic benefits, and it may include mechanisms for making industry more sustainable (Realf and Abbas, 2004). To achieve the goals of sustainable development, biorefineries have to play a dominant role in the coming millennia (Fernando et al., 2006).

Three types of biorefineries known as phase I, II and III have been described by Kamm and Kamm (2004) and van Dyne et al. (1999). The phase I and II biorefinery plants use grain as feedstocks such as corn and wheat. The difference is that phase I biorefinery has fixed processing capabilities and produces a fixed amount of ethanol and other feed products, while phase II biorefinery has the capability to produce various end products and has far more processing flexibility. Typical examples for phase I and II biorefinery are corn dry milling and corn wet milling, respectively. A phase III, the most promising and to be developed biorefinery, uses a mix of biomass feedstocks and yields an array of products by employing combination of technologies (Kamm and Kamm, 2004). It allows a mix of agriculture feedstocks, has the ability to use various types of processing methods, and has the capability to co-produce a mix of high-value chemicals in low volume while co-producing bulk products like ethanol in high volume.

Lignocellulosic feedstock (LCF) biorefinery is one important phase III biorefinery. In a LCF biorefinery, cellulosic biomass including dedicated plants, co-products or wastes is initially cleaned and degraded into three fractions (cellulose, hemicellulose and lignin) via chemical digestion or enzymatic hydrolysis. The cellulose and hemicellulose are further processed to produce useful products such as fuels and chemicals, and the lignin residues have only limited uses such as a fuel for direct combustion to generate steam and electricity.

The technical development and perspectives of LCF biorefineries have been extensively discussed in the literature studies (Kadam et al., 2008; Kaparaju et al., 2009; Laser et al., 2009a; Laser et al., 2009b). All these studies indicate that multiple products biorefineries are the future of biomass refining. Furthermore, several studies has focused on environmental assessment of a LCF biorefinery (Cherubini and Ulgiati, 2010; Uihlein and Schebek, 2009); Lynd and Wang (2004) developed a product-nonspecific framework to evaluate the potential of bio-based products to displace fossil fuels.

Nevertheless, none of these studies has provided a sustainability assessment of such a refinery involving environmental, economic and social aspects, which are still in a new era of biorefinery research.

1.6 Research Questions and Thesis Outline

A number of questions are often raised by the public as well as researchers in the field of biofuel studies, such as:

- While biofuels are strongly promoted, what about the food security in the third-world countries?
- Instead of producing ethanol, why don't we just combust biomass for electricity generation?
- Are all the bio-based productions carbon-neutral?

These are all very relevant questions; however, not all are addressed in this thesis. For instance, question 1 has always been a dilemma for social scientists and economists working in the field of biofuels; and question 2 has been addressed in some literature studies. The main objective of this thesis is to indicate the directions of biomass refining for sustainable development, and how to utilize bio-based fuels in a sustainable way. Therefore, some of the aforementioned questions are out of the scope of this work. This thesis focuses mainly on the environmental aspects of bioethanol production and biorefinery. The economic feasibility of such productions is addressed to certain extent. To this end, three main research questions have been formulated:

- I. Is fuel ethanol from lignocelluloses better than gasoline, from an environmental point of view?
- II. How can bio-based production be optimized with regard to energy efficiency, environmental performance and economic feasibility?
- III. How can we design a methodology to achieve a more comprehensive sustainability assessment of biomass refining?

These main questions are interrelated and comprise many smaller questions, which are addressed from Chapter 2 to 7, as indicated in Table 1.1.

Table 1.1 Overview research questions addressed in each chapter of this thesis

Chapter	Research question		
	I	II	III
2	•		•
3	•		•
4	•		
5		•	
6	•	•	
7		•	•

Chapter 2 investigates the influence of allocation methods on the outcomes of LCA by using fuel ethanol from corn stover as a case study, as it is a main second-generation application growing fast in the U.S. The life cycles of the fuels under study include gasoline production, corn and stover agriculture, cellulosic ethanol production, blending ethanol with gasoline to produce E10 (10% of ethanol) and E85 (85% of ethanol), and finally the use of gasoline, E10, E85, and ethanol in a midsize vehicle. A substantially broad set of environmental impacts ranging from greenhouse gas emissions to toxicity aspects is covered.

Chapter 3 presents an LCA and a Life Cycle Costing (LCC) of bioethanol from sugarcane in Brazil involving the cellulosic technology and a complete set of environmental impacts of importance. Two scenarios are compared: base case – ethanol production from juice sugar after cane milling, steam and electricity are generated from the combustion of bagasse; future case – both juice sugar and bagasse are used for ethanol production, heat and power are generated from the combustion of lignin residues and wastes. The full life cycles of gasoline and three ethanol fuels (E10, E85 and E100) were analyzed. The results are used to better understand which scenario provides a better option from environmental and economic point of view.

Chapter 4 focuses on LCA of another promising cellulosic feedstock – switchgrass. The same system boundaries, methodology and impact categories as described in previous two chapters were applied. Moreover, sensitivity analyses were conducted on allocation method, transport distance and whether or not taking soil preparation into consideration.

Chapter 5 presents a detailed energy analysis of corn stover-based ethanol production using advanced cellulosic technologies. The method used differs from the one in LCA from major studies on the subject as published in Science (Farrell et al., 2006) in two

respects. First, it accounts for all the co-products so mainly avoids the allocation problems which plague all LCA studies explicitly and other studies implicitly. Second, the system boundaries only involve the content of the energy products used in the system but not the production processes of these energy products, like oil refining and electricity generation. We normalized the literature studies to this unified method. The detailed analysis of energy inputs suggests opportunities for system optimization.

Chapter 6 summarizes and evaluates the five studies on LCA and two studies on energy analysis of bioethanol from lignocelluloses, in which cellulosic technologies were used; the same system boundaries were defined; and the same allocation procedures were applied. The resulting net energy values from the two energy analyses were compared with literature values. The results provide indications on the environmental performance and energy efficiency of second-generation bioethanol.

Chapter 7 involves the technical design of a lignocellulosic feedstock biorefinery producing ethanol, succinic acid, acetic acid and electricity from corn stover and analyzes the refinery from environmental and economic point of view. The results help optimize the biorefinery in terms of technology, energy efficiency and environmental impact; bridge technical process design to system analysis; and provide indications on the sustainability of such a refinery.

Chapter 2

Allocation Issues in LCA Methodology: A Case Study of Corn Stover-Based Fuel Ethanol

* This chapter is published in International Journal of Life Cycle Assessment 2009; 14: 529-539. Co-authors: Ester van der Voet, Gjalt Huppes and Helias A. Udo de Haes

Abstract

Facing the threat of oil depletion and climate change, a shift from fossil resources to renewables is ongoing to secure long-term low carbon energy supplies. In view of the carbon dioxide reduction targets agreed upon in the Kyoto protocol, bioethanol has become an attractive option for one energy application, as a transport fuel. A number of studies on LCA of fuel ethanol have been conducted, and the results vary to a large extent. In most of these studies, only one type of allocation is applied. However, the effect of allocation on outcomes is of crucial importance to LCA as a decision supporting tool. This is only addressed in a few studies to a limited extent. Moreover, most of the studies mainly focus on fossil energy use and GHG emissions. In this paper, a case study is presented wherein a more complete set of impact categories is used. Land use has been left out of account as only hectare data would be given which is obviously dominated by agriculture. Moreover, different allocation methods are applied to assess the sensitivity of the outcomes for allocation choices.

This study focuses on the comparison of LCA results from the application of different allocation methods by presenting an LCA of gasoline and ethanol as fuels and with two types of blends of gasoline with ethanol, all used in a midsize car. As a main second-generation application growing fast in the USA, corn stover-based ethanol is chosen as a case study. The life cycles of the fuels include gasoline production, corn and stover agriculture, cellulosic ethanol production, blending ethanol with gasoline to produce E10 (10% of ethanol) and E85 (85% of ethanol), and finally the use of gasoline, E10, E85, and ethanol. In this study, a substantially broader set of seven environmental impacts is covered.

LCA results appear to be largely dependent on the allocation methods rendered. The level of abiotic resource depletion and ozone layer depletion decrease when replacing

gasoline by ethanol fuels, irrespective of the allocation method applied, while the rest of the impacts except global warming potential are larger. The results show a reduction of global warming potential when mass or energy based allocation is applied; in the case of economic allocation, it gives contrary results. In the expanded systems, global warming potential is significantly reduced comparing to the ones from the allocated systems. A contribution analysis shows that car driving, electricity use for cellulase enzyme production and ethanol conversion contribute largely to global warming potential from the life cycle of ethanol fuels.

The reason why the results of global warming potential show a reverse trend is that the corn/stover allocation ratio shifts from 7.5 to 1.7 when shifting from economic allocation to mass/energy based allocation. When mass/energy allocation is applied, both more credits (CO_2 uptake) and more penalties (N_2O emission) in agriculture are allocated to stover compared to the case of economic allocation. However, more CO_2 is taken up than N_2O (in CO_2 eq.) emitted. Hence, the smaller the allocation ratio is between corn and stover, the lower the share of the overall global warming emissions being allocated to ethanol will be. In the system expansion approach, global warming potentials are significantly reduced, resulting in the negative values in all cases. This implies that the system expansion results are comparable to one another because they make the same cut-offs but not really to the results related to mass, energy, and economic value based allocated systems.

The choice of allocation methods is essential for the outcomes, especially for global warming potential in this case. The application of economic allocation leads to increased GWP when replacing gasoline by ethanol fuels, while reduction of GWP is achieved when mass or energy based allocation is used as well as in the system where biogenic CO_2 is excluded. Ethanol fuels are better options than gasoline when abiotic resource depletion and ozone layer depletion are concerned. In terms of other environmental impacts, gasoline is a better option, mainly due to the emissions from the application of nutrients and the toxic substances associated with agriculture. A clear shift of problems can be detected – saving fossil fuels at the expense of emissions related to agriculture, with GHG benefits depending on allocation choices. The overall evaluation of these fuel options, therefore, depends very much on the importance attached to each impact category.

This study focuses only on corn stover-based ethanol as one case. Further studies may include other types of cellulosic feedstocks (i.e. switchgrass or wood), which require less intensive agricultural practice and may lead to better environmental performance of fuel

ethanol. Furthermore, this study shows that widely used but different allocation methods determine the outcomes of LCA studies on biofuels. This is an unacceptable situation from a societal point of view and a challenge from a scientific point of view. The results from the application of just one allocation method are not sufficient for decision making. Comparison of different allocation methods is certainly of crucial importance. A broader approach beyond LCA for the analysis of biorefinery systems with regard to energy conservation, environmental impact, and cost-benefit will provide general indications on the sustainability of bio-based productions.

2.1 Introduction

Facing the threat of oil depletion and climate change, the production and use of bioethanol from renewable resources as a fuel instead of gasoline has been strongly promoted on a global scale. Bioethanol, however, is connected to environmental problems of its own. Thus, the question is raised, what indeed the environmental benefits of bioethanol are and how to compare different fuel options from an environmental point of view. A number of studies were conducted on the environmental impact of bioethanol, focusing particularly on two main aims behind the use of biofuels: life cycle fossil energy efficiency and greenhouse gas (GHG) emissions (Gnansounou et al., 2008; Kim and Dale, 2005a; Liska et al., 2009; Macedo, 1998; Nguyen and Gheewala, 2008a; von Blottnitz and Curran, 2007; Zah et al., 2007). With respect to these two main aims, the use of bioethanol is not unchallenged. For instance, a review study was published in “Science” on the production of ethanol from corn (Farrell et al., 2006); this is a relevant case because of the tremendous scale of investment in the production of ethanol from corn in the U.S.. The study indicates that the replacement of crude oil appears to be rather effective (about 95%). However, the emissions of greenhouse gases are diverging among the reviewed studies, ranging from 32% higher to 20% lower compared with the use of gasoline. In addition, criticism is expressed on the production of biofuels regarding land use requirements. This holds true particularly for the first-generation of bioethanol, using carbohydrates from dedicated crops like corn, wheat, sorghum, potato, sugar cane, sugar beet, cassava, etc. (Gnansounou et al., 2008; Halleux et al., 2008; Kim and Dale., 2005a, Kim and Dale., 2005b; Leng et al., 2008; Macedo, 2008).

Especially the land use requirements, causing competition with land for food and nature elsewhere, are the driving forces for the technology development of second-generation bioethanol, which uses celluloses from low-value agricultural products or wastes, like corn stover, wheat straw, bagasse from sugar cane, wood, or grass. Some studies have been performed on these new production routes (Fu et al., 2003; González García et al., 2009a; González García et al., 2009b; Kemppainen and Schonnard, 2005; Luo et al., 2009b; Searcy and Flynn, 2008; Sheehan et al., 2004; Spatari et al., 2005). These studies show, to a varying degree, reduction of fossil fuel use and of GHG emissions, in comparison with the use of gasoline. Since the carbon dioxide (CO₂) uptake in agriculture is counteracted by the nitrous oxide (N₂O) emitted in agriculture and the CO₂ emissions generated in other parts of the life cycle, the reduction of GHG emissions depends on the greenhouse gases emitted in the whole chain, which may be substantial in relation to the emissions at final use.

However, the studies on both the first- and second-generation bioethanol raise a number of further questions. First of all, there is insufficient consistency regarding the definition of system boundaries. For instance, an ethanol system may be incomplete by not including the production of cellulase enzyme which is used to degrade cellulosic feedstocks. Secondly, some questions can be raised with regard to the allocation methods used in these studies for the attribution of environmental impacts from processes generating several other products as co-products. A high sensitivity to the allocation method has been reported for LCA results when evaluating carbon intensity and fossil energy consumption for bioethanol pathways (Beer and Grant, 2007; Kim and Dale, 2002; Malça and Freire, 2006). Nevertheless, these studies focus mostly on the first-generation feedstocks such as corn, wheat, and sugar beet, where allocation is less important to results. The environmental performances are not evaluated with more complete set of impact categories.

In the present study, corn stover-based fuel ethanol is investigated using LCA and compared with gasoline from fossil origins. The full life cycles of fuel ethanol and gasoline are analyzed, including the production, transport, and use of the raw materials, fuels, and electricity. Advanced technologies are assumed in both agriculture practice and ethanol refinery. The influence of different allocation methods on results is a core issue of this study. Whereas most case studies focus just on GHG emissions and resource depletion, in this case, a larger set of environmental impacts are included. The investigation of potential tradeoffs among impact categories is another main issue in this study.

2.2 Methodology

LCA is a tool for the analysis of environmental impacts of a functional unit, taking into account the complete life cycle of a product (good or service) delivering the functional unit. It is, therefore, well suited to answer the question raised in the introduction, ‘how to compare different fuel options from an environmental point of view?’ Typically, LCA studies on one given topic do yield varying results due to differences in data and in methodological assumptions. In order to cope with this and to render studies better comparable, extensive efforts are undertaken in the LCA community to standardize assumptions and procedures and build up reference databases. However, in different situations, different approaches to modelling may apply; hence, explicit choices are always required.

The present study concerns the general comparison of technologies for the car driving function without specific local circumstances playing a role. For this purpose, the ISO

14040-44 series (2006), elaborated into methodological choices and procedures by Guinée et al. (2002), is followed.

2.2.1 Functional unit and alternatives

The functional unit in this study is defined as power to wheels for one kilometre driving of a midsize car. In practice, ethanol is mainly used in one of the two ways in vehicle fuel (Homewood, 1993; Keller, 1984): (1) blended with gasoline, typically 5-20% by volume, for use in existing vehicles with no engine modifications; (2) blended with gasoline, typically 85-100% by volume, for use in vehicles with specifically modified engines. In this study, ethanol is assumed to be used in both ways, as a mixture of 10% ethanol with 90% gasoline by volume (termed E10) and as a mixture of 85% ethanol with 15% gasoline by volume (termed E85). As a reference alternative, a hypothetical case of pure ethanol is also taken into account. Therefore, the fuel alternatives are gasoline, E10, E85, and ethanol, in amounts required to deliver the same amount of energy ‘to the wheels’.

2.2.2 System boundaries

All relevant processes are included within the boundary of the fuel systems, as shown in Figure 2.1. Furthermore, those for capital goods and wastes management are included as well. The emissions and wastes associated with the production and disposal of the passenger car are outside of the system boundaries.

2.2.3 Data sources and software

Data used in this study are obtained from different sources. The U.S. Life Cycle Inventory Database (<http://www.nrel.gov/lci/>) is the source for agriculture data. Data on the ethanol production process from corn stover are based on a detailed technical process design, using data from NREL (Aden et al., 2002). This production process can be characterized as ‘future technology’ – the design is not implemented at a significant scale yet and, therefore, may be on the optimistic side. Emissions from capital goods production are from the EIPRO database (Tukker et al., 2006). Gasoline production data are provided by the Swiss Centre of Life Cycle Inventories (<http://www.ecoinvent.org/>). Emission data of car driving using gasoline, E10 and E85, are acquired from the reports on emission test of different fuels (Kelly et al., 1996; Reading et al., 2002).

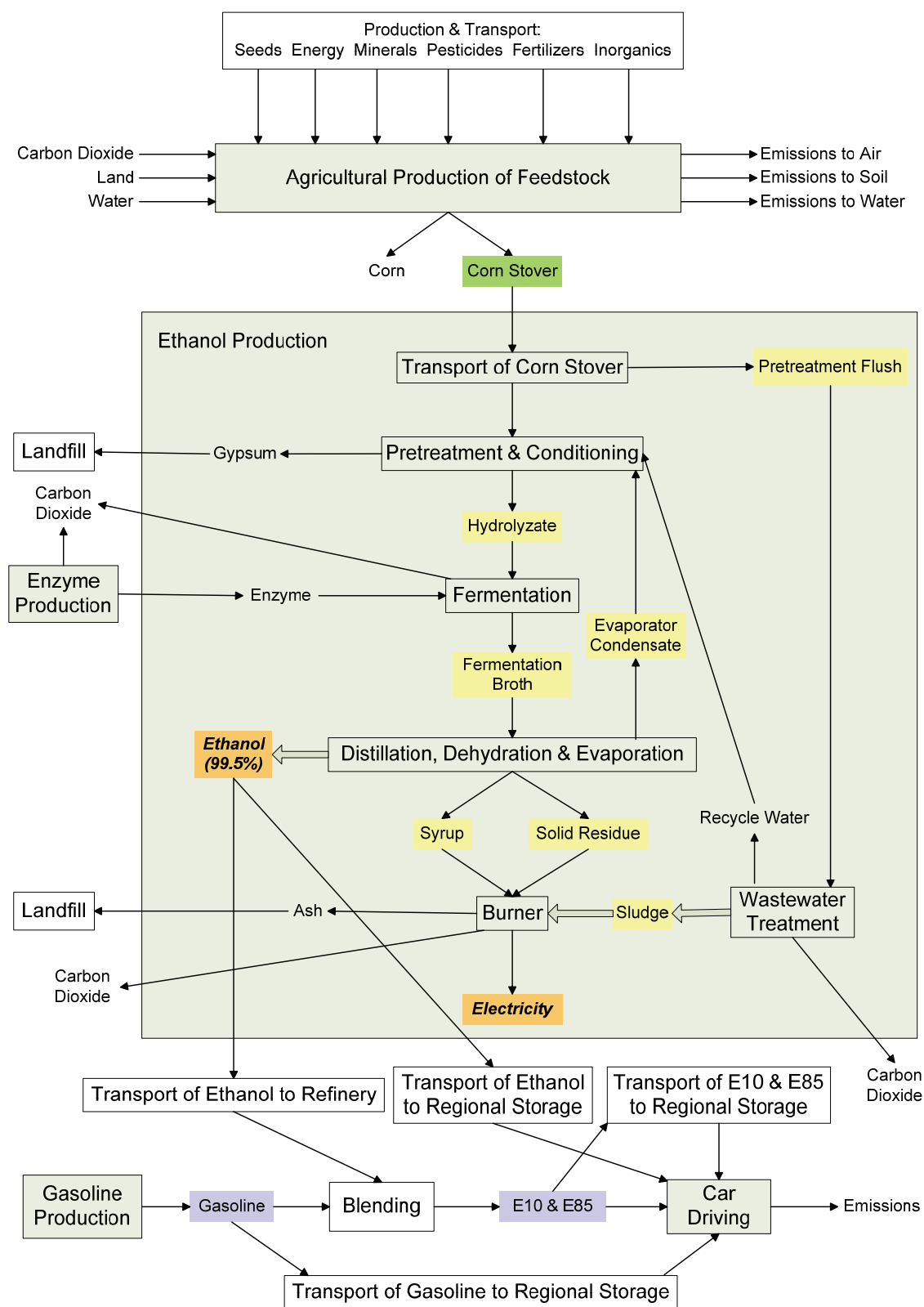


Figure 2.1 The life cycle of ethanol from corn stover

The completeness of data may differ between sources; therefore, one source, the Ecoinvent database, is used when possible, as this source has a long learning experience and involves a very broad range of processes, around 4,000. Data gaps resulting from general data unavailability are filled by estimation based on a variety of assumptions as noted below. The software package created by Heijungs called “Chain Management by Life Cycle Assessment” (<http://cml.leiden.edu/software/software-cmlca.html>) is used for the analysis.

2.2.4 Key assumptions

In this study, the ethanol production plant is assumed to be located in the middle of the Corn Belt farmland, State of Iowa, Midwest of the U.S.. The stover is assumed to be collected within an 80 km (50 miles) radius around the plant (Aden et al., 2002). Corn stover is transported by lorries with a load of 16 tonnes, and the transport of the rest of the materials and products is by road using lorries with a load of 32 tonnes. The average transport distance for the stover to the ethanol plant is derived from the above data, yielding a distance of 56 km (112 km both ways); 20 km is assumed to be the transport distance of ethanol to the refinery. For the distance between the refinery and the regional storage, the value from the Ecoinvent is followed (34 km). Therefore, for comparison, the transport distance of E10, E85, and ethanol to their regional storages is assumed to be 34 km. For gasoline, E10 and E85 emission data are based on a standard test procedure, covering a mix of driving on urban roads and on motorways. For ethanol, the emission data are estimated based on the assumption of driving with nearly 100% ethanol.

2.2.5 Allocation methodology

The allocation procedure in a multiproduct process is the most critical issue in LCA. The ISO 14040-44 series (2006) recommends avoiding allocation whenever possible either through subdivision of certain processes or by expanding the system limits to include the additional functions related to them. This was done in our case in the following manner:

- Assuming continuous corn production instead of crop rotation to avoid having to allocate over a variety of crops and their destinations; this assumption is not unrealistic.
- Assuming the electricity produced from wastes is used in the ethanol refinery itself instead of being sold to the grid; this may not be fully according to reality.
- Expanding the system to include the ‘corn for food and feed’ as an additional function.

If ‘avoiding’ allocation is not possible, the ISO series (2006) recommends using methods that reflects the physical relationship such as mass and energy content or using other relevant variables to allocate, such as economic value of the products, which is similar to the cost allocation methods in managerial accounting (Guinée et al., 2004). We used energy and mass allocation as well as economic allocation in this case study. Regarding the allocation procedure, the refinery of crude oil to produce gasoline, diesel, and other co-products was considered in the gasoline lifecycle. In the ethanol life cycle, multi-output processes are the following:

- Agricultural production, where both corn and stover are produced.
- Ethanol production, where both ethanol and electricity are produced.

For the gasoline production, the allocations were taken as currently implemented in the Ecoinvent database by its designers. The Ecoinvent default allocation includes differentiated allocation factors based on physical-causal relationships, common physical parameters (mass or heating values), and/or the economic values of the valuable outputs of the multi-output processes, after processes have been split up in order to avoid allocation (Jungbluth et al., 2005). For ethanol from corn stover, allocation based on mass, energy content, and economic value was applied in addition to system expansion as described below. The mass ratio between stover and corn produced in agriculture is roughly 1:1 (Kim and Dale, 2006b), and the same is true for the energy content (Pordesimo et al., 2005). The prices of the collected stover and corn currently are \$0.033/kg (Graham et al., 2007) and \$0.148/kg (Ethanol Market, 2007), respectively. However, in the current agriculture practice, only 28% of the stover is harvested (Graham et al., 2007), and the rest is left in the field for the soil fertility. Sheehan et al. (2002) stated that as much as 60% of the stover can be collected and converted to fuel ethanol. As the technologies assumed in the ethanol production are advanced, the value of 60% is taken by assuming advanced agriculture practice still leaving soil fertility intact. The carbon fixed in the non-harvested stover has been left out of account in the analysis. The results in the percentages of stover and corn for partitioning based on mass/energy and economic value are summarized in Table 2.1

Table 2.1 Partitioning ratio for economic and mass/energy allocation

Percentage Allocation	Stover (%)	Corn (%)
Economic value	11.8	88.2
Mass/energy content	37.5	62.5

The system expansion approach was developed for the agricultural process in the system only. System expansion implies taking all the outputs of the multi-outputs process into the functional unit and adding products to make the total of functions equal among all the alternatives. In the ethanol system, corn (used for food and fodder) is produced besides stover (used for ethanol). Hence, the gasoline alternative needs to be expanded with the equivalent amount of food and fodder, which we assumed to be corn and stover again. As corn and stover are produced in the same agriculture process, it is impossible to producing solely corn or stover. A mixture with different amounts is assumed to fulfil the same function in all systems, and the amount is estimated based on the nutritional values. The amount of ethanol for driving 1 km is produced by utilizing 0.393 kg of stover, while 0.655 kg of corn is produced in the agriculture. Hence, when driving with gasoline the functional unit is ‘1 km of driving + 1.048 kg of corn and stover (total nutritional value 13.6 kJ)’, while driving with ethanol 0.393 kg of additional biomass needs to be produced. The nutritional value of corn is 14.3 kJ/kg (Organic Facts, 2009), and the one of stover is estimated to be 10.7 kJ/kg based on the composition difference in corn and stover. As corn has higher nutritional value, the total amount of biomass for food and fodder is less than 1.048 kg. For the case of E10 and E85, the method of estimation is applied. The functional unit used in all four alternatives is defined as ‘one kilometre of car driving + nutritional value 13.6 kJ of corn and stover’ as illustrated in Table 2.2. The chains of corn and stover for food and fodder are not followed beyond the farm, which is considered sufficient for the comparative purpose of this study.

Table 2.2 Function units of current system and added biomass for all fuel options

Item	Current system			Added biomass	
	Fuel	Corn	Stover	Corn	Stover
Alternative	(kg)	(kg)	(kg)	(kg)	(kg)
Gasoline, corn & stover	0.066	0.000	0.000	0.655	0.393
E10, corn & stover	0.069	0.045	0.000	0.624	0.374
E85, corn & stover	0.092	0.514	0.000	0.301	0.180
Ethanol, corn & stover	0.099	0.655	0.000	0.203	0.122

The co-produced electricity in the ethanol production is fully used in the system due to the electricity requirement in enzyme production. Therefore, this case is considered as a closed loop, and rendering allocation is unnecessary. In more general cases where these amounts differ, allocation cannot be resolved in this way: electricity delivered to the grid and taken from the grid has to be specified separately, and allocation choices will have to be made.

2.2.6 Impact assessment and interpretation

The following impact categories are included in this study:

- Abiotic resource depletion potential (ADP)
- Global warming potential (GWP)
- Ozone layer depletion potential (ODP)
- Photochemical oxidation potential (POCP)
- Human and eco-toxicity potential (HTP and ETP)
- Acidification potential (AP)
- Eutrophication potential (EP)

We left 'land use' out of account for two reasons. One is that land use shifts induced elsewhere do not fit into the LCA framework. This is a limitation that all LCA types of studies have by necessity due to the use of the functional unit instead of full totals in all markets concerned. At the LCA level, we could have included hectares of land use which would lead to obvious results – agriculture is dominant for the land use.

Weighting is not included in this study, as we want to show differences per impact category due to different allocation methods applied. A contribution analysis was performed in which the contributions of life cycle stages or groups of processes to the total result are examined, expressing the contribution as a percentage of the total. The major parts of the four main alternatives are agriculture production, enzyme production, ethanol production, gasoline production, and car driving.

2.3 Results and Discussion

In this section, the results of the inventory analysis and impact assessment based on different allocation methods are presented, and the results of the contribution analysis are discussed.

2.3.1 LCA results

1) Mass, energy content and economic value based allocation

Figure 2.2 gives the overall results when applying allocation based on mass, energy content, and economic value between corn and stover as well as system expansion. In this case, mass and energy ratios between corn and stover are identical. It is worth noting that the function unit used in the system expansion approach is different from the ones in the allocation approaches.

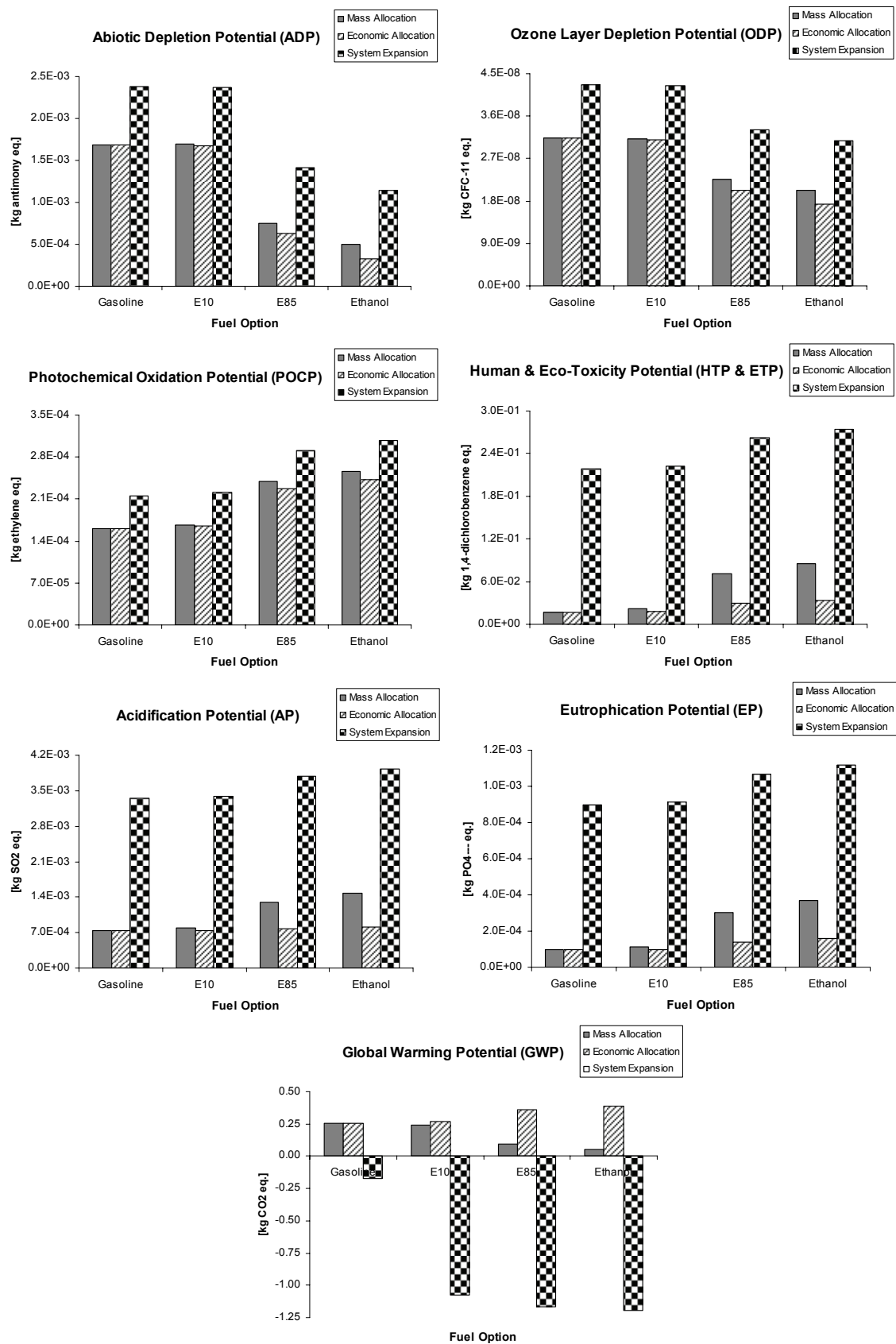


Figure 2.2 Overall results of the environmental impact of all fuel options

The results show that the level of ADP and ODP are reduced when replacing gasoline by ethanol fuels irrespective of the allocation method applied. This is obviously due to the replacement of fossil resources by renewables – corn stover in this case. Crude oil, natural gas, and coal are the main contributors of the ADP level, while the ODP level is mainly contributed by the emissions from the crude oil production onshore. In the case of economic allocation, the reduction is more significant due to the smaller share of agricultural emissions allocated to stover.

For the rest of the impact categories except GWP, applying ethanol fuels leads to worse environmental performance, also irrespective of the allocation method. When shifting from gasoline to ethanol fuels, the emissions causing POCP from natural gas production and oil exploitation decrease, but the ones from ethanol production contribute even more to POCP level. Moreover, agriculture contributes largely to human and eco-toxicity, acidification, and eutrophication due to the use of agrochemicals; thus, gasoline is a better option in terms of these impacts. The application of economic allocation leads to a better environmental performance in these impact categories because most of the agriculture related emissions are allocated away to corn, but still, gasoline is the better option.

The most interesting outcome in this study refers to GHG emissions. When mass and energy content based allocation is applied, the GWP score is significantly better for ethanol fuels compared to gasoline. The application of economic value based allocation gives opposite results: now, the biofuels perform worse than gasoline. The reason is that the corn/stover ratio shifts from 1.7 to 7.5 when shifting mass/energy allocation to economic allocation. When mass/energy allocation is applied, both more credits (CO_2 uptake) and more penalties (N_2O emission) in agriculture are allocated to stover compared to the case of economic allocation. However, more CO_2 is taken up than N_2O (in CO_2 eq.) emitted. Hence, the smaller the allocation ratio between corn and stover, the less the GWP score for stover ethanol becomes. This finding shows that the outcomes are highly sensitive to the allocation method applied. Therefore, allocation issues are of crucial importance in LCA studies applied to biofuels and should be discussed explicitly in any such case study.

We have chosen in this case study to follow the ‘normal’ LCA procedure when dealing with CO_2 uptake and CO_2 emissions: the uptake counts as an extraction from the environment; therefore, the emissions of the biogenic CO_2 are counted just the same as CO_2 emissions from fossil sources. In the field of energy research, there is a custom of ignoring both CO_2 extractions from the atmosphere and emissions of biogenic CO_2 . In

a straightforward system that does not require allocation; the net result should be the same. However, when allocation is needed, this may no longer be the case. As the allocation methods applied strongly affect the results of GWP, a comparative computation of the system excluding biogenic CO₂ was made, and the result is given in Figure 2.3. When biogenic CO₂ is excluded, the results show a reduction of GWP when replacing gasoline with ethanol fuels irrespective of the allocation method applied. What in fact has happened by excluding biogenic CO₂ is that CO₂ escapes the chosen method of allocation. Instead, CO₂ is allocated in all cases on the basis of the carbon balance of the chain. Implicitly, another way of allocation has entered the story and has been mixed with the other types of allocation. It is very relevant to acknowledge this.

Further computations show that when the allocation ratio between stover and corn becomes 0.29:0.71, GWP of gasoline and ethanol (on basis of energy content in both fuels) are the same and, thus, also for all mixtures. This can be seen as a breakeven point, which means when the allocation ratio is higher than 0.29:0.71, GWP will decrease with increasing ethanol content. For this special case to result, the price of the stover has to increase to at least \$0.1/ kg, three times higher than the current price of \$0.033/kg, while the price of corn remains the same. When the price of the stover reaches the one of corn, the results of the impact assessment will be the same as the current results with mass or energy based allocation applied in agriculture. Nevertheless, the price will be largely dependent on the U.S. policy on biofuels.

2) System expansion

It is worth noting that the functional unit defined in this approach does not only comprise one kilometre of car driving but also the same amount of energy in the added food and fodder in all the alternatives, as described in Section 2.2.5. These additional products lead to substantially larger environmental impact than outcomes given above. The results are shown in Figure 2.3 in comparison with other approaches.

The levels of all impact categories except GWP are higher in the expanded systems than the allocated systems when replacing gasoline by ethanol fuels. The reason for this is that in the other approaches, only the life cycles of the fuels are taken into account, while in the system expansion approach, the functional unit does not only include one kilometre driving but also additional agricultural production of food and stover. The CO₂ uptake for the growth of food and fodder are ultimately released to the atmosphere, but that does not show as the system only includes the co-production of food and fodder, not the downstream of food and fodder digestion. Thus, global warming potential is significantly reduced, resulting in the negative values in all cases. This implies

that the system expansion results are comparable to one another because they make the same cut-offs but not really to the results related to the allocated systems based on mass, energy content and economic value.

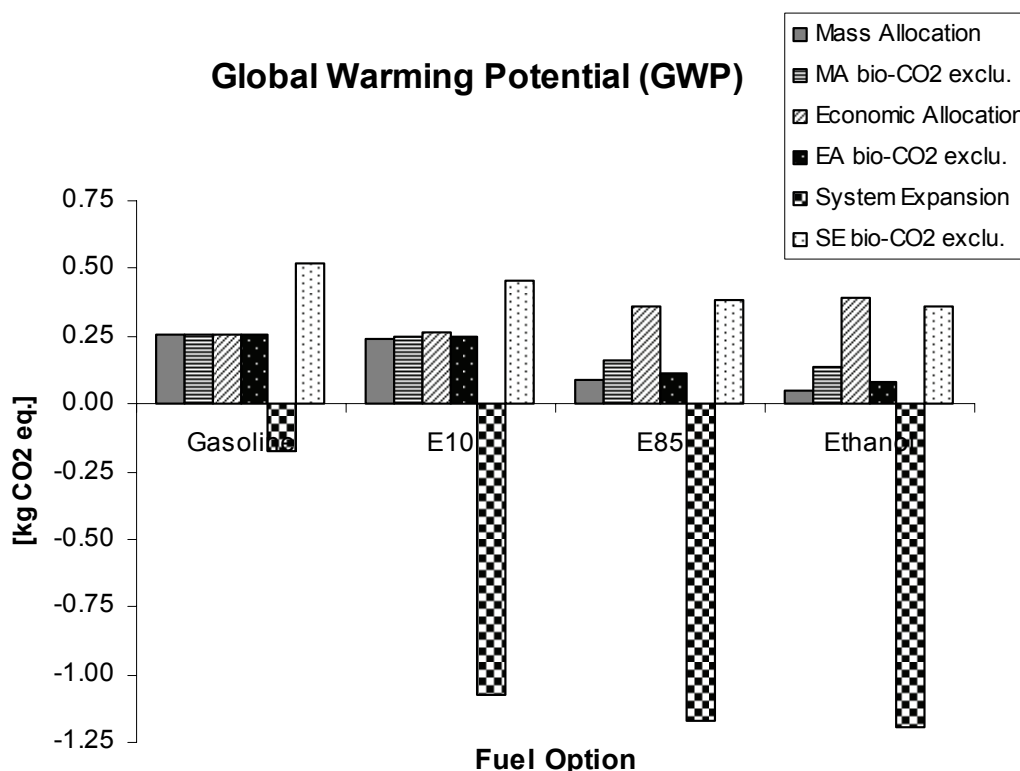


Figure 2.3 Comparative results of global warming in all cases

2.3.2 Contribution analysis

A contribution analysis was conducted to identify the major sub-processes which contribute significantly to the environmental impact of the total system. This can be done for all the impact categories; however, here only the results of global warming potential using economic value based allocation are shown as an example (see Figure 2.4).

In the gasoline life cycle, car driving (82%) is the main contributor to GWP. In the life cycle of E10, the contributions of fossil resource extraction (7%), CO₂ uptake (-5%), electricity generation (6%), and fermentation (2%) are also significant, as shown in Figure 2.4. In the life cycle of E85 and ethanol, the results of the contribution analysis are similar however, of course, stronger. Besides CO₂ uptake, electricity generation is the largest contributor due to the high electricity consumption in the enzyme

production process. Figure 2.4 also shows the significant contributions of car driving, fermentation, N₂O emissions from agriculture, and fossil fuel use to GWP. The contribution analysis indicates that the bottlenecks are N₂O emissions from agriculture, enzyme production, and electricity generation in the ethanol refinery.

The emissions from the production of capital goods do not seem to be important. The results show little difference from the ones not including the emissions from the capital goods production in ethanol process.

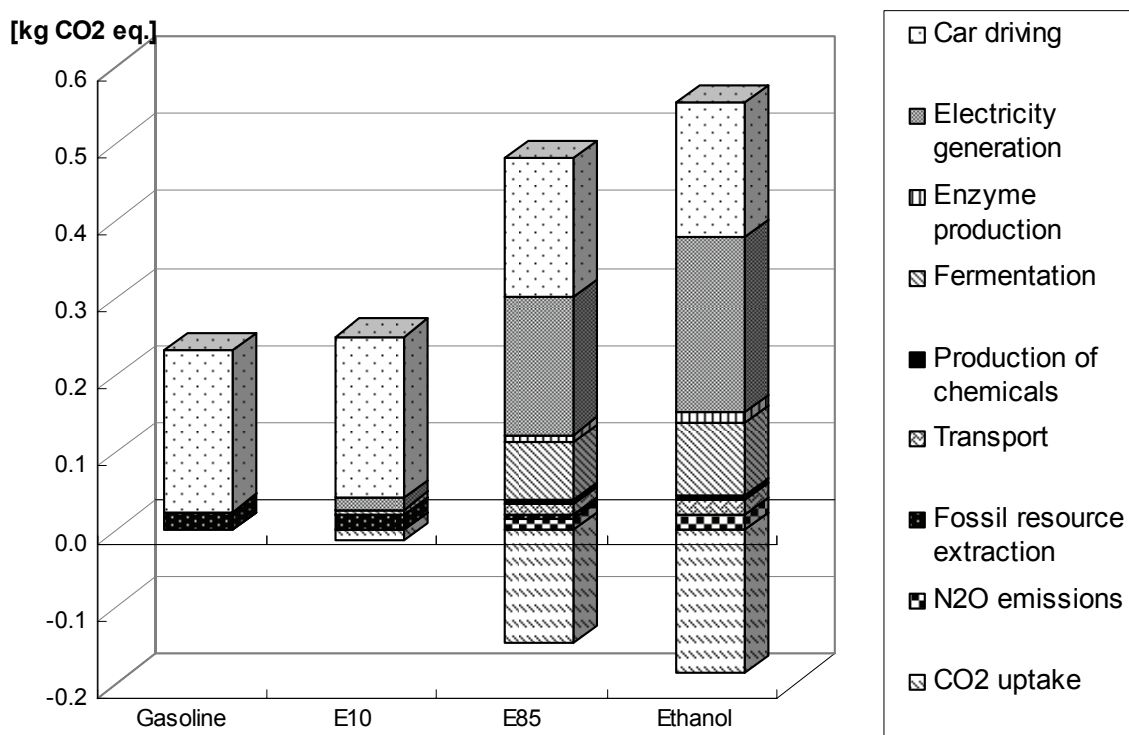


Figure 2.4 Contributions of the main processes to global warming potential (economic value based allocation)

2.4 Conclusions

The levels of abiotic resource depletion and ozone layer depletion decrease when shifting from gasoline to ethanol fuels, irrespective of the allocation method applied, only the degrees of reduction are different; while the levels of photochemical oxidation, human and eco-toxicity, acidification, and eutrophication potential increase in all cases. Here, we may conclude a clear case of problem shifting – solving one problem (oil depletion) at the expense of increasing others (mostly agriculture-related emissions).

The choice of the allocation methodology is essential for the outcomes related to GHG

emissions. Since this is an important issue and one of the main reasons for considering biofuels instead of fossil fuels, it is important to realize this and give allocation a special place in life cycle-based studies of biofuels. Subsequent replacement of gasoline by ethanol increases global warming potential when economic allocation is applied based on current prices. In contrast, reduction of global warming potential is achieved when mass or energy content based allocation is applied. In the agricultural production, carbon dioxide is taken up for the growth of corn and stover, and global warming potential are caused mainly by nitrous oxide released from the soil. When economic value based allocation is applied, both less credit (CO_2 uptake) and fewer penalties (N_2O emission) are allocated to stover comparing to the case of mass or energy based allocation. However, more CO_2 is taken up in the agriculture than N_2O (in kg CO_2 eq.) emitted which results in the increment of global warming potential. When biogenic CO_2 is altogether excluded from the system, as is customary in energy analysis studies of biofuels, a reduction of GWP is achieved irrespective of the allocation method applied. However, it is important to notice that by doing this, in fact, a different allocation method has entered (allocation based on carbon balance) and is mixed with the other allocation methods.

In expanded systems where both driving, food and fodder production are taken into account, all the environmental impacts except global warming potential are larger than the ones in allocated systems when replacing gasoline by ethanol fuels. The negative global warming potential is mainly due to the carbon dioxide uptake in the agriculture. In terms of abiotic resource depletion, global warming potential and ozone layer depletion, ethanol fuels have better environmental performance than gasoline; however, gasoline is a better fuel when the rest of the impacts are concerned. The overall evaluation depends on the importance attached to each impact category.

If larger cellulosic ethanol markets can be established in the U.S. with a higher price for stover as feedstock, the ratio of economic allocation will shift towards the one of mass/energy allocation. If this situation is reached, a replacement of gasoline by ethanol will consistently show an increasing reduction of global warming potential irrespective of the allocation method applied.

GHG emissions in agriculture are, besides biogenic CO_2 uptake and emissions, largely determined by the emission of nitrous oxide (N_2O). In the ethanol production process, GHG emissions are mainly due to electricity generation and fermentation. The production of the enzyme used for hydrolysis requires a substantial amount of electricity for air compression. The production of this electricity from either fossil resources or the

combustion of wastes in the plant also generates a considerable amount of CO₂ emission in the chain. The main bottleneck processes in the chain are nitrous oxide emissions in agriculture and electricity use required in enzymes production for ethanol production; these two processes should therefore receive most attention when focusing on improving the GHG performance of the chain.

We now have three allocation methods which can be applied and are applied in the environmental analysis of biofuels: (1) mass or energy based allocation, (2) economic value based allocation, and (3) system expansion. These can be combined with what is usual in many studies – leaving biogenic carbon out of the analysis. These lead to opposing outcomes for scores on climate change and diverging outcomes on most of the other environmental impacts.

2.5 Recommendations and Perspectives

This study shows that corn and stover agriculture is an intensive process. The production of other types of cellulosic feedstock may have a less intensive agricultural management. Further analysis should focus on different feedstock for the second generation bioethanol production such as sugarcane bagasse, switchgrass, wood and cassava, etc.

The outcomes are highly sensitive to the allocation methods applied, especially with regard to global warming, which is one of the main reasons to consider biofuels. This is unacceptable from a societal point of view and a challenge from a scientific point of view. Nevertheless, this has not yet raised the awareness of many decision makers who use LCA as a support tool. The results from applying one allocation method are certainly not sufficient in this case and may be in many other cases in the cellulosic ethanol LCA. It is relevant to notice that the so far uncontested practice of ignoring biogenic CO₂ in the chain is, in fact, another allocation choice: allocation based on the carbon balance. It is important that LCA practitioners realize this and deal with it in an appropriate manner. Mixing allocation methods in one case study is not advisable.

It is also advisable to broaden the attention to include more issues than GHG emissions, fossil fuel depletion and energy balance in studies on biofuels. This study has shown that there is a clear shifting of problems from oil depletion toward eutrophication and toxicity due to the use of agrochemicals. The use of land and water has not been included in this study but here, important problem displacement issues may also occur. To assess the sustainability of biofuel chains, this broader perspective must not be ignored.

LCA as it stands has its limitations not only in allocation issues but also in variable multi-input multi-output systems, such as complex biorefineries. A broader approach beyond LCA for the analysis of biorefinery systems with regards to energy conservation, environmental impact, and cost-benefit will provide general indications on the sustainability of bio-based productions.

Chapter 3

Life Cycle Assessment and Life Cycle Costing of Bioethanol from Sugarcane in Brazil

* This chapter is published in Renewable and Sustainable Energy Reviews 2009; 13(6-7): 1613-1619. Co-authors: Ester van der Voet and Gjalb Huppes

Abstract

Brazil has always been the pioneer in the application of bioethanol as a main fuel for automobiles, hence environmental and economic analyses of the Brazilian ethanol industries are of crucial importance. This study presents a comparative life cycle assessment (LCA) on gasoline and ethanol as fuels, and with two types of blends of gasoline with bioethanol, all used in a midsize car. The focus is on a main application in Brazil, sugarcane based ethanol. The results of two cases are presented: base case – ethanol production from juice sugar from the cane and electricity generation from bagasse; future case – ethanol production from both juice sugar and bagasse and electricity generation from lignin residues and wastes. In both cases sugar is co-produced. The life cycles of fuels include gasoline production, agricultural production of sugarcane, ethanol production, sugar and electricity co-production, blending ethanol with gasoline to produce E10 (10% of ethanol) and E85 (85%), and finally the use of gasoline, E10, E85 and pure ethanol as transport fuels. Furthermore, a life cycle costing (LCC) was conducted to give an indication on fuel economy in both cases. The results show that in the base case less GHG is emitted; while the overall evaluation of these fuel options depends on the importance attached to different impacts. The future case is certainly more economically attractive, which might have been the driving force for development in the ethanol industry in Brazil. Nevertheless, the outcomes depend very much on the assumed price for crude oil. In LCC a steady-state cost model was used and only the production cost was taken into account. In the real market the prices of fuels are largely dependent on the taxes and subsidies. Technological development can help lowering both the environmental impact and the prices of the ethanol fuels.

3.1 Introduction

The concept of biofuels, especially bioethanol, has been promoted all over the world, and the rationale behind mainly focuses on the reduction of fossil resource use and greenhouse effect. With respect to these two aims the feasibility of bioethanol in terms of environmental impact has been challenged (Farrell et al., 2006; Kim and Dale, 2005a; Macedo, 1998; Pimentel, 2003; Shapouri et al., 2002; Sheehan et al., 2004; von Blottnitz and Curran, 2007). The major outcomes of these studies are the reduction of fossil resource extraction and greenhouse gas (GHG) emissions to some extent. The current technology in industry is able to convert carbohydrates from dedicated crops such as corn, wheat, sorghum, potato, sugarcane, sugar beet and cassava to ethanol (Hu et al., 2004a; Hu et al., 2004b; Kim and Dale, 2002; Kim and Dale, 2005a; Kim and Dale, 2005b; Pimentel, 2003; Reinhardt and Uihlein, 2002; Shapouri et al., 2002). However, the land use requirement of such an application causes the competition with food and nature, which has become the main driving force of the development and implementation of advanced process technologies to produce ethanol from celluloses from low value agricultural co-products or wastes like corn stover, wheat straw, sugarcane bagasse, wood or grass. Several LCA studies focusing on these advanced technologies have been conducted (Fu et al., 2003; Kadam, 2002; Kemppainen and Schonnard, 2005; Sheehan et al., 2002; Spatari et al., 2005; Tan and Culuba, 2002), concluding a reduction of fossil fuel use and GHG emissions. However, other environmental impacts including land requirements caused by bioethanol production and application received much less attention. Furthermore, economic feasibility has not been of concern in the LCA studies. Hence a study with a complete set of impact categories and an indication of fuel economy is in urgent need.

Since early 1970s Brazil has been the major fuel ethanol producer in the world depending on sugarcane as feedstock. Ethanol from sugarcane with its bio-renewable nature and optimized production technology is already proven as a replacement for fossil fuels in Brazil (Efe et al., 2005). The advanced process technology has also been developed to produce ethanol from cellulosic feedstock – bagasse. Hence the main research question is raised as ‘Is the second-generation bioethanol from sugarcane better than first-generation?’ To answer this question it is of crucial importance to research on the environmental impact and economic feasibility of sugarcane ethanol as a transport fuel. Here the term ‘second-generation’ bioethanol means the involvement of using both sucrose and bagasse for ethanol production, unlike the first-generation bagasse is combusted for heat and power generation.

This paper focuses on bioethanol from sugarcane involving the cellulosic technology and a complete set of environmental impacts of importance. The full life cycles of bioethanol and gasoline are analyzed, including the production and transport of the raw materials and fuels, the production of equipments and energy in the plant, and the application of the fuels. The agriculture and the ethanol production data based on the local conditions in Brazil are used. The LCA methodology used, especially allocation procedures, follows the guidelines described in the Handbook on Life Cycle Assessment (Guinée et al., 2002).

3.2 Methodology

Life cycle assessment (LCA) is a method for determining the environmental impact of a product (good or service) during its entire life cycle – from extraction of raw materials through manufacturing, logistics and use to scrapping and recycling. In LCA substantially broader environmental aspects can be covered, ranging from global warming potential and fossil resource depletion to acidification and toxicity aspects, hence it is a good tool for quantifying environmental impacts of a defined product system. However, LCA as it stands has its limitations such as the difficulties in data acquisition and validation, and the misleading results due to the choice of methodology especially on allocation issues.

Life cycle costing (LCC) is a process to determine the sum of all the costs associated with an asset or part thereof, including acquisition, installation, operation, maintenance, and refurbishment and disposal costs. In LCC a steady-state cost model is engaged, and only production cost is taken into account, thus it cannot be used to model the dynamic effect in the real markets.

The present study concerns the comparison of technologies and costs for the car driving function, with Brazilian local circumstances playing a role. Not only was the comparison between driving on gasoline and ethanol fuels made, but also the one between ethanol from two processes involving different technologies was made. The two cases engaged are: base case – bioethanol production from sucrose (juice sugar), and heat and electricity generation from bagasse using the current technology; future case – bioethanol production from both sucrose and bagasse, and heat and electricity generation from lignin residues and wastes. In the process of ethanol from bagasse advanced technology was assumed, meaning that genetically modified organism (GMO) is used to ferment both pentose and hexose sugar to increase the yield. In both cases sugar is co-produced. The following issues are of specific interest.

3.2.1 Functional unit and alternatives

The functional unit in this study is defined as power to wheels for one kilometre driving of a midsize car. Not the full car is taken into account but only its energy requirements in driving. In practice, ethanol is mainly used in one of two ways in vehicle fuel (Homewood, 1993; Keller, 1984): (1) blended with gasoline, typically 5-20% by volume, for use in existing vehicles with no engine modifications; (2) blended with gasoline, typically 85-100% by volume, for use in vehicles with specifically modified engines. In this study ethanol is assumed to be used in both ways, as a mixture of 10% ethanol with 90% gasoline by volume (termed E10), and as a mixture of 85% ethanol with 15% gasoline by volume (termed E85). As a reference alternative, a hypothetical case of 100% ethanol is also taken into account. Therefore the fuel alternatives are gasoline, E10, E85 and 100% ethanol, in amounts required to deliver the same amount of energy 'to the wheels'.

3.2.2 System boundaries

All relevant processes are included within the boundary of the fuel systems, including those for capital goods and wastes management. Base case and future case are shown in Figures 3.1 and 3.2, respectively.

In the base case the ethanol production includes sugarcane milling, juice clarification, fermentation and purification of ethanol; as well as the co-production of sugar from sucrose and electricity from bagasse and wastes. In the future case, the ethanol production includes sugarcane milling, juice clarification, pre-treatment and hydrolysis of bagasse, fermentation and purification of ethanol; as well as the co-production of sugar from sucrose and electricity from wastes. In both cases 48% of the sucrose is used to produce ethanol, and 52% is for sugar co-production. The major difference between the two cases is the use of bagasse, in the base case completely for electricity generation, and in the future case mainly for ethanol production. Only the lignin residues from bagasse used together with wastes for electricity generation in the future case. Since the production and disposal of the car is outside the system boundaries, neither waste management nor recycling is included.

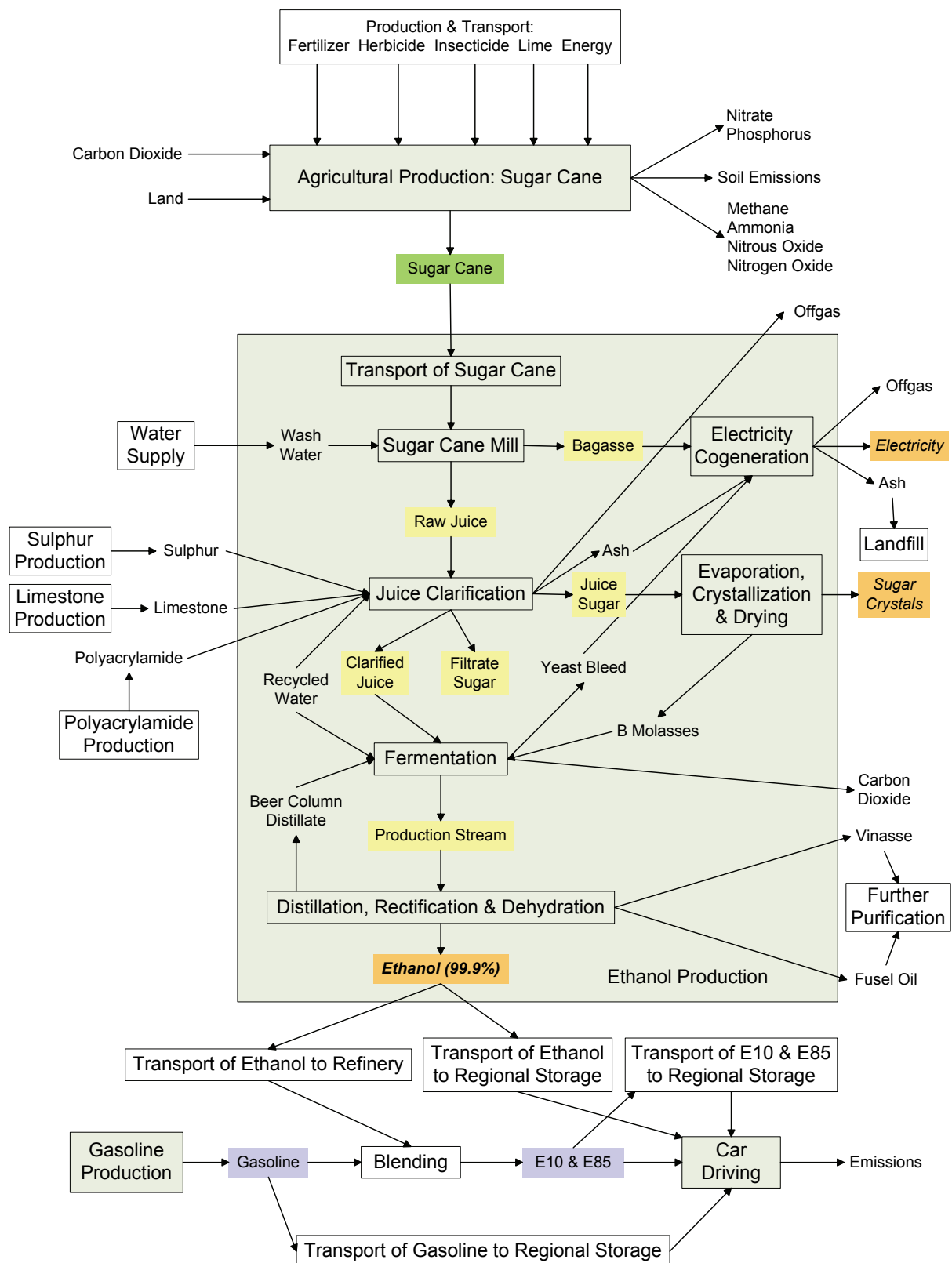


Figure 3.1 The life cycle of bioethanol from sugarcane in the base case

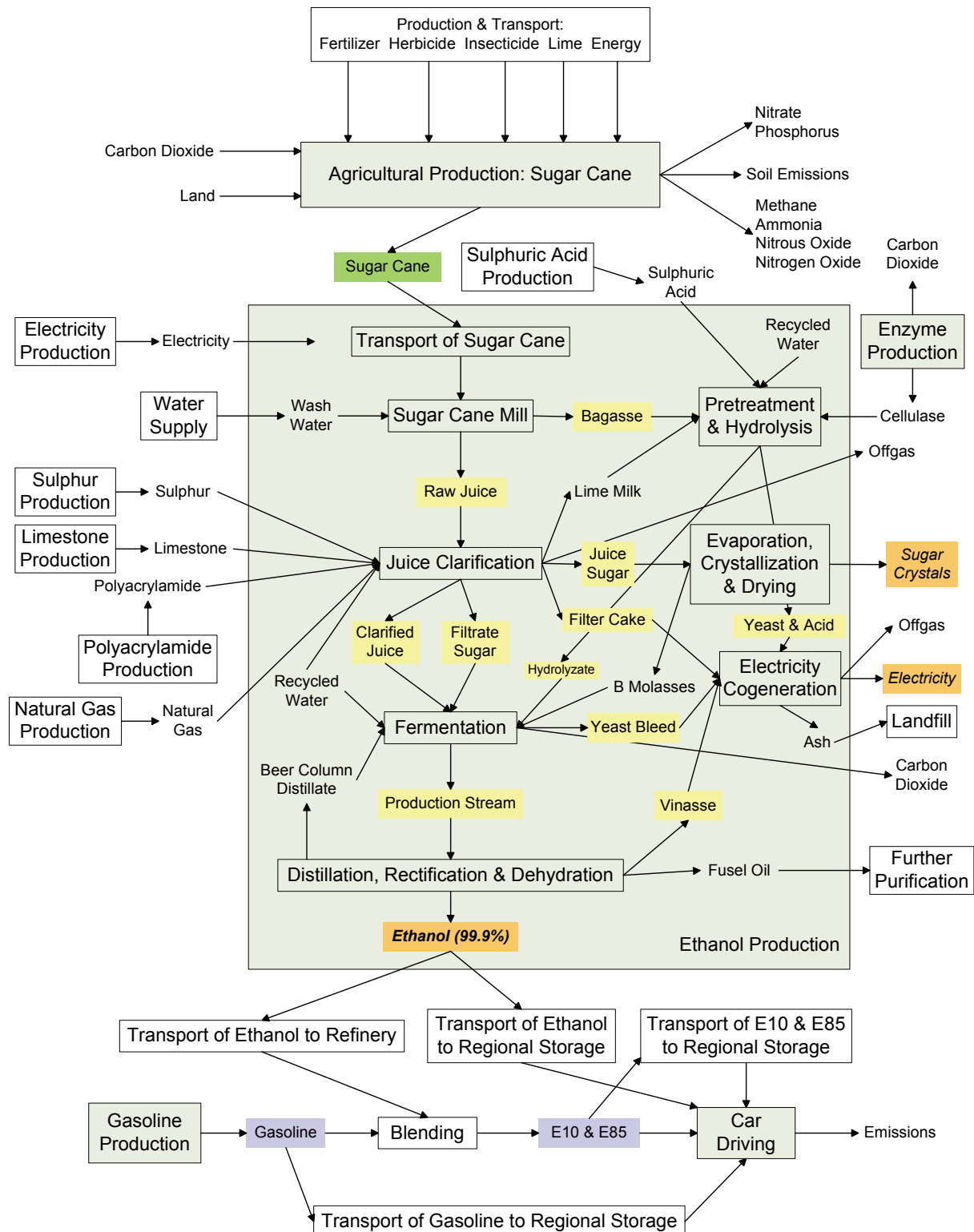


Figure 3.2 The life cycle of bioethanol from sugarcane in the future case

3.2.3 Data sources and software

Data used in this study are obtained from different sources. Agriculture data are from Macedo et al. (2004), or estimated using the methods in report on agriculture published by the Swiss Centre of Life Cycle Inventories (Nemecek et al., 2004). Data on transport of sugarcane are also from Macedo et al. (2004). Process and cost data on ethanol, sugar and electricity productions are reported by Efe et al. (2005). Emissions from capital goods production are from EIPRO database (Tukker et al., 2006). Gasoline production data are provided by Ecoinvent (<http://www.ecoinvent.org/>), and cost data (year 2005) is obtained from Energy Information Administration (<http://www.eia.doe.gov/>). Emission data of car driving using gasoline, E10 and E85 are acquired from the reports on emission test of different fuels (Kelly et al., 1996; Reading et al., 2002). The completeness of data may differ between sources; therefore one source, the Ecoinvent database, is used when possible, as this source has a long learning experience and involves a very broad range of processes, around 4,000. Data gaps resulting from general data unavailability are filled by making a variety of assumptions as noted below. The software package called “Chain Management by Life Cycle Assessment” (<http://cml.leiden.edu/software/software-cmlca.html>) is used for the analysis.

3.2.4 Key assumptions

In this study, the life time of the ethanol plant is assumed to be 10 years, and the ethanol produced is aimed at a purity of 99.9% in both cases. 48% of sucrose from sugarcane is utilized for ethanol production and 52% is crystallized into sugar crystals (Efe et al., 2005). Ethanol production plant is assumed to be located 20 km away from the sugarcane field (Macedo et al., 2004). Hence the transport distance of sugarcane from the field to the plant is 20 km. The transport of materials and products is by road using lorry with various loading capacities, depending on the needs. 20 km is assumed to be the transport distance of ethanol produced to the refinery. For the distance between the refinery and the regional storage the value from the Ecoinvent is followed (34 km). Therefore, for comparison the transport distance of E10, E85 and 100% ethanol to their regional storages is assumed to be 34 km. For gasoline, E10 and E85 emission data are based on a standard test procedure, covering a mix of driving on urban roads and on motorways. For 100% ethanol the emission data are based on assumptions and calculations.

3.2.5 Allocation methodology

According to the LCA methodology, allocation is required for multi-product processes. In the gasoline life cycle this refers to the oil refinery including drilling oil well, the

production of crude oil, the transport of crude oil to refineries, and the refinery of crude oil to produce gasoline, diesel and other co-products. In the gasoline life cycle allocation must be applied to the refinery producing gasoline and other co-products. For gasoline production the allocations were taken as currently implemented in the Ecoinvent database by its designers. In the ethanol life cycle this refers to five sub-processes: sugarcane milling, juice clarification, fermentation, ethanol purification, electricity generation and sugar purification. In these processes economic allocation based on the market value of the process outputs was applied, as specified by the Handbook on Life Cycle Assessment (Guinée et al., 2002).

3.2.6 Impact assessment

This study mainly focused on the following impact categories:

- Abiotic resource depletion potential (ADP)
- Global warming potential (GWP)
- Ozone layer depletion potential (ODP)
- Photochemical oxidation potential (POCP)
- Human and eco-toxicity potential (HTP and ETP)
- Acidification potential (AP)
- Eutrophication potential (EP)

3.2.7 Life cycle costing (LCC)

A LCC was conducted with the same system specification, indicating the cost (tax excluded) of 1 km distance driven by a midsize car using gasoline, E10, E85 and 100% ethanol. In LCC a steady-state cost model is used, which means no discounting and depreciation were taken into account. As the life time of the ethanol refinery is assumed to be 10 years, the capital investment is divided over 10 years. Since in the ethanol plant co-produces sugar and electricity in the base case and sugar in the future case, respectively, the fixed capital investment and operating costs were allocated between ethanol and co-products based on their economic values. It is worth noting that in the future case is designed with assumed advanced process technologies; hence all the data on cost were estimated based on the base case.

3.3 Results and Discussion

3.3.1 LCA

The comparative results of the LCA for all the fuel alternatives in the base and the future case are shown in Figure 3.3.

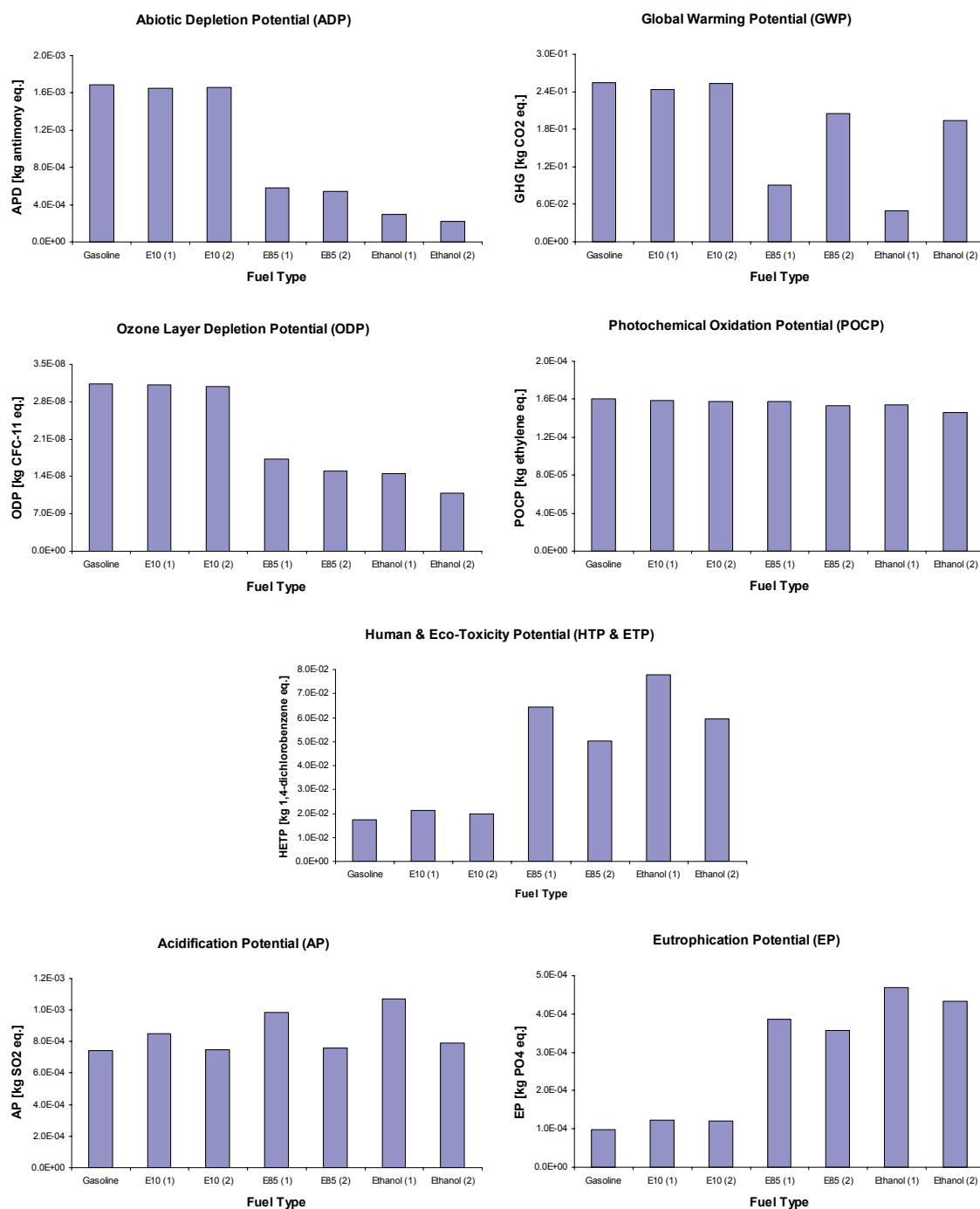


Figure 3.3 Overall comparison of the environmental impact of all fuel options

The results show that in the base case the levels of ADP and GWP substantially decrease when replacing gasoline by ethanol fuels, about 83% and 81%, respectively. This is due to the replacement of fossil resources by renewable biological resources. In the future case ADP decreases even more (87%). GWP also decrease, but much less than in the base case (24%) (See below). The reason for the significant decrease in GHG emissions is that the growth of sugarcane takes up a large amount of CO₂, counter-acted only partly by N₂O emissions from agriculture. For most of the other impact categories, applying ethanol fuels causes a larger environmental impact. The agricultural process contributes largely to human and eco-toxicity, acidification and eutrophication potential. Ozone layer depletion is much lower for ethanol from sugarcane because it is mainly caused by the emissions from crude oil production onshore. The POCP level is not significantly changed in both cases. When replacing gasoline by ethanol fuels, emissions causing POCP from natural gas production and crude oil exploitation decrease, but emissions from ethanol storage, fermentation, bagasse treatment and electricity cogeneration increase.

When considering the comparison between the base and future case in terms of environmental impact, in the categories except GWP the future case shows a better performance. More ethanol is made out of the same harvested material: to produce 1 kg of ethanol, only 12.6 kg of sugarcane is needed in the future case, while 30.1 kg is needed in the base case. Regarding GHG emissions, in the base case 77.4 MW of electricity is cogenerated from the combustion of bagasse, while only 18.4 MW is used for the ethanol production and the rest (59 MW) is assumed to be sold to the local grid. A significant part of the process emissions from the co-generation process are allocated to the co-produced electricity. However, in the future case only 13.2 MW of electricity is coproduced from wastes, while 22 MW is needed for the plant; hence 8.8 MW is purchased from the grid. In this case, although more ethanol is produced due to the use of bagasse, net GHG emissions decrease less compared to the base case. This result is different from our previous work on the LCA of bioethanol from corn stover. In the stover-ethanol case, stover is a by-product from corn production. Therefore, a large part of the agricultural emissions and extractions are allocated to corn. When economic value based allocation (stover/corn ratio 0.14/0.86) is applied both less credits (CO₂ uptake) and less penalties (N₂O emission) are allocated to stover. In the case of sugarcane-ethanol, no allocation is required for the agricultural process. Furthermore, sugarcane agriculture is much less intensive compared to corn agriculture in terms of the use of fertilizers, which results in less GHG emissions.

3.3.2 LCC

Based on the cost data in 2005, the gasoline production cost was calculated to be 0.59 \$/kg. Ethanol production costs are 0.30 and 0.26 \$/kg in the base case and the future case, respectively. The costs of 1 km driving for all the fuel alternatives in both cases are shown in Table 3.1.

Table 3.1 Costs of one kilometre driving for all the fuel alternatives

Case	Gasoline	E10	E85	Ethanol	Unit
Base case	0.0393	0.0388	0.0313	0.0294	\$/km
Future case	0.0393	0.0385	0.0282	0.0254	\$/km

As a whole, driving with ethanol fuels is cheaper than driving with gasoline due to the low production cost of ethanol from sugarcane. The future case is economically more attractive than the base case. The reason for this is that although in the future case ethanol plant does not co-produce extra electricity, it produces ethanol 2.4 times as the one produced in the base case. As the price of the crude oil was nearly doubled in 2008 compared to the one in 2005 (Energy Information Administration: <http://www.eia.doe.gov/>), a sensitivity analysis was conducted with the current oil price. In this analysis all the capital investment and operation costs were assumed to remain the same. Moreover, with the growing market of sugarcane-ethanol, the price of sugarcane can increase substantially. Hence another sensitivity analysis was performed with the assumption of doubling the sugarcane price and taking the 2005 price for crude oil. The third sensitivity analysis was conducted with the assumption of doubling the prices of both crude oil and sugarcane. The results of the analysis are shown in Tables 3.2-3.4.

Table 3.2 Costs of one kilometre driving with double crude oil price

Case	Gasoline	E10	E85	Ethanol	Unit
Base case	0.0816	0.0784	0.0402	0.0294	\$/km
Future case	0.0816	0.0781	0.0370	0.0294	\$/km

Table 3.3 Costs of one kilometre driving with double sugarcane price

Case	Gasoline	E10	E85	Ethanol	Unit
Base case	0.0393	0.0403	0.0483	0.0511	\$/km
Future case	0.0393	0.0395	0.0388	0.0390	\$/km

Table 3.4 Costs of one kilometre driving with double both prices

Case	Gasoline	E10	E85	Ethanol	Unit
Base case	0.0816	0.0799	0.0572	0.0511	\$/km
Future case	0.0816	0.0790	0.0472	0.0383	\$/km

The results show that in all three scenarios driving on ethanol fuels is much cheaper in both the base and the future case. The example of E85 fuel shows the upward trend of costs of driving when the prices of crude oil and sugarcane are doubled separately and simultaneously. Furthermore, the differences in fuel economy in base cases are smaller than the ones in future cases. Due to the implementation of advanced process technologies in the future case, production costs of ethanol has been brought down significantly.

3.4 Conclusions and Recommendations

From the LCA results it can be concluded that in terms of abiotic resource depletion, global warming potential, ozone layer depletion and photochemical oxidation ethanol fuels are better options than gasoline, while gasoline is a better fuel where human and eco-toxicity, acidification and eutrophication potential are concerned. The future case is promoted due to the use of bagasse to enhance the production efficiency of ethanol; in this study to produce 1 kg of ethanol 30.1 kg of sugarcane is needed in the base case, while only 12.6 kg is needed in the future case. When GHG emissions are concerned, however, the combustion of bagasse for electricity generation (base case) is a much better option than converting bagasse to ethanol (future case); while in all the other aspects the results are better for the future case. The overall evaluation of these fuel options depends on the importance attached to different impacts.

The results of LCC indicate that driving with ethanol fuels is more economical than gasoline, and the future case is economically more attractive than the base case, which has been the driving force for the promotion of advanced technologies converting bagasse to ethanol. Nevertheless, the outcomes depend very much on the assumed price for crude oil, which was considered high in the year of 2005. In the year of 2008 the oil price was nearly doubled compared to 2005, which makes driving on ethanol fuels even more economical. In LCC a steady-state cost model was used and only the production cost was taken into account, hence it can provide a first indication on the economic feasibility of the process. In the real market the prices of fuels are largely dependent on the taxes and subsidies.

In order to achieve an overall evaluation of the environmental impact of different fuel options, weighting factors attached to different impact categories need to be established. As weighting is a rather arbitrary step, we have not attempted it here.

It has to be kept in mind that the LCA methodology as it stands cannot capture all the relevant impacts. Land and water use and issues related to indirect land use changes and competition with food products do not fit well into the LCA framework but require a broader approach. Furthermore, technological development in both agriculture and ethanol production can help lowering both the environmental impact and the prices of the ethanol fuels, especially for the future case.

Life Cycle Assessment of Switchgrass-Derived Ethanol as Transport Fuel

* This chapter is accepted for publication in International Journal of Life Cycle Assessment. Co-authors: Yu Bai and Ester van der Voet

Abstract

The increasing gasoline price, the depletion of fossil resources and the negative environmental consequences of driving with petroleum fuels have driven the development of alternative transport fuels. Bioethanol which is derived from cellulosic feedstocks has attracted increasing attention as one such alternative. This study assesses the environmental impact of using ethanol from switchgrass as a transport fuel and compares the results with the ones of gasoline to analyze the potential of developing switchgrass-ethanol as an environmentally sustainable transport fuel.

The standard framework of LCA from ISO was followed. To compare the environmental impact of driving with E10 and E85 with gasoline, 'power to wheels for one kilometre driving of a midsize car' was defined as the functional unit. The product system consists of all relevant processes, from agriculture of switchgrass, throughout the production of ethanol, blending ethanol with gasoline to produce E85 and E10, to the final vehicle operations. The transport of all the products and chemicals are also included in the system boundaries. An allocation based on energy content was applied as a baseline, and market price based allocation was applied for a sensitivity analysis.

With regard to of global warming potential, driving with switchgrass-ethanol fuels leads to less GHG emissions than gasoline: 65% reduction may be achieved in the case of E85. Except for global warming and abiotic resource depletion, driving with ethanol fuels from switchgrass does not offer environmental benefits in the other impact categories compared to gasoline. Switchgrass agriculture is the main contributor to eutrophication, acidification and toxicity aspects. The emissions from bioethanol production cause a greater impact in photochemical smog formation for ethanol fuelled driving.

Bioethanol derived from switchgrass indeed leads to less GHG emissions than gasoline on a life-cycle basis; however, the problem has been shifted to other impacts. Improvement of switchgrass yields and development of ethanol production technologies may be the key to lower environmental impact in the future. For a more comprehensive evaluation of using bioethanol as transport fuel, more impact categories need to be included in the life cycle inventory analysis. A comparison with bioethanol from other feedstocks, based on similar methodological choices and background data, would provide more insight in the environmental benefits of switchgrass as a feedstock.

4.1 Introduction

An increasing demand for energy has led to an increase in the price of crude oil and an increased risk for depletion of fossil resources (EIA, 2009). The development of biofuels as transport fuel has the potential to reduce both greenhouse gas (GHG) emissions and the reliance on fossil fuels. Bioethanol is the most common biofuel, which has large potential to substitute gasoline as a transport fuel. So far, many studies on the life cycle assessment of bioethanol as a transport fuel focus on the first-generation bioethanol, which is derived from conventional crops, such as corn, wheat, sugar cane and sugar beet (Halleux et al., 2008; Luo et al., 2009b; Patyk and Reinhardt, 2002; Shapouri et al., 2002). It has been signalled that producing energy from such crops is very land- and water intensive ((Nguyen and Gheewala, 2008b; Renouf et al., 2008; Silalertruksa and Gheewala, 2009). Global demand for food is expected to keep increasing in the future (Rosegrant et al., 2001), and demand for transportation fuels is expected to increase even more rapidly (EIA, 2009), which implies a potential competition between land for food and land for energy.

To avoid conflict in demand between food and energy, cellulosic technology has been developed recently to convert ethanol from lignocelluloses rather than sugar or starch (Faaij, 2006). The application of the second-generation bioethanol has the potential to reduce fossil fuel use and to achieve better environmental performance, while at the same time avoiding competition with food supply, as cellulosic feedstocks are mainly from agriculture residues and lignocellulosic plants which do not need the same soil fertility as for conventional crops. Some LCA studies of the second-generation bioethanol as transport fuels have been conducted, and the feedstocks are mainly bagasse, corn stover and switchgrass (Kadam, 2002; Luo et al., 2009a; Sheehan et al., 2004; Spatari et al., 2005; Wu et al., 2006b). Switchgrass is one of the popular lignocellulosic feedstocks for the second-generation ethanol production. Although it is not a residue but a crop, it can be grown on marginal lands which cannot be used for food production. Since switchgrass does not need high soil nutrient concentrations, it does not have the annual preparation requirements and requires less chemical inputs than food crops (Mitchell et al., 2008; Sokhansanj et al., 2009).

Previous LCA studies of switchgrass-ethanol focus on greenhouse gas emissions. The research by Spatari et al. (2005) shows that, compared to gasoline, GHG emissions reduction can reach 57% when using E85 for vehicle driving, and greater reduction can be achieved in the future with the improvement of the switchgrass yield and the ethanol production. Wu et al. (2006b) use the GREET model to analyse the life cycle GHG emissions of transport fuel from switchgrass, and the results indicate that for E85, the

GHG reductions were 60-62% compared to gasoline. Without regard to final vehicle operations by ethanol fuels, LCA studies even show a reduction of GHG emissions of 94% per MJ on average, compared to gasoline (Schmer et al., 2008).

However, the environmental impacts of switchgrass-derived ethanol as a transport fuel do not only include global warming. Other impact categories should also be taken into account to evaluate the switchgrass-ethanol system comprehensively. This study carries out a life cycle assessment on switchgrass-ethanol to evaluate the environmental performance of using ethanol as a transport fuel compared with gasoline with a more complete set of impacts.

4.2 Methodology

4.2.1 Functional unit and alternatives

The functional unit in this study is defined as ‘power to wheels for one kilometre driving of a midsize car’. Neither the production nor the disposal of the car is taken into account but only its energy requirements in driving, similar to the assumptions by Luo et al., 2009b. For the usage of ethanol as transport fuel, two applications were reported (Fu et al., 2003). The first one is that for standard gasoline engine, typically 5 to 20 percent ethanol mixed in gasoline can be used directly. The other is blending high percentage (85% to 100%) ethanol into gasoline. For the latter application, specific flexible fuelled vehicles (FFVs) with internal combustion engine designed to run on more than one fuel are required. With the progress of vehicle design and transport fuel using bioethanol in the future, E10 as well as E85 are taken into account in this study. Pure ethanol is also considered, but only as a reference; and conventional transport fuel gasoline is included for comparative purpose. Therefore, the alternative systems in this study consist of E100, E85, E10 and gasoline.

4.2.2 System boundaries

Figure 4.1 shows the product system including all relevant processes, from agriculture of switchgrass, throughout the production of pure ethanol, E85, and E10, to final vehicle operations, and all the transport sections.

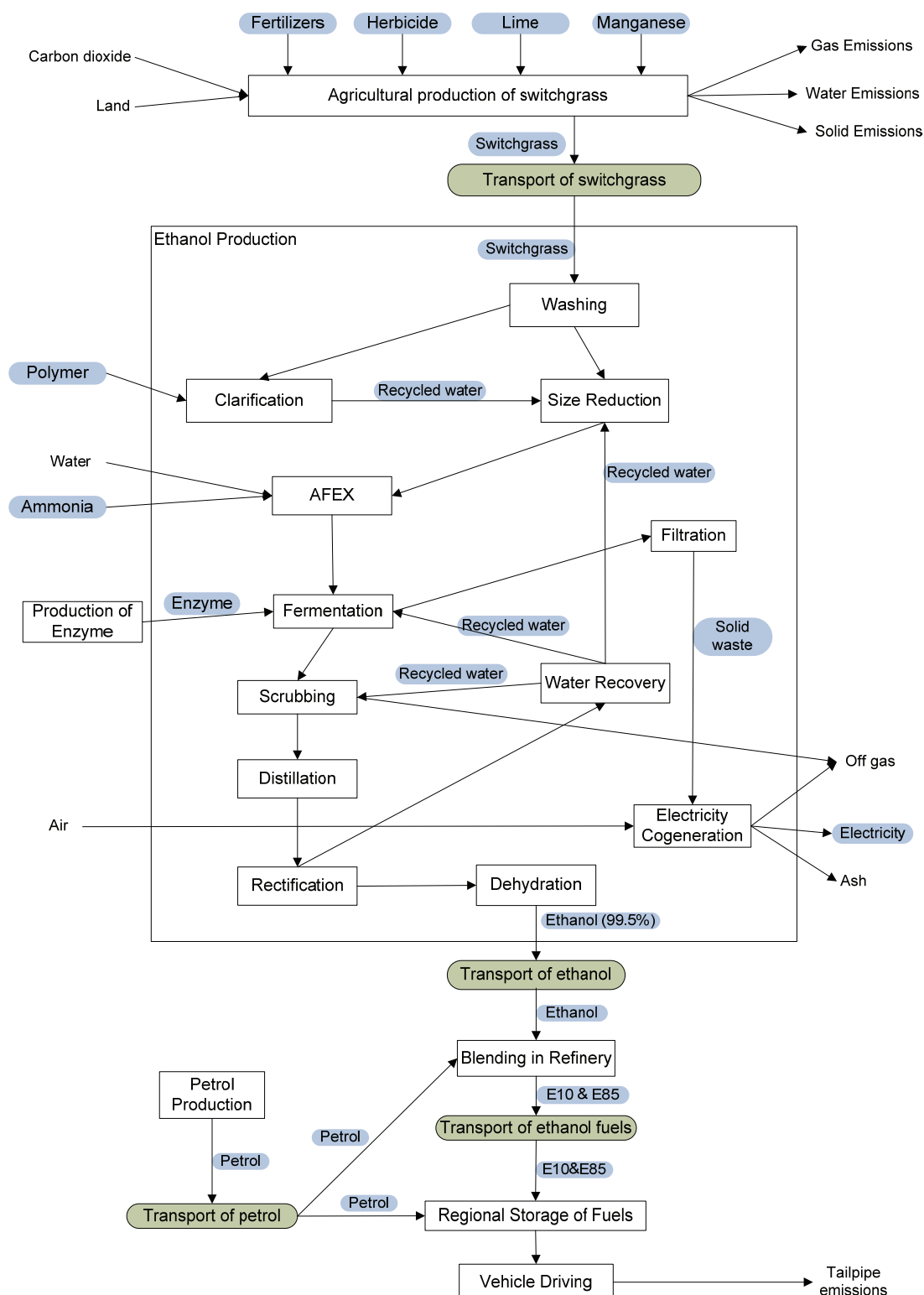


Figure 4.1 The life cycle of ethanol from switchgrass

The technical data of the ethanol production plant can be found in the report by Guerra Miguez et al. (2009). The switchgrass agriculture process was built on the base case scenario of switchgrass from the report by Bullard and Metcalfe (2001). However, to provide a more realistic approach in the management of switchgrass agriculture, one modification was made – in the base case, the fertilizer input is applied only in the preparation year, but from the literature it appears that application also in the other harvesting years is more realistic. Annually, 100 kg per hectare of nitrogen fertilizers are assumed to be applied. The inputs, outputs and emissions associated to the agricultural activities are summarized in Table 4.1 and 4.2, respectively.

Table 4.1 Inputs and outputs in the switchgrass agriculture over 20 years

Soil preparation (year 1)	
Seed	10 kg/ha
Fertilizer – ammonium nitrate	100 kg/ha
Fertilizer – P_2O_5	40 kg/ha
Fertilizer – K_2O	80 kg/ha
Lime	3000 kg/ha
Herbicide – advance (bromoxynil/ioxynil/fluroxypyr)	2 kg/ha
Herbicide – triflex-tra (MCPA + MCPB)	7.7 kg/ha
Herbicide – isoproturon	2 kg/ha
Yield	0 t/ha
Production (year 2-20)	
Fertilizer – ammonium nitrate	100 kg/ha
Manganese ($MnSO_4$)	4 kg/ha
Herbicide – advance (bromoxynil/ioxynil/fluroxypyr)	2 kg/ha
Herbicide – triflex-tra (MCPA + MCPB)	7.7 kg/ha
Herbicide – isoproturon	2 kg/ha
Yield (25% moisture)	year 2 and 3: 12 t/ha year 4-20: 16 t/ha
Total yield over 20 years (25% moisture)	296,000 t/ha
CO_2 from air	1.54 kg/kg DM ^a
Energy	17 MJ/kg DM ^b

^a C-content is 42% w/w

^b The energy content corresponds to the higher heating value (HHV) of the dry biomass

Table 4.2 Environmental emissions in the switchgrass agriculture over 20 years

	Soil preparation (year 1)	Production (year 2-20)	Total 20 years
Emissions to air (kg/ha)			
Nitrogen oxides	1.02	1.02	20.5
Dinitrogen monoxide	4.88	4.88	97.5
Ammonia	2.43	2.43	48.6
Emissions to water (kg/ha)			
Nitrate	48.00	48.00	960.00
P to ground water	0.06	0.06	1.20
P to surface water	0.28	0.25	5.03
P from erosion to surface water	0.71	0.71	14.20
Cadmium (Cd)	3.90×10^{-5}	1.72×10^{-6}	7.17×10^{-5}
Copper (Cu)	3.21×10^{-3}	1.85×10^{-3}	3.84×10^{-2}
Zinc (Zn)	1.52×10^{-2}	5.53×10^{-3}	0.12
Lead (Pb)	2.60×10^{-4}	2.14×10^{-5}	6.67×10^{-4}
Chromium (Cr)	2.11×10^{-2}	6.04×10^{-3}	0.14
Emissions to soil (kg/ha)			
Cadmium (Cd)	1.79×10^{-5}	7.93×10^{-7}	3.29×10^{-5}
Copper (Cu)	1.21×10^{-3}	7.01×10^{-4}	1.45×10^{-2}
Zinc (Zn)	2.22×10^{-3}	8.05×10^{-4}	1.75×10^{-2}
Lead (Pb)	7.83×10^{-4}	6.52×10^{-5}	2.02×10^{-3}
Nickel (Ni)	1.48×10^{-3}	7.69×10^{-4}	1.61×10^{-2}
Chromium (Cd)	1.78×10^{-3}	5.09×10^{-4}	1.14×10^{-2}

The conversion of switchgrass to ethanol consists of four steps – feedstock pretreatment, enzyme hydrolysis, fermentation and production recovery. An AFEX (Ammonia Fibre Explosion) operation was chosen and optimized to recover 99% ammonia that is used for pretreatment; SSCF (Simultaneous Saccharification and Co-Fermentation) operation was used to produce ethanol. The lignin residues and different wastes produced during the process are used in a cogeneration unit in order to supply all the steam and electricity required in the plant. The surplus electricity is the co-product from the final step and can be sold to the local grid (Guerra Miguez et al., 2009). The end-use stage of ethanol fuel life cycle is fuel combustion via vehicle operation. In this unit process, a midsize car was chose and only the tailpipe emissions were taken into account to serve the purpose of this study – ethanol as transport fuel.

The transport of materials and products is by road using lorry with various loading capacities. The distances between the switchgrass farm and the ethanol production plant, as well as the one between the ethanol plant and the refinery were both assumed to be 20 kilometres. The transport distance of the regional storage from the refinery follows the data from the Ecoinvent database (<http://www.ecoinvent.org/>), which is 33.7 km.

4.2.3 Life cycle inventory: data sources and software

The data for the switchgrass agriculture are mainly from the report by Bullard and Metcalfe (2001). Switchgrass is assumed to be planted on the prepared land for 20 years, after which the land needs to be prepared again. The emissions during cultivation were calculated by using the input data from the base case scenario, via the methods described in the Ecoinvent report (Nemecek and Kägi, 2007). The data for the ethanol production process were taken from the Guerra Miguez et al. (2009), including the material and energy inputs and outputs, as well as the use of equipments. The technical data used for the production of the cellulase enzyme were obtained from Wooley et al. (1999). The tailpipe emissions in practice are very complex, due to the different vehicle types, road situations and driving behaviours etc. The data for tailpipe emissions of vehicle driving used in this study are based on a standard test procedure, covering a mix of driving on urban roads and on motorways, and some assumptions and calculations (Kelly et al., 1996; Luo et al., 2009a; Reading et al., 2002).

The background data were from the Ecoinvent database version 1.3. The software tool CMLCA (Chain Management Life Cycle Assessment) developed by Heijungs (2009) was used for inventory analysis and impact assessment.

4.2.4 Life cycle inventory: allocation

When bioethanol is produced, electricity is generated as a co-product. For multi-functional systems in LCA, allocating the material and energy inputs and environmental emissions between the main product and co-products/by-products is a vital issue. There is a stepwise allocation procedure in ISO 14044 (2006). Since the system has multiple outputs, we have to find a way to account for the co-product as well. This can be done by systems expansion as applied by Luo et al. (2009a). It can also be done by physical or economic allocation. In line with EU Directive (Directive 2009/28/EC, 2009), we use co-product allocation based on the energy content of the two products – ethanol and electricity. However, in order to understand the influence of different allocation methods in LCA study, a sensitivity analysis using economic allocation based on market prices was also conducted, as allocation based on mass is not applicable in this case.

4.2.5 Life cycle impact assessment

The following environmental impact categories have been assessed:

- Abiotic resource depletion potential (ADP)
- Global warming potential (GWP)
- Ozone layer depletion potential (ODP)
- Photochemical oxidation potential (POCP)
- Human and eco-toxicity potential (HTP and ETP)
- Acidification potential (AP)
- Eutrophication potential (EP)

4.2.6 Interpretation

The choices and assumptions made during the analysis in this study were evaluated. A contribution analysis is performed to understand the contributions of specific pollutants and production processes to the total impact scores, to find the reasons of the changes of environmental impacts from gasoline fuelled to ethanol fuelled vehicle driving. Furthermore, various sensitivity analyses, determining the influence of the variations in assumptions, method choices and process data on the results, have been applied (Guinée et al., 2002; ISO 14040, 2006).

4.3 Results and Discussion

4.3.1 LCA results

The comparative results from the LCA of ethanol fuel and gasoline are shown in Figures 4.2 and 4.3.

GHG mitigation is one of the most important issues globally. As can be seen in Figure 4.2, switchgrass-derived ethanol as transport fuel produces less GHG emissions than conventional gasoline, and driving with E85 reduces substantially more GHG emissions than with E10. The primary (and obvious) reason of this significant decrease is the large amount of CO₂ uptake in switchgrass agriculture. When driving with E10, about 5% reduction of GWP is achieved compared to gasoline. A significant reduction of GHG emissions (65%) is achieved when driving with E85. In this result, the difference in fuel efficiency is included – for driving 1 km with E85 0.099 kg of fuel is required, which is much larger than the 0.0665kg of gasoline. With regard to abiotic resource depletion, replacing gasoline by fuel ethanol reduces the use of crude oil, which is the primary source for gasoline production. Emissions from crude oil production are avoided, causing a significant decrease in impacts in terms of ODP for ethanol fuelled driving.

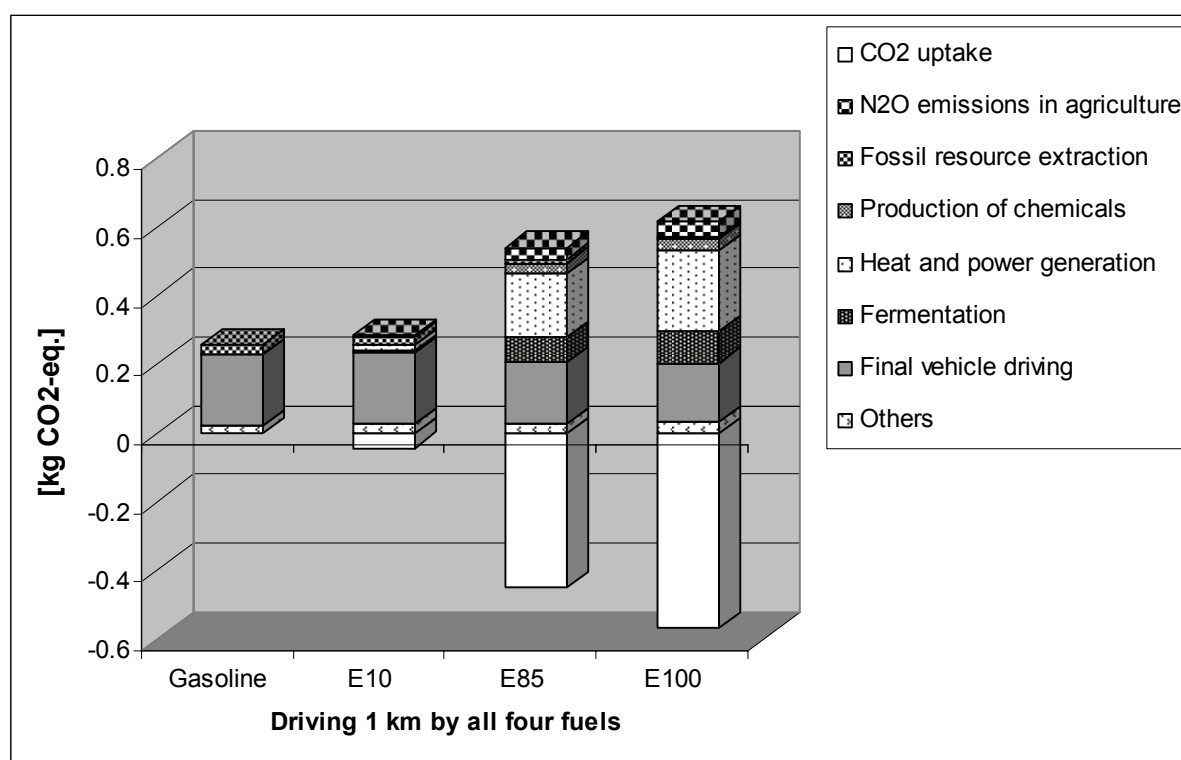


Figure 4.2 Contributions of the main processes to GWP using all four fuels

Figure 4.3 indicates that except for GWP, ADP and ODP, driving with ethanol fuel from switchgrass does not offer advantages over gasoline regarding other environmental impacts. On the contrary, the emissions in these impact categories are substantially higher. The higher level of photochemical oxidation caused by using ethanol fuels is mainly due to the acetaldehyde emission during bioethanol fermentation, which contributes 77% to POCP of vehicle driving with E85. The higher eutrophication score results from switchgrass agriculture, especially the nitrate leaching to ground water and nitrogen oxide (NO_x) to air from N-fertilizer application. Agriculture is also the main contributor to human and eco-toxicity, due to the use of agro-chemicals.

The result for acidification deserves special attention. Driving 1 km with E10 leads to the lowest impact in all four fuel alternatives. This can be explained as follows: AP is largely contributed by the upstream emissions of ammonia from agriculture and sulphur dioxide (SO_2) from oil refinery, and the downstream emissions of nitrogen oxides (NO_x) from vehicle driving. The impact of ammonia from agriculture is more significant than SO_2 from oil refinery. Thus when shifting from gasoline to ethanol fuel for vehicle driving, the resulting AP level should increase. However, since in E10 only a small amount of ethanol is blended into gasoline, the difference in their upstream emissions is insignificant. The downstream NO_x emissions are rather higher for gasoline on a per

litre basis, but for the ethanol blends also show an increase proportional to the amount of fuel used to drive. The amount of fuel needed to drive 1 km is significantly higher in E85 and E100 than it is in E10. All these different mechanisms result in the lowest score (optimum fuel composition) for E10.

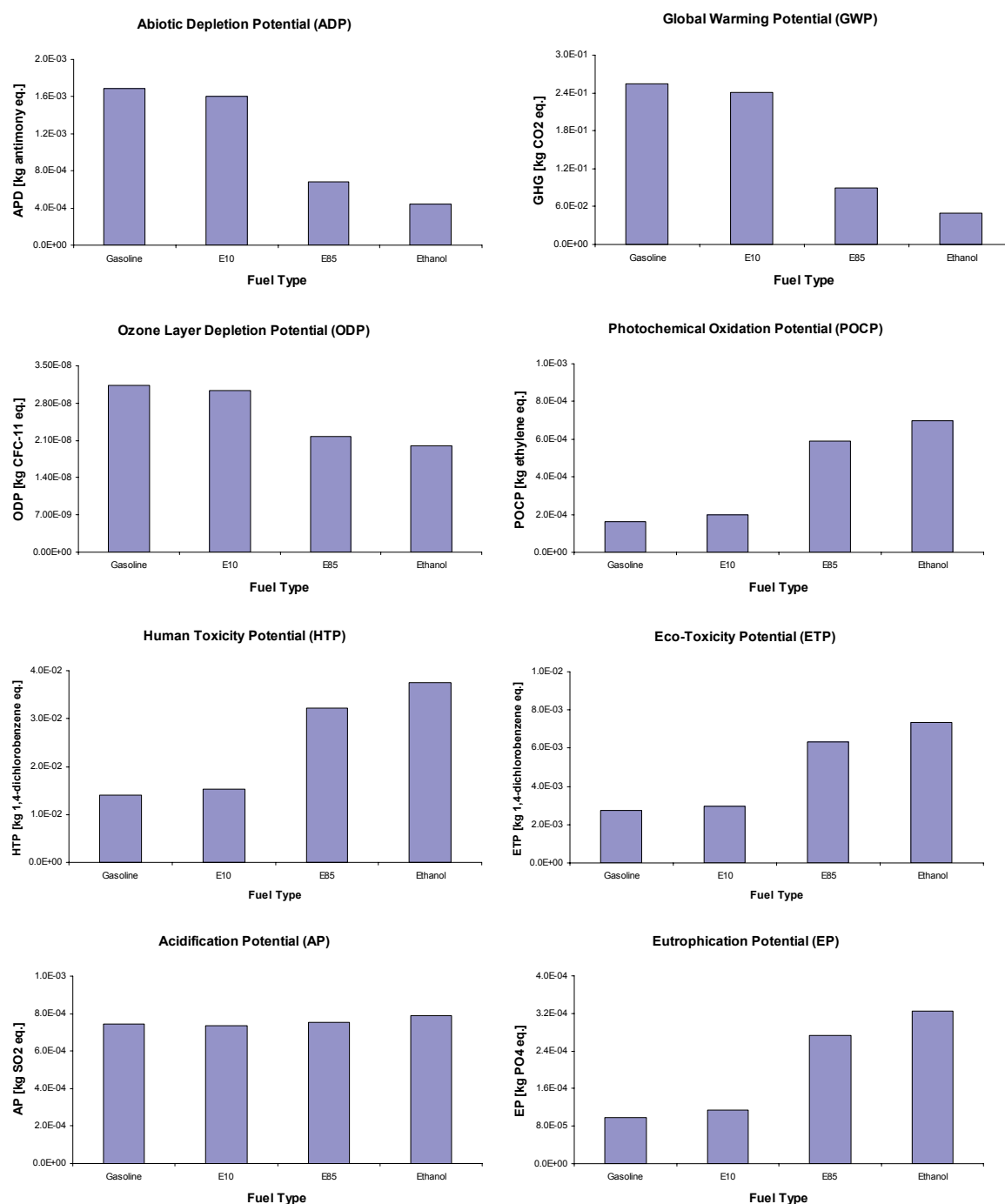


Figure 4.3 Overall comparison results of the environmental impact of gasoline, E10, E85 and E100

4.3.2 Sensitivity analysis

1) Allocation method

The multi-functionality in this study occurs in the ethanol production process, in which electricity is co-produced. The partitioning ratio between ethanol and electricity is calculated to be 0.855/0.145 when applying allocation based on the energy content of the products. As stated in ISO 14040-44 series (2006), whenever more than one allocation method can be applied, a sensitivity analysis is required. In this case economic allocation can also be applied; a sensitivity analysis was conducted for comparative purposes. The average price of ethanol and electricity are taken as 0.357 €/kg and 0.01 €/kWh, respectively (Lynd et al., 2005), thus the allocation ratio between ethanol and electricity is 0.742/0.258. The resulting GWP for driving 1 km with E10 and E85 is given in Table 4.3.

Table 4.3 Comparison results of E10 and E85 in GWP with different allocation methods

	Partitioning factor		GWP of 1 km driving (kg CO ₂ eq.)	
	Ethanol	Electricity	E10	E85
Energy allocation	0.855	0.145	0.241	0.090
Economic allocation	0.742	0.258	0.240	0.075

The results indicate that the choice of allocation methods has influence on the outcomes. GWP is used here to give an example of this effect. As allocation occurs in the ethanol production process, the influence of allocation method on GWP on driving with E85 is larger than E10. When driving 1 km with E85, 17% reduction of GHG emission is achieved by switching from energy content to economic values based allocation. The analogous results are also observed in other impact categories.

2) Soil preparation

As switchgrass is a newly developed feedstock for bioethanol production, for the base scenario in this study, a key step in switchgrass agriculture is the soil preparation before planting and harvesting for large scale production. In this base scenario the first year is used only for land preparation; the switchgrass yield for the second and third year is assumed to be 12 t/ha, and 16 t/a in the consequent years. For large scale production of conventional crops such as corn and sugar cane, such land preparations are usually not taken into account. In order to observe the effect of soil preparation on the outcomes, an alternative scenario in which soil preparation is excluded was assumed for sensitivity analysis. In this alternative scenario, 100 kg/ha N-fertilizer is applied as one important input every year, and herbicides for weeding and manganese for soil buffer are applied

annually. The switchgrass yield is assumed to be 16 t/ha (with 25% moisture) per year. The soil preparation year without harvesting of switchgrass is outside the system boundary. The two scenarios including and excluding soil preparation are shown graphically in Figure 4.4, and the comparative results are given in Table 4.4.

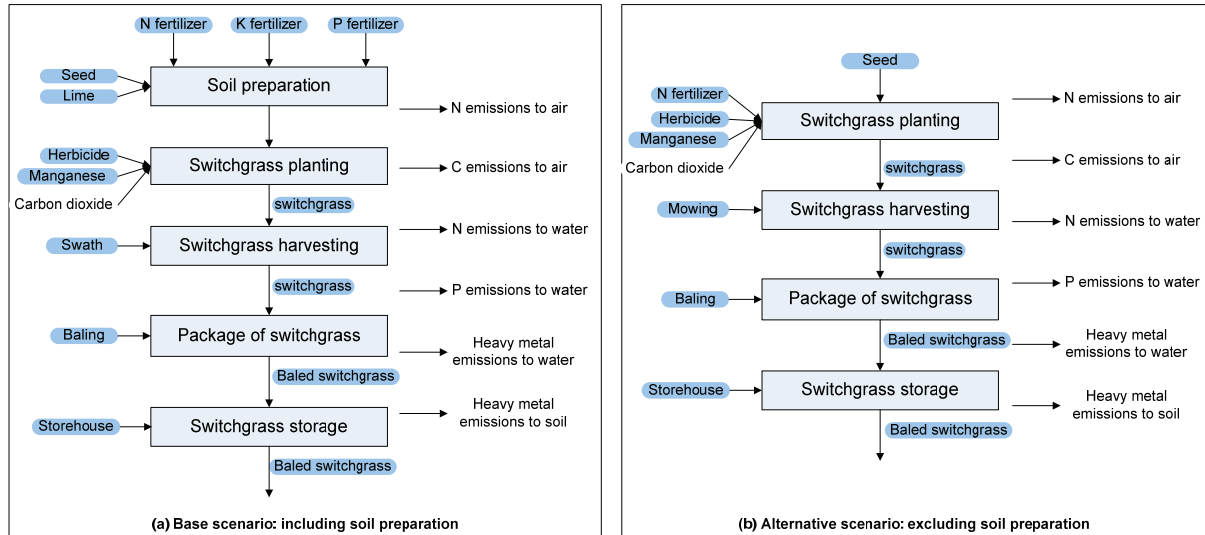


Figure 4.4 The differences between the two scenarios: (a) including soil preparation (b) excluding soil preparation

Table 4.4 Comparison results of environmental impacts for 1 km driving by E100 in the two scenarios

Impact category	Unit	Base scenario	Alternative scenario	Range (%)
ADP	kg antimony eq.	6.79×10^{-4}	6.52×10^{-4}	-3.98
GWP	kg CO ₂ eq.	8.96×10^{-2}	8.14×10^{-2}	-9.15
OPD	kg CFC-11 eq.	2.18×10^{-8}	2.15×10^{-8}	-1.37
POCP	kg ethylene eq.	5.91×10^{-4}	5.86×10^{-4}	-0.85
AP	kg SO ₂ eq.	7.52×10^{-4}	7.03×10^{-4}	-6.52
EP	kg PO ₄ eq.	2.69×10^{-4}	2.51×10^{-4}	-6.69
HTP	kg 1,4-DCB eq.	3.22×10^{-2}	2.89×10^{-2}	-10.3
ETP	kg 1,4-DCB eq.	6.33×10^{-3}	5.75×10^{-3}	-9.12

The results indicate that excluding soil preparation leads to better results from the perspective of GHG emissions reduction. The first reason is that some farming activities are only performed for soil preparation, like hoeing and ploughing. These farming activities, which cause CO₂ and N₂O emissions, are excluded in the alternative scenario. The second one is that the average switchgrass yield is higher in the alternative

scenario than the one in the base case, meaning that less GHG are emitted per kg of switchgrass harvested. The resulting GHG emission of 1 km driving with E100 is 9% lower than the one in the base case. However, the change of driving with E10 is rather small, since only 10% (v/v) bioethanol is mixed with gasoline. Similar reductions can be observed in the other impact categories. Besides GWP, other two large reductions appear in HTP and ETP, due to the reduction of heavy metal emissions from fertilizers and lime application in the switchgrass agriculture. The main reason for the reduction in acidification potential is that NO_x emissions from agriculture in alternative scenario are much less than the ones in base scenario. The primary emissions in eutrophication are the phosphate and phosphorus emissions, and in the alternative scenario, no P fertilizers are applied in the production years. The changes of ODP and POCP are very small as the main contributor to these two impacts is the ethanol production process.

3) Transport distance

The transport distances assumed are important for the outcomes, as lorries fuelled with diesel are the major transport vehicles, which lead to significant environmental impact. Since the system under study has not been established in practice, the transport distances both from the switchgrass farm to the ethanol production plant and from the ethanol plant to the oil refinery are assumed to be 20 km. The sensitivity of transport distance was analyzed to observe the influence of the transport section in this study. To compare with 20 km, 40 km and 80 km transport distances were assumed. The comparative results are shown in Table 4.5.

Table 4.5 Comparison results of environmental impacts and increases of E85 with different transport distances

Impact category	Unit	20 km	40 km		80 km	
ADP	kg antimony eq.	6.79×10^{-4}	6.97×10^{-4}	+2.65%	7.31×10^{-4}	+7.66%
GWP	kg CO ₂ eq.	8.96×10^{-2}	9.16×10^{-2}	+2.23%	9.57×10^{-2}	+6.81%
OPD	kg CFC-11 eq.	2.18×10^{-8}	2.22×10^{-8}	+1.83%	2.28×10^{-8}	+4.59%
POCP	kg ethylene eq.	5.91×10^{-4}	5.96×10^{-4}	+0.93%	6.03×10^{-4}	+2.03%
AP	kg SO ₂ eq.	7.52×10^{-4}	7.61×10^{-4}	+1.23%	7.86×10^{-4}	+4.52%
EP	kg PO ₄ eq.	2.69×10^{-4}	2.72×10^{-4}	+0.94%	2.75×10^{-4}	+2.23%
HTP	kg 1,4-DCB eq.	3.22×10^{-2}	3.24×10^{-2}	+0.68%	3.29×10^{-2}	+2.17%
ETP	kg 1,4-DCB eq.	6.33×10^{-3}	6.42×10^{-3}	+1.46%	6.58×10^{-3}	+3.93%

It can be seen that the increase of transport distance lead to worse environmental performance in all impact categories, especially with regard to the level of ADP, GWP and AP. This is because increasing transport distances leads to higher demand of diesel used in the lorries, which contributes largely to ADP. One key consequence of the increasing use of diesel is the CO₂ emissions, resulting in the increase of GWP. All these changes were obtained for E85 fuelled driving. For E10 fuelled driving, changes occurred in all impact categories are only up to 1%.

4.4 Conclusions and Recommendations

In this study, the LCA methodology was used to evaluate ethanol from switchgrass as a transport fuel on its environmental performance. The assessment results indicate that driving with switchgrass-ethanol fuel as a replacement of gasoline contributes significantly to the reduction of GHG emissions, mainly due to the CO₂ uptake from atmosphere in the switchgrass agriculture. Driving one kilometre using E85 reduces GHG emissions by 65% compared to driving with gasoline. The reduction of dependency on fossil fuels in ethanol fuelled driving leads to better performance on abiotic resource depletion and ozone layer depletion. However, switchgrass ethanol fuel performs worse with regard to other impacts, including photochemical oxidation, eutrophication, human and eco-toxicity. For acidification, driving with E10 gives the lowest impact. Sensitivity analyses show that the application of different allocation methods affects the LCA outcomes; the exclusion of soil preparation lowers the environmental impact of ethanol fuels; and increasing transport distance leads to worse environmental performance.

The results from this LCA study on switchgrass-ethanol as transport fuel are comparable with other LCA studies on the second-generation bioethanol. There are potentially significant benefits offered by using ethanol derived from lignocellulosic feedstocks, especially in term of GHG emissions (Fu et al., 2003; Kadam, 2002; Luo et al., 2009a; Sheehan et al., 2004; Spatari et al., 2005; Wu et al., 2006b). However, these benefits are offset by worse impacts in other categories, such as eutrophication, photochemical oxidation and toxicity aspects. In order to reduce these environmental impacts, more advanced technologies with optimization of energy use and emissions in both the switchgrass agriculture and the ethanol refinery still need to be developed.

The overall life cycle environmental performance of using bioethanol as a transport fuel requires further research, in which a number of critical impacts in biofuel LCA studies shall be considered that are presently out of scope, such as water and land use. Land use change (direct: LUC, indirect: ILUC) can be accompanied by sometimes large changes

in GHG emissions from soils, as Fargione et al. argue (2008). Searchinger et al. (2008) show that including GHG emissions from LUC and ILUC may change a net GHG benefit into a net cost. We have not attempted to include these emissions in this study. To do this, methodology development in LCA is of crucial importance.

Chapter 5

An Energy Analysis of Ethanol from Cellulosic Feedstock – Corn Stover

* This chapter is published in Renewable and Sustainable Energy Reviews 2009; 13(8): 2003-2011. Co-authors: Ester van der Voet and Gjalt Huppes

Abstract

The shift from fossil resources to renewables for energy and materials production has been the driving force for research on energy analysis and environmental impact assessment of bio-based production. This study presents a detailed energy analysis of corn stover-based ethanol production using advanced cellulosic technologies. The method used differs from that in LCA and from major studies on the subject as published in “Science” in two respects. First, it accounts for all the co-products together so mainly avoids the allocation problems which plague all LCA studies explicitly and other studies implicitly. Second, the system boundaries only involve the content of the energy products used in the system but not the production processes of these energy products, like oil refining and electricity generation. We normalized the six literature studies to this unified method. The resulting values of the total energy product use in both the agricultural production and the biomass conversion to ethanol are lower than these literature values. LCA type of values including energy conversion would systematically be higher, in our case study around 45%. The net energy value of cellulosic ethanol production is substantially higher than the ones of the corn-based technologies, and it is slightly higher than the ones from incineration and gasification for electricity production. The detailed analysis of energy inputs indicates opportunities to optimize the system. This form of energy analysis helps establish models for the analysis of more complex systems such as biorefineries.

5.1 Introduction

Facing the threat of oil depletion and climate change, a shift from fossil resources to renewables is ongoing to secure long-term supplies, with biofuel as one of the options. Several studies on life cycle assessment (LCA) of bioenergy have been conducted, focusing particularly on two main impacts – reduction of fossil resource extraction and greenhouse gas (GHG) emissions. However, our previous studies show that LCA as a tool supporting decision-making has its limitations when multi-product systems are concerned, requiring some form of allocation. With the upcoming biorefineries, the product systems involve variable multiple inputs and outputs. Hence LCA in general cannot be applied. Therefore, an analysis methodology is needed in order to optimize integrated biorefineries with regard to energy conservation, environmental impact and profitability.

Since both the environmental impact and production costs are closely related to the amount of fossil fuels used in the life cycle of a product, energy analysis can give a key insight at relatively low cost. Several studies have been conducted on the energy analysis through the life cycle of corn (*Zea mays*, or maize)-based ethanol (de Oliveira et al., 2005; Groboski, 2002; Patzek, 2004; Pimentel and Patzek, 2005; Shapouri and McAloon, 2002; Wang, 2001). Two studies stand out because they report negative net energy values (Patzek, 2004; Pimentel and Patzek, 2005), indicating that more fossil energy inputs are required in the production processes than the energy contained in the ethanol produced. The rest show positive net energy values to a varying extent. To permit a direct meaningful comparison of the data and assumptions across these six studies, Farrell et al. (2006) aligned methods and removed the differences in the underlying data. They indicate that calculations of net energy are highly sensitive to assumptions about both system boundaries and key parameter values and, as to content, conclude that large-scale use of fuel ethanol certainly requires more sustainable practices in agriculture and advanced technologies, shifting from corn to cellulosic ethanol production.

The cellulosic ethanol production refers to the processes converting cellulosic feedstocks (i.e. corn stover, wheat and rice straw, sugarcane bagasse, wood or grass) to ethanol. A recent paper on a comparative energy assessment of corn- and stover-based ethanol concludes that stover is a better feedstock than corn from a perspective of energy conservation (Lavigne and Powers, 2007). In our study corn stover was chosen as the feedstock for ethanol production. Aiming at giving an indication on the efficiency of the stover-ethanol life cycle and how to optimize the system in terms of energy production, this study focuses on an energy analysis providing an overview of the total use of energy products, in all (sub-) processes or sections of the stover-ethanol life cycle.

The results are used to compare different systems and to optimize the corn agriculture and the fuel ethanol production.

5.2 Methodology

5.2.1 System boundaries and allocation

All relevant processes in the biomass production (corn agriculture producing corn and stover) and the conversion to ethanol are within the system boundaries of the ethanol life cycle, as shown in Figures 5.1 and 5.2. Capital goods production and wastes management are also included. The system under study is not ‘cradle-to-gate’ as usual in LCA, but ‘energy products-to-gate’. Primary energy conversion processes were left out of account, though an overall comparison was made to show the quantitative effect of this exclusion.

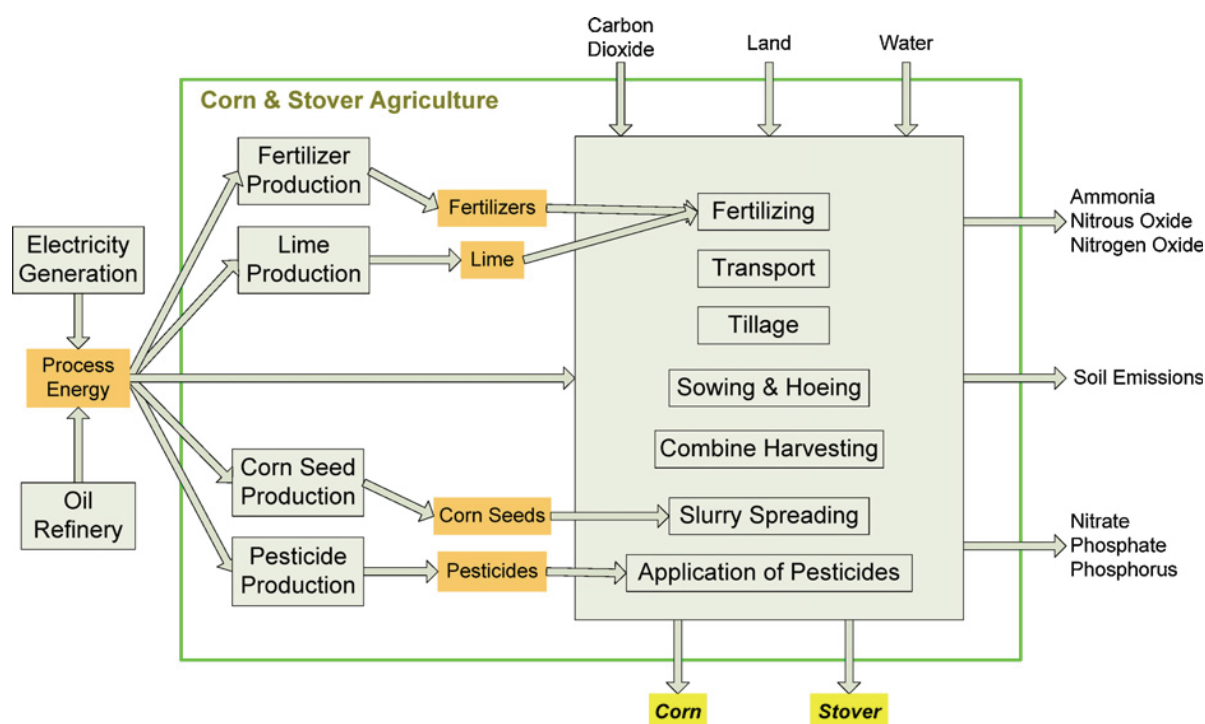


Figure 5.1 Corn and stover agriculture

There is no allocation involved in the foreground processes, as all co-products are included, making the outcomes independent of arbitrary allocation choices which otherwise would have to be made. The systems compared involve differing amounts of the four main products – corn, stover, electricity and ethanol. Implicitly, allocation is involved in the data used for the background processes, however, with a limited quantitative effect on outcomes.

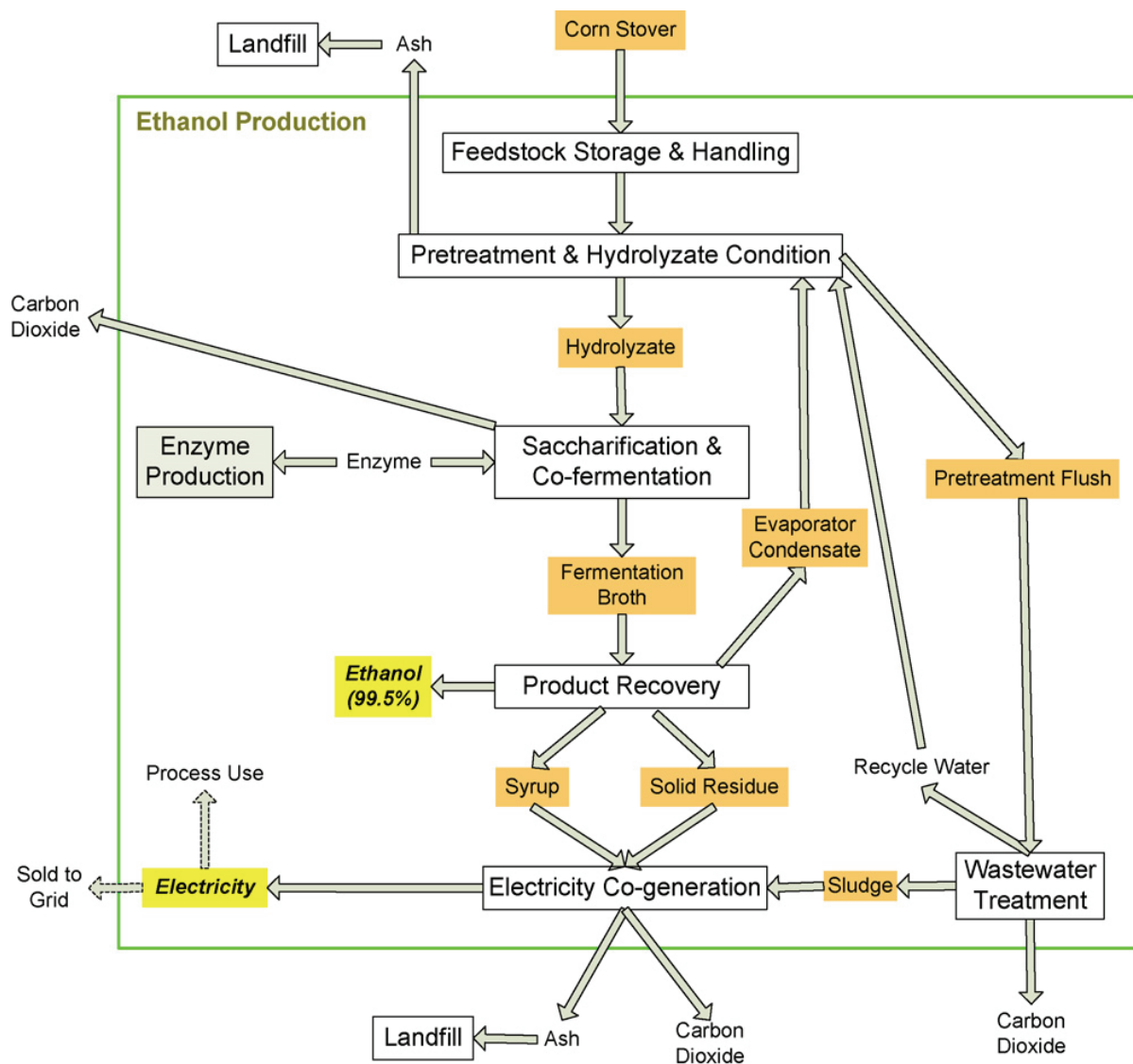


Figure 5.2 Bioethanol production from stover

In order to make comparisons, we analyzed these co-products from an energy content point of view. Other measures might be used, like economic value, adding broadness but not requiring other types of modelling. Adding specific applications of corn, stover, ethanol and electricity will surely lead to different outcomes of such more application focused studies. We left these out of account here, but they could easily be included. For the sake of simplicity we focus only on energy; environmental effects have been left out of account as well. In the modelling framework as applied, such effects can be specified in the usual ways as have been developed in the realm of LCA.

5.2.2 Data sources

Data used in this study were obtained from different sources. U.S. Life-Cycle Inventory Database (<http://www.nrel.gov/lci/>) is the main source for the agriculture data, and the data from the Swiss Centre of Life Cycle Inventories (<http://www.ecoinvent.org/>) are used for adjustment when necessary. Data on the transport of stover and the production of ethanol and electricity are from NREL report (Aden et al., 2002).

5.2.3 Energy analysis

1) Comparison with Literature Values

In order to compare the results with the literature values, the energy use in the corn agriculture was calculated on a ‘per hectare’ basis for 14 cost categories. The crop yield taken in this study is 8,687 kg corn/ha (Lal, 2005), which means the annual yield of the harvested stover is 5,112 kg/ha (Sheehan et al., 2002). In the other studies these data are slightly different and mostly stover is not specified. The total energy input in ethanol production was calculated based on the production of one litre of ethanol. Although the ethanol is produced from stover instead of corn, the results can provide an indication on the scale of values, and more importantly, how efficient cellulosic technologies are as compared to corn-based ethanol. Furthermore, net energy values without and with co-product credits were calculated and compared with the literature values. In the case of ethanol production from stover, electricity is the only co-product from the biorefinery.

2) Calculations of energy inputs

In order to find out the energy intensive sub-processes and improve process efficiency, a detailed analysis was performed. The calculations of energy inputs are based on the production of 1 kg of ethanol, which requires 3.97 kg of stover, while 6.62 kg of corn is co-produced in the agriculture. The agriculture process was divided into two sections – production of the agriculture inputs and the agricultural production. When producing 1 kg of ethanol, 1.23 kWh of electricity is co-generated. All the sub-processes are indicated in Figures 5.1 and 5.2.

5.3 Results and Discussion

5.3.1 Results of energy use

The results of energy use in corn agriculture and the total energy use in ethanol production compared to the literature values are shown in Tables 5.1 and 5.2, respectively.

Table 5.1 Comparison of the energy use in the corn agriculture with the literatures

	This Study	Patzek	Pimentel	Shapouri	Graboski	de Oliviera	Wang
Corn production (kg/ha)	8687	7310	8655	8746	8799	7850	7846
Stover harvest (kg/ha)	5212	-	-	-	-	-	-
Energy Use (MJ/ha · year)							
Fertilizer production	7988	9160	12431	9804	8077	8681	10305
Lime production	1067	583	1318	-	369	445	-
Pesticide production	197	953	3766	1060	777	1025	970
Seed production	158 ^a	1968	2176	228	215	2048	-
Transport	398	400	707	73	738	-	168
Gasoline	-	1005	1695	1277	1290	960	1501
Diesel	3071 ^b	2957	4197	2719	3205	2907	4310
LPG	-	1205	-	765	1357	1512	1072
Natural gas	116 ^c	779	-	670	597	504	1626
Electricity	382	688	143	820	1571	657	225
Irrigation	-	-	1339	49	-	-	-
Labour	-	1390	1934	574	628	-	-
Farm machinery	3249 ^d	6050	4259	-	320	-	-
Input packaging	-	-	-	-	74	-	-
Total	16626	27138	33954	18041	19220	18738	20177

^a This value was taken from the Ecoinvent database, as it is not provided in the U.S. database.

^b In the U.S. database, gasoline and LPG are used together with Diesel for the operation of agricultural machinery. However, the Ecoinvent database was used to calculate the energy inputs in all the agricultural operation, where only diesel is used as fuel.

^c Also calculated from the Ecoinvent database.

^d Calculated by this study, as it is not provided in the U.S. database.

Table 5.2 Comparison of the total energy use in the ethanol production

Energy Use (MJ/L)	This Study	Patzek	Pimentel	Shapouri	Graboski	de Oliviera	Wang
Total	0.5	17.0	17.0	15.2	16.6	14.1	12.5

It can be seen from Table 5.1 that the total energy use in the agriculture is in the same scale as the values in the literature, though it lies on the low side. The major differences appear in the pesticide production, gasoline and LPG consumption. Since the U.S. database only provides the total amount of the pesticides used without specifying the type of the herbicides and insecticides and the energy needed to produce the pesticides, the Ecoinvent database was used to estimate the energy engaged in the production, which can be somewhat optimistic. In the U.S., it is common to use gasoline and LPG together with diesel for the operation of agricultural machineries. However, in the Ecoinvent database the fuel for the agriculture operation is mainly diesel, and the total fuel consumption was lower than the data from the U.S. database. The major reason why the U.S. life-cycle inventory database was used together with the Ecoinvent database is to obtain a summary of energy inputs in all the sub-processes in the agriculture, as shown in Section 5.3.2.

For the total energy use in the stover-based ethanol production, it takes only 0.5 MJ of process energy to produce 1 litre of ethanol. Although some sub-processes such as pretreatment of cellulosic feedstock are highly energy intensive, the large amount of steam required is co-generated from the combustion of lignin residues and wastes, no external steam and electricity is needed. This results in much lower value of energy use than the literature values for the ethanol from corn. Due to the incompleteness of the data in the sub-processes of the ethanol production provided by the literature, only the values of the total energy use can be compared. Nevertheless, this gives an indication on how efficient the cellulosic process is. The net energy summaries compared to the literature values is shown in Tables 5.3 and 5.4.

Table 5.3 Net energy summary excluding co-products, no allocation

Energy Use (MJ/L)	This Study	Patzek	Pimentel	Shapouri	Graboski	de Oliviera	Wang
Agriculture	10.0	9.9	10.0	5.3	5.6	6.3	6.6
Biorefinery	0.5	17.0	17.0	15.2	16.6	14.1	12.5
Total Input	10.5	26.9	27.0	20.5	22.2	20.4	19.1
Ethanol*	21.2	21.2	21.2	21.2	21.2	21.2	21.2
Total Output	21.2	21.2	21.2	21.2	21.2	21.2	21.2
NEV	10.7	-5.7	-5.8	0.7	-1.0	0.8	2.1

* Normalized energy value for ethanol based on lower heating value (LHV).

Table 5.4 Net energy summary including co-products, no allocation

Energy Use (MJ/L)	This Study	Patzek	Pimentel	Shapouri	Graboski	de Oliviera	Wang
Agriculture	10.0	9.9	10.0	5.3	5.6	6.3	6.6
Biorefinery	0.5	17.0	17.0	15.2	16.6	14.1	12.5
Total Input	10.5	26.9	27.0	20.5	22.2	20.4	19.1
Ethanol ^a	21.2	21.2	21.2	21.2	21.2	21.2	21.2
Co-products in agriculture ^b	85.2	25.9	25.9	24.0	24.6	24.6	24.6
Co-products in biorefinery ^c	0.2	4.1	1.9	7.3	4.1	4.1	4.0
Total Output	106.6	51.2	49.0	52.5	49.9	49.9	49.8
NEV	96.1	24.3	22.0	32.0	27.7	29.5	30.7

^a Normalized energy value for ethanol based on lower heating value (LHV).

^b In this study it refers to the corn as a co-product in the agriculture; in all the other six studies it refers to the harvested stover (60%, dry mass basis) as a co-product, and the values were estimated in this study.

^c In this study it refers to electricity; in the literature studies it refers to a range of products from corn milling, such as dried distiller grains, corn gluten feed, corn oil, etc.

The results show that when the co-products are not taken into account, three literature studies results in a negative net energy value. The positive value obtained in our study is the highest due to the low process energy requirement in the ethanol refinery. When the co-products are taken into account, all studies give positive net energy values. This indicates that outcomes of net energy calculations depend on whether or not taking the energy value of co-products into account. Farrell et al. (2006) only reckon with the co-products from the biorefinery, but not the stover produced from the corn agriculture. In our study all the co-products are included, also for the six literature studies.

The reason why the energy use in the agriculture per litre of ethanol in our study is the highest is that the yield of ethanol from stover is lower than the one from corn. In order to produce 1 litre of ethanol more stover is needed. While in our study the energy use for the biomass conversion processes is substantially lower, due to its advanced nature. In this study, the resulting net energy value is much higher mainly due to the co-product (corn), which is consumed in the ethanol production of the first-generation to which the other studies refer. Although the average ethanol yields in the six studies is 0.4 L ethanol/kg corn, while in our study the yield is only 0.3 L ethanol/kg stover, cellulosic ethanol is more energy efficient. Moreover, it can be seen that co-generation of steam

and electricity from lignin residues and plant wastes to supply process energy is an important pathway to increase energy efficiency.

One further question may then be raised as, ‘Is it better to use stover for ethanol production or for heat and power generation?’ In order to answer this, two reference systems were defined to generate electricity, incinerating the same amount of stover as required for the production of 1 kg of ethanol, that is 63.5 MJ (3.97 kg) of stover. The energy use and the electricity generated in this system were calculated. The systems in comparison with the stover-ethanol system are defined in Figure 5.3 and the results are shown in Table 5.5.

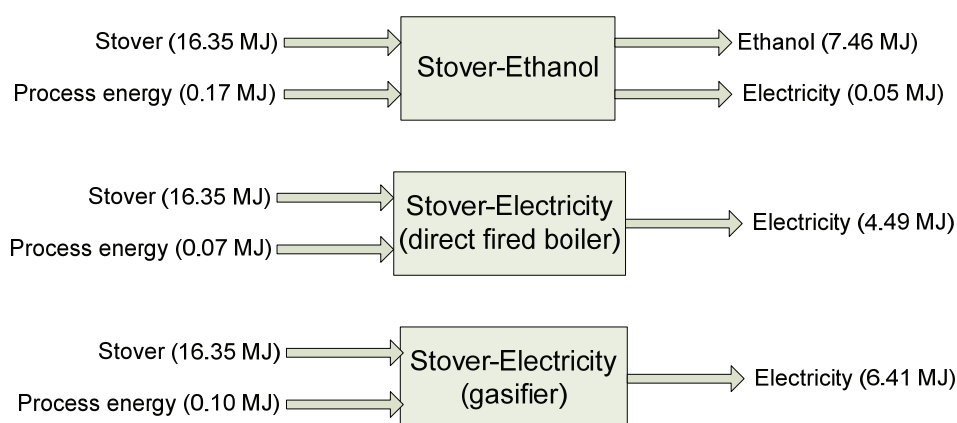


Figure 5.3 The defined comparable systems

Table 5.5 Energy input, output and net energy values of the applications of stover

System definition	Process Energy Use (MJ/kg stover)	Electricity generated (MJ/kg stover)	Ethanol produced (MJ/kg stover)	Net energy value (NEV)* (MJ/kg stover)
Stover-ethanol	0.17	0.05	7.46	7.34
Stover-electricity (direct fired boiler)	0.07	4.49	-	4.42
Stover-electricity (gasifier)	0.10	6.41	-	6.31

* Net energy value (NEV) = energy in ethanol + energy in electricity – process energy use

Table 5.5 shows that in terms of net energy generation the benefit of converting a given amount of stover to ethanol is a better option than utilizing it for power generation from the two electricity options, disregarding the further use of end products, here only

ethanol and electricity. The energy cost for stover-ethanol production is higher, but so are its energy proceeds. If the applications of ethanol and electricity are considered, the efficiency of ethanol use may be much lower than the one of electricity use, as combustion processes have a low energy efficiency score. Furthermore, the possibility of using low temperature steam for urban heating is not specified here. This finding indicates that creating more valuable products from lignocellulosic biomass than only energy is a promising option when energy use is optimized. With further optimization of the ethanol production process, higher net energy value might still be achieved.

5.3.2 Survey of energy inputs

The energy inputs in different sub-processes (sections) in the agriculture and the ethanol production are shown in Figures 5.4 and 5.5, respectively. The lower heating value (LHV) is the basis for the energy production analysis.

In Figure 5.4 the total energy use given (12,646 kJ) refers to the sum of the energy content of the fuels used in the agriculture, but not the primary energy – the energy sources (i.e. crude oil, coal, uranium, biomass, etc.) in the oil refinery and electricity production processes. This system boundary is different from the one in life cycle assessment (LCA), which is ‘cradle-to-gate’. As we want to compare the results in this study with the literature values, the choice of the system boundary is also consistent with the one in the literature studies.

How do our scores relate to the LCA (‘cradle-to-gate’) type of outcomes, with an expanded system definition? When the values of the total energy input in the refinery and the electricity production are used instead of only the ones of the energy outputs, the embodied energy is added to these flows. In this case the total energy use in the agriculture becomes 18,394.49 kJ for the production of 6.62 kg of corn and 3.97 kg of stover. The summary of the energy use from the two comparable system definitions is given in Table 5.6.

Table 5.6 Energy use in ‘cradle-to-gate’ and in ‘energy-product’ analysis

Methodology	Cradle-to-gate	Energy-product
Energy use	(MJ/kg ethanol)	(MJ/kg ethanol)
Agriculture	18.39	12.65
Biorefinery	0.51	0.51
Total	18.90	13.10

84

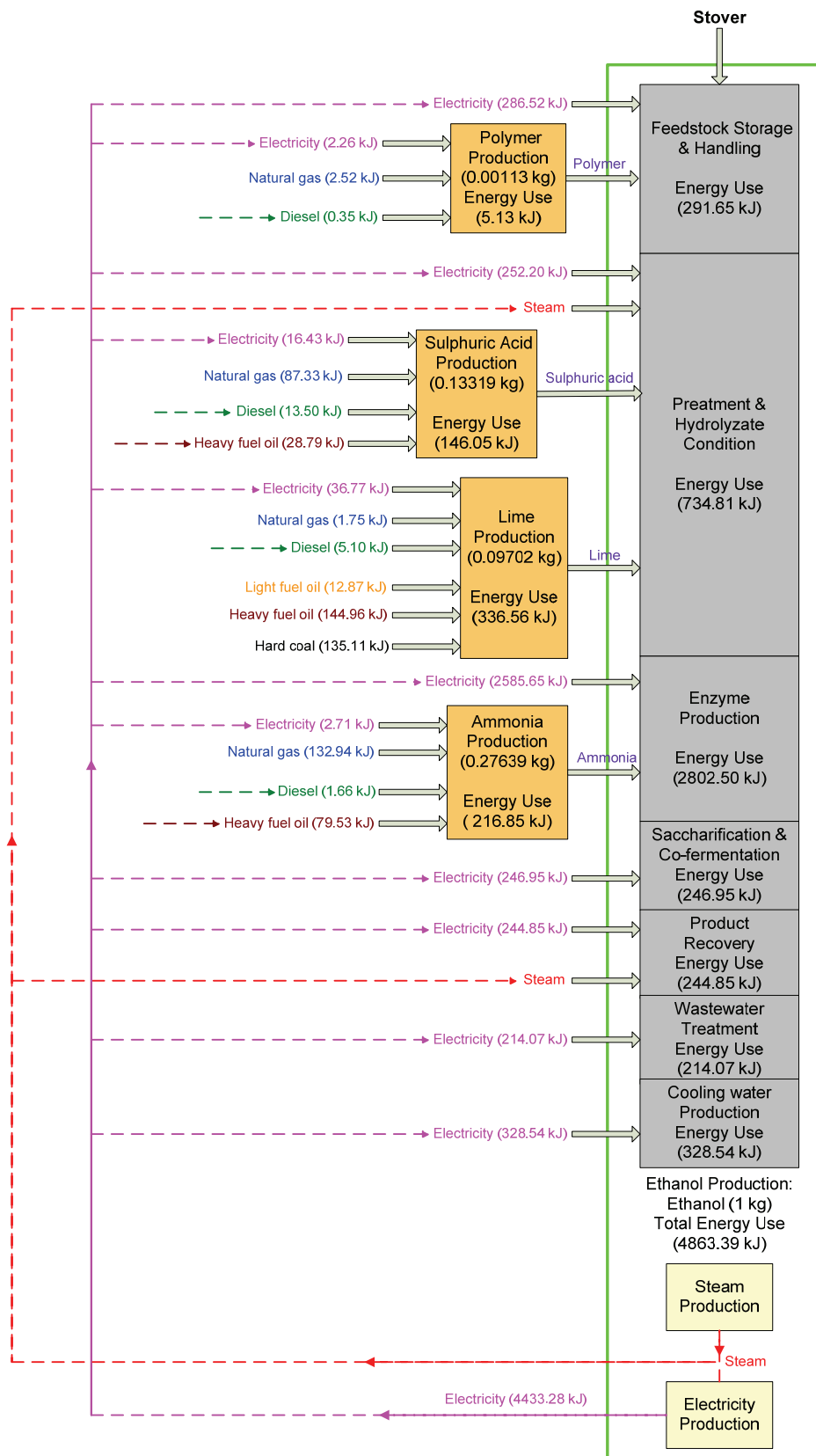


Figure 5.5 Energy inputs in the ethanol production from stover (unallocated)

The reason why the value for the biorefinery does not differ in the two cases is that the energy use (mainly steam and electricity) is supplied by the heat and power production within the refinery. The small amount of energy required for the upstream production of the chemicals used in the refinery is negligible. In the corn-stover agriculture, fertilizer production, tillage and harvesting are the most energy intensive processes. The reason why fertilizer production contributes most to the energy use in the agriculture is the large amount of natural gas used for steam reforming in the production of ammonia, which is then used in the production of nitrogen fertilizers. Tillage and harvesting require a large amount of diesel, which is needed for the operation of agricultural machineries.

In Figure 5.5 the total electricity consumed is 4,217 kJ/kg ethanol, and the co-generated electricity is 4,433 kJ/kg ethanol. The surplus of 216 kJ can be sold to the grid, which corresponds to the number 0.05 MJ/kg stover in Table 5.5 and is not expressed per litre of ethanol but per kilogram of stover. The total energy consumed is shown as 4,863 kJ/kg ethanol, however, among this 4,217 kJ/kg is electricity and is supplied by the refinery itself. Therefore, the actual energy input from outside the system is only 646 kJ/kg ethanol.

In the ethanol production, the causes of the large energy inputs are the steam and electricity used in pre-treatment, product recovery and enzyme production. Steam is needed for stover pre-hydrolysis due to the high temperature requirement in hydrolysis reactor, and for condensation and the preparation of the boiler feed water. Since aerobic fermentation is used in the enzyme production, electricity is used to pump air into the fermenter continuously.

After all the bottlenecks in the ethanol life cycle are defined, possible solutions are provided as follows for process optimization to reduce energy consumption:

- To produce ammonia by nitrogen fixation instead of steam reforming;
- To increase the engine efficiency of the agricultural machines to reduce the fuel use;
- To use less energy intensive crops like sugarcane or grass instead of corn stover;
- To use non-thermal methods for pre-treatment, i.e. chemical or mechanical methods;
- To increase the boiler efficiency of the distillation and rectification columns;
- To apply anaerobic fermentation for cellulase production to prevent aeration.

All the aforementioned means of improvement have their own limitations compared to the technologies engaged in the present study. For instance, nitrogen fixation might be

more costly than steam reforming; investment and initiatives need to be made to increase the efficiency of machineries; the supply of different feedstocks depends on its regional availability and cost for transport; the application of anaerobic fermentation might bring the yield of cellulase down. With all the incentives to reduce energy consumption and the limitations mostly in process economy, technology development shall be further investigated.

5.4 Conclusions and Recommendations

This study presents a detailed energy analysis of stover-based ethanol production using advanced cellulosic technologies. Unlike the ‘cradle-to-gate’ approach in LCA methodology, the system boundaries defined in the present study as well as in the literatures, with which we compared our results, only involve the energy content of the energy product but not the primary energy inputs to the production processes of these energy products. Furthermore, for the calculation of net energy values, Farrell’s study only reckons with the co-products from the biorefinery but ignores the ones from the agriculture for all six literature studies, in their case stover. In our study this has been corrected. The resulting values of the total energy use in both the agriculture and the ethanol production are lower for the case of stover-based ethanol than the ones for corn-based ethanol production. In the corn agriculture the lower energy use in our study is mainly due to less fuel use in the operation of the agriculture machineries. The reason for this is that the data provided by the U.S. Life-Cycle Inventory Database have been optimized. In the second generation stover-ethanol production, the much lower total energy use is due to the highly optimized process design in terms of energy efficiency. When all co-products are taken into account, the net energy value becomes much higher than the ones in the literatures covering the corn cases, which shows that ethanol production from cellulosic feedstocks is more energy efficient than corn-based ethanol. Moreover, co-generation of steam and electricity from lignin residues and wastes is an important pathway to increase energy efficiency in the cellulosic ethanol process.

The survey of energy inputs indicates the bottlenecks in the ethanol production chain – fertilizer production, tillage and harvesting in the agriculture, and pre-treatment, enzyme production and product recovery in the biorefinery. The detailed investigation of the energy inputs in all the energy intensive processes provides the opportunity to optimize the system in terms of net energy production.

The production of the nitrogen fertilizer consumes more than 90% of the energy in the fertilizer production, thus the possibilities of reducing nitrogen fertilizer use and improved production processes require more attention. For instance, organic farming

replacing synthetic fertilizers by green manure may result in less energy use and lower environmental impact. Regarding the agriculture processes, optimization should focus on the design of the machineries in order to achieve higher efficiency to reduce fuel consumptions. Furthermore, stover might not be a good feedstock option for cellulosic ethanol production due to its highly intensive agriculture. More promising feedstocks can be sugarcane and switchgrass.

In the ethanol production, advanced technologies involving two steps pre-treatment (dilute acid pre-hydrolysis and enzymatic saccharification) and genetically modified organisms (GMO) for fermentation are used. The process has been conceptually designed and optimized with regard to production yield and energy efficiency, but yet it needs to be established in practice. To further optimize the system, strain development of microorganism to achieve a high yield and innovations of pre-treatment and recovery options can be the focus. It is worth noting that the goal of energy conservation may bring side effects such as worse environmental performance, low profitability or unacceptable opinions from the society. Therefore, it is crucial to develop a model for optimization with a complete set of criteria, among which a reduced energy requirement and a better energy generation technology can be important ones.

The present study also indicates that in terms of net energy value created, ethanol refining is a better option than combustion of cellulosic feedstocks. There are opportunities to further increase the value derived from biomass processing by co-producing high-value products next to ethanol, especially using agricultural wastes as they are already available in varying compositions. In such a complex multi-feedstock and multi-product biorefinery system, the production of high volume of low-value products (like fuels) and low volume of high-value co-products (like pharmaceutical precursors) can be combined. Together with collective feedstock supply, waste treatment and integrated power generation, a biorefinery complex could potentially maximize the total value derived from cellulosic feedstocks and minimize the energy consumption and environmental impacts.

**Energy and Environmental Performance of
Bioethanol from Different Lignocelluloses**

* This chapter is submitted to International Journal of Chemical Engineering for publication. Co-authors: Ester van der Voet and Gjalt Huppes

Abstract

Climate change and the wish to reduce the dependence on oil are the incentives for the development of alternative energy sources. The use of lignocellulosic biomass together with cellulosic processing technology provides opportunities to produce fuel ethanol with less competition with food and nature. Many studies on energy analysis and life cycle assessment of the second-generation bioethanol have been conducted. However, due to the different methodology used and different system boundary definitions, it is difficult to compare their results. To permit a direct comparison of fuel ethanol from different lignocelluloses in terms of energy use and environmental impact, seven studies conducted in our group were summarized in this paper, where the same technologies were used to convert biomass to ethanol; the same system boundaries were defined; and the same allocation procedures were followed. A complete set of environmental impacts ranging from global warming potential to toxicity aspects is used. The results provide an overview on the energy efficiency and environmental performance of using fuel ethanol derived from different feedstocks in comparison with gasoline.

6.1 Introduction

Climate change and the wish to reduce the dependence on oil are the incentives for the development of alternative energy sources. In view of the carbon dioxide reduction target agreed upon in the Kyoto protocol, a shift from fossil fuels to renewable resources is ongoing to secure the long-term energy supply at both national and international level. The European Commission demonstrated in 2007 that a 20% target for the overall share of energy from renewable sources and a 10% target for energy from renewable sources in transport would be appropriate and achievable objectives (Renewable Energy Road Map, 2007), though both targets have become subject of dispute since then. In the near term, liquid biofuels will still largely contribute to the target in the transport sector due to the limited available technologies for fuels from other renewable sources. Especially bioethanol with its bio-renewable nature, optimized production technology and potential of greenhouse gas (GHG) mitigation already proved itself as an attractive alternative fuel.

Most of the current practice only concerns the first-generation ethanol from conventional crops like corn, wheat, sorghum, potato, sugarcane, sugar beet, etc. Criticism is expressed on the first-generation bioethanol with regard to land use requirement and competition with food and nature. These issues have become the driving forces for the technology innovation towards the second-generation ethanol from lignocellulosic feedstocks, both as agricultural co-products and wastes and dedicated energy crops. EC Directive 2009 addressed the importance of commercializing second-generation biofuels (Directive 2009/28/EC, 2009). The United States, as one of the leading nations in promoting biofuels, proposed that cellulosic ethanol must achieve 44% of the total biofuel production by 2020 (DOE/EIA-0383, 2008).

With the development of the cellulosic technology being able to convert agricultural co-products of often lower value to ethanol, two major questions are raised when comparing the second-generation bioethanol to fossil fuel and the first-generation bioethanol: (1) Is the second-generation ethanol a better option for energy conservation? (2) What are the environmental benefits of the second-generation ethanol? In order to answer the first question efforts were exerted on energy analysis of ethanol from corn stover (Lavigne and Powers, 2007; Luo et al., 2009c), switchgrass (Farrell et al., 2006; Pimentel and Patzek, 2005; Wang, 2001, Wu et al., 2006) and woodchip (Cardona Alzate and Sánchez Toro, 2006; Pimental and Patzek, 2005). Most of these studies yield a positive net energy value (NEV), which indicates lignocelluloses are more favourable feedstocks than dedicated crops i.e. corn grain. However, Pimentel and Patzek (2005)

exceptionally reported negative NEV from switchgrass- and wood-ethanol systems concluding cellulosic ethanol processes are more energy intensive than ethanol from corn grain. With respect to the second question many life cycle assessment (LCA) studies were conducted on ethanol from lignocelluloses such as corn stover (Kim et al., 2009; Luo et al., 2009a; Searcy and Flynn, 2008; Sheehan et al., 2004; Spatari et al., 2005), Switchgrass (Kim et al., 2009; Wu et al., 2006), Miscanthus and willow (Styles and Jones, 2008), sugarcane bagasse (Botha and von Blottnitz, 2006; Luo et al., 2009b), cereal straw (Gabrielle and Gagnaire, 2008), woodchip and wood wastes (Beer and Grant, 2007; Fu et al., 2003; Kempainen and Schonnard, 2005), flax shives (González García et al., 2009a) and hemp hurds (González García et al., 2009b). All these studies, to different extent, show environmental benefits especially in terms of reduced fossil resource depletion and GHG emissions.

However, these studies on both energy analysis and LCA of the second-generation bioethanol raise a number of questions. First of all, there is insufficient consistency regarding the definition of the system boundaries, with different choices made without explicit arguments. For instance, an ethanol refining system does not include the environmental impact from the production of cellulase enzyme for degrading cellulosic feedstocks (Sheehan et al., 2002), leaving out a major energy requiring process. Secondly, in different studies allocation methods are different and not systematic and mostly are unclearly stated. A high sensitivity to allocation method has been reported for LCA results when evaluating carbon intensity and fossil energy consumption for bioethanol pathways (Beer and Grant, 2007; Kim and Dale, 2002; Luo et al., 2009a; Malça and Freire, 2006). The differences and ambiguities in the definition of system boundaries and allocation methodology made most of the studies incomparable.

To allow for a direct and meaningful comparison of different analysis, Farrell et al. (2006) aligned methods and assumptions for six selected studies (de Oliveira et al., 2005; Groboski, 2002; Patzek, 2004; Pimentel and Patzek, 2005; Shapouri and McAloon, 2002; Wang, 2001), and removed the differences in the underlying data. Their focus, however, is mostly on corn-based ethanol. They indicate that calculations of NEV are highly sensitive to assumptions about both system boundaries and key parameter values and, as to content, conclude that large-scale use of fuel ethanol certainly requires more sustainable practices in agriculture and advanced technologies, shifting from corn based to cellulosic ethanol production.

In order to have an overview of the energy intensity and the environmental performance of bioethanol production from different lignocellulosic feedstocks, we

have conducted five LCA studies at CML (Bai et al., 2010; Luo et al., 2009a; Luo et al., 2009b; González García et al., 2009a; González García et al., 2009b) and two studies on energy analysis (Luo et al., 2009c; Hadzhiyska et al., 2009) of bioethanol from lignocelluloses, in all of which the same technologies were used to convert cellulose and hemicellulose to ethanol and to generate heat and power from lignin residues and wastes; the same system boundaries were defined; and the same allocation procedures were followed. In all the LCA studies a comprehensive set of environmental impacts is used, ranging from abiotic resource depletion and GHG emissions to acidification and toxicity aspects. The present study summarizes and compares the results obtained from these five LCA studies and the two on energy analysis, also in comparison with the literature studies.

6.2 Life Cycle Assessment (LCA)

6.2.1 Methodology

All five case studies compared in the present study focus on LCA of fuel ethanol from lignocellulosic feedstocks, with application of different allocation methods and/or scenario analysis. In all these studies advanced cellulosic processing technology was assumed to convert biomass to ethanol, the system boundaries are identical, and the same allocation procedure was applied. Therefore they are well comparable. The feedstocks in these studies are summarized as follows:

- Corn stover (Luo et al., 2009a)
- Sugarcane and bagasse (Luo et al., 2009b)
- Switchgrass (Bai et al., 2010)
- Flax shives (González García et al., 2009a)
- Hemp hurds (González García et al., 2009b)

In this section the methodologies used in all five studies are described. It is worth noting that the 2nd study by Luo et al. (2009b) presents a comparative LCA of ethanol production from solely sugar (current practice) and sugar plus bagasse (future case). As combining sugar and bagasse as feedstock for ethanol production is proposed to be a common practice in Brazil in the future, we did not perform an LCA on ethanol derived solely from bagasse. Thus the future case presented in this study was used to compare with other four studies, even though the feedstock includes not only the lignocellulose (bagasse) but also sugar.

1) Functional unit and alternatives

The functional unit in all studies is defined as power to wheels for one kilometre driving of a midsize flexible fuelled vehicle (FFV), which means that engine modification can be left out of account. Four fuel alternatives are considered: (1) conventional gasoline; (2) a blend of 90% gasoline with 10% ethanol by volume (termed E10); (3) a blend of 15% gasoline with 85% ethanol by volume (termed E85); (4) pure ethanol. In practice pure ethanol is not used as transport fuel, hence it is only a hypothetical case here for easy comparison with gasoline.

2) System boundaries

The systems defined in all five studies are based on a ‘cradle-to-grave’ approach, which includes the crude oil extraction and refinery, the agriculture production of lignocellulosic biomass, harvest and transport of the biomass to the ethanol refinery, the production of ethanol and its co-products, blend and transport all fuels to the regional storages, and the final use phase of fuels in vehicle driving. The production and transport of chemicals used in all processes are also taken into account. Moreover, emissions from capital goods production and waste management are included. However, emissions and wastes associated with the production and disposal of the FFV are outside the system boundaries.

In all five studies different co-products are produced from either the agricultural production or the ethanol refinery, as listed in Table 6.1. In fact, in all studies electricity is also co-generated from the ethanol refinery, however, only in the one by Bai et al. (2010) there is a surplus of electricity, in the other studies it is fully utilized by the operation of the refinery and no surplus can be considered as co-product. In the 2nd study by Luo et al. (2009b) extra electricity needs to be purchased from local grids due to the insufficiency of the co-generated electricity inside the refinery.

3) Data sources and software

Life cycle inventory (LCI) data used in all studies are obtained from different sources, as summarized in Table 6.2. The completeness of data may differ between sources; therefore, the Ecoinvent database from the Swiss Centre of Life Cycle Inventories (<http://www.ecoinvent.org/>) is used as a standard whenever possible, as this source has long learning experience and involves a very broad range of processes (around 4,000). Software package Chain Management by Life Cycle Assessment (CMLCA) is used for the analysis (<http://cml.leiden.edu/software/software-cmlca.html>).

Table 6.1 Product and co-products from the agriculture and the ethanol refinery

Study	Products	Agriculture		Ethanol refinery	
		Product	Co-products	Product	Co-products
Luo et al., 2009a		Corn	Stover	Ethanol	-
Luo et al., 2009b		Sugarcane	-	Ethanol	Sugar
Bai et al., 2010		Switchgrass	-	Ethanol	Electricity
González García et al., 2009a		Shives	Fibres & linseed	Ethanol	-
González García et al., 2009b		Hurds	Fibres & dust	Ethanol	-

Table 6.2 Data sources for the life cycle inventories of the five studies

Subsystem	Data source
Corn agriculture	U.S. Life-Cycle Inventory Database: http://www.nrel.gov/lci/
Sugarcane agriculture	Macedo et al., 2004
Switchgrass agriculture	Bullard and Metcalfe, 2001; Nemecek and Kägi, 2007
Flax agriculture	Nemecek et al., 2004; Hauschild, 2000; Audsley et al., 1997; Arrouays et al., 2002; EMEP/CORINAIR, 2006
Hemp agriculture	Nemecek et al., 2004; Hauschild, 2000; Audsley et al., 1997; Arrouays et al., 2002; EMEP/CORINAIR, 2006
Biomass transport	Spielmann et al., 2004
Stover-ethanol production	Aden et al., 2002
Sugarcane-ethanol production	Efe et al., 2005
Switchgrass-ethanol production	Guerra Míguez et al., 2009
Flax shives-ethanol production	Aden et al., 2002
Hemp hurds-ethanol production	Aden et al., 2002
Ethanol transport	Spielmann et al., 2004
Gasoline production & transport	Swiss Centre of Life Cycle Inventories: http://www.ecoinvent.org/
Emissions from capital goods production	Tukker et al., 2006 (EIPRO Database)
Emissions from vehicle driving	Kelly et al., 1996; Reading et al., 2002.
Background processes	Swiss Centre of Life Cycle Inventories: http://www.ecoinvent.org/

4) Allocation method

The allocation procedure in multi-product processes has been always one of the most critical issues in LCA. The ISO 14040 and 14044 (2006) recommend a step-wise procedure for allocation. First of all, allocation should be avoided whenever possible

through subdivision of certain processes or by expanding system boundaries so as to include the additional functions related to them. If allocation cannot be avoided, methods reflecting underlying physical relationships shall be applied, of how process inputs and outputs change due to a quantitative change in products and functions delivered. This is often filled in as allocation based on mass or energy content of the co-products. To the extent that physical relations cannot be established, other relevant variables like economic values of the co-products can be used to allocate. This last option is similar to the cost allocation methods used in managerial accounting (Huppes, 1993; Guinée et al., 2004).

In all five studies, one allocation method is applied, followed by a sensitivity analysis when two or more allocation methods can be applied. In some studies methods based on mass or energy content cannot be applied systematically. For instance, in the case of electricity as a co-product in ethanol refinery, mass allocation is not applicable; in the case of sugar as a co-product, energy content allocation cannot be used. Therefore, in the present study, in order to permit a fair comparison, economic allocation, which is used in all five studies, is applied. In no case the more general ISO requirements on physical allocation have been used or met. The multi-product processes in these studies are given as follows:

- The corn agriculture, where corn and stover are produced;
- The ethanol production from sugarcane and bagasse, where ethanol and sugar are produced;
- The ethanol production from switchgrass, where ethanol and electricity are produced;
- The flax agriculture, where flax fibres, shives and linseed are produced;
- The hemp agriculture, where hemp fibres, hurds and dust are produced.

For the gasoline production, the allocations were taken as currently implemented in the Ecoinvent database by its designers, using different methods for different parts of the product system. This is a shortcoming but is less relevant when comparing different biofuel options. The partitioning factors based economic values in the five studies are given in Table 6.3. In the studies by González García et al. (2009a; 2009b) the authors also conducted a sensitivity analysis on the price change of shives and hurds. For the comparison in the present study, an averaged price of flax shives and the price of hemp hurds in the base case scenario were taken.

Table 6.3 Partitioning factors for economic allocation in all five studies

Study	Multiple products	Partitioning factor
Luo et al., 2009a	Stover/corn	0.118/0.882
Luo et al., 2009b	Ethanol/sugar	0.837/0.163
Bai et al., 2010	Ethanol/electricity	0.894/0.106
González García et al., 2009a	Shives/fibres/linseed	0.042/0.911/0.047
González García et al., 2009b	Hurds/fibres/dust	0.122/0.863/0.015

5) Impact assessment

The categories selected for impact assessment in all five studies are as follows:

- Abiotic resource depletion potential (ADP)
- Global warming potential (GWP)
- Ozone layer depletion potential (ODP)
- Photochemical oxidation potential (POCP)
- Human and eco-toxicity potential (HTP and ETP)
- Acidification Potential (AP)
- Eutrophication Potential (EP)

The environmental impacts addressed here reflect the differences between operations of vehicles fuelled with gasoline, E10, E85 and pure ethanol. The results were normalized to the ‘world total’ in order to compare the importance of each impact. Overall evaluation requires weighting, which has not been applied in this study. The Handbook on Life Cycle Assessment (Guinée et al., 2002) states: “Weighting is an optional step for all non-comparative assertions; there is no best available method and there is no recommended set of weighting factors.” Nevertheless, for actual decision making some sort of weighting always is required.

6.2.2 Results comparison and discussion

The LCA results of fuel ethanol from the five different feedstocks compared with gasoline for each impact category are presented in Figure 6.1. In order to compare the relative size of results in different impact categories, they are normalized to ‘world total 1995’ and are all set to the same scale. This normalized score indicates the percentage the system would contribute to the world total score on that impact, for the reference year taken.

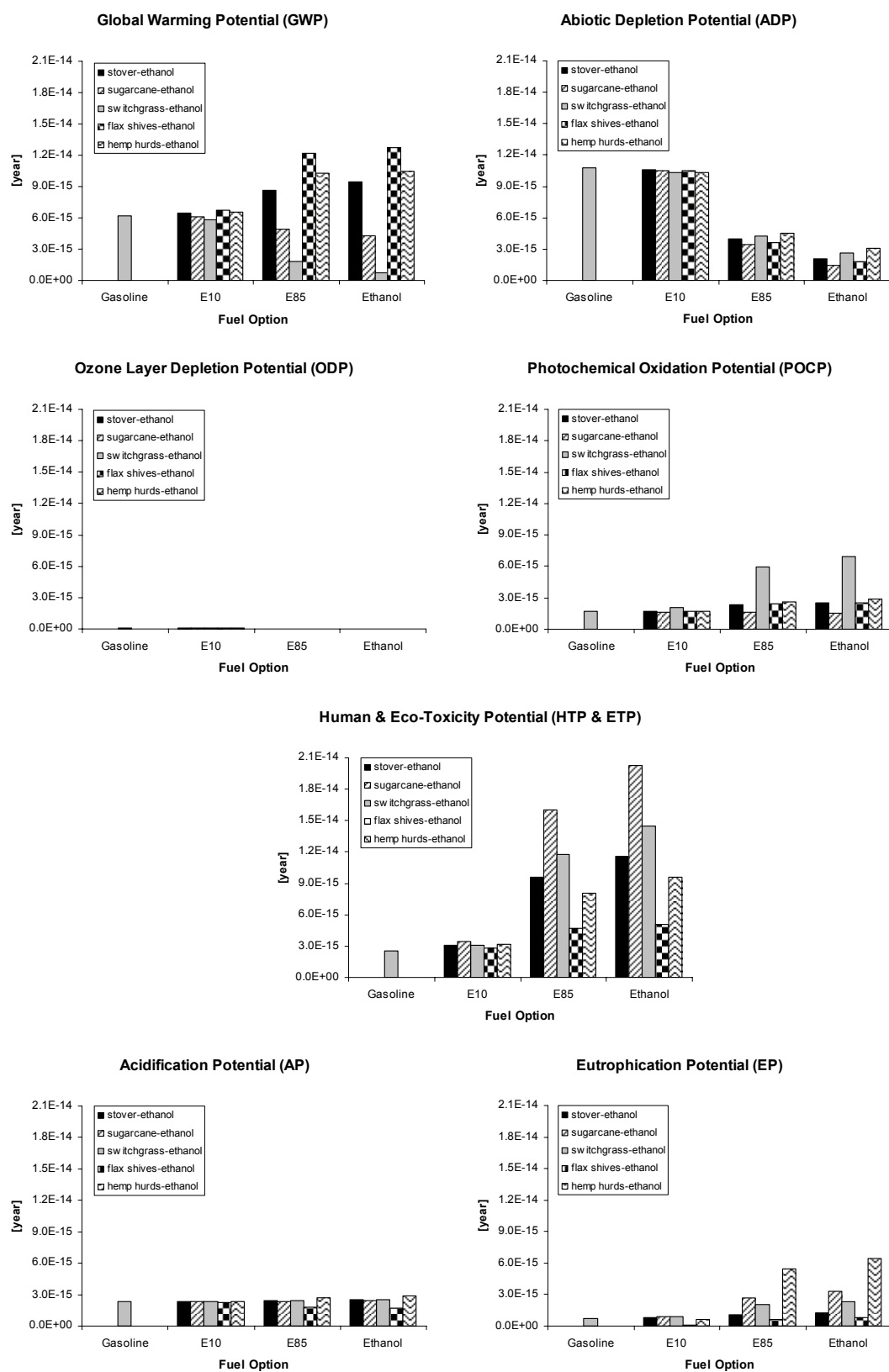


Figure 6.1 Overall comparison of environmental impact of all fuel options in all studies

1) Global warming potential (GWP)

Global warming has always been considered as the most important category in biofuel LCA studies, a simple type of weighting. The results of GWP always draw special attention also due to the diversity of the results between different studies. This stands also true in the present study. When sugarcane and switchgrass are the energy crops, ethanol fuels show better performance than gasoline. The reason for the decrease of GHG emissions is the large amount of CO₂ taken up by the growth of sugarcane and switchgrass. Moreover, switchgrass seems to be a better feedstock than sugarcane because in the ethanol production from switchgrass, there is surplus electricity which is sold to the local grid. However in the sugarcane-ethanol refinery, the co-generated electricity is not enough to supply the refinery and additional electricity needs to be purchased from the grid. If the electricity supplied by the grid is also bio-based in the future, its contribution to GHG emissions could be less.

However, when fuel ethanol is produced from corn stover, flax shives and hemp hurds, the application of ethanol fuels leads to worse performance. Here the economic allocation applied in the agriculture production in these three studies plays an important role. As compared to corn, flax and hemp, stover, shives and hurds have much smaller partitioning factors due their low prices (see Table 6.3). Hence when economic allocation is applied, most of the CO₂ uptakes in agriculture are allocated on corn, flax and hemp fibres. Flax shives turned out to be the worst feedstock due to its smallest allocation factor (0.042). The substantial influence of allocation methods on the outcome of GWP is illustrated in Section 3).

2) Other impact categories

In the other six impact categories the results of driving on fuel ethanol from different feedstocks are also diverse. The level of ADP is significantly reduced when replacing gasoline with fuel ethanol, irrespective of the feedstock used. Apparently this is due to the replacement of fossil resources by biomass. The levels differ among the five studies insignificantly. The reasons for these differences can be the energy efficiency in the agriculture as well as the ethanol refinery. To have a better understanding in which sub-processes are energy intensive, a detailed energy analysis is required.

Normalized ODP shows substantially lower level than other impacts, which means, it contributes relatively less to the world total and is negligible in comparison. Among all the ethanol fuels, sugarcane-derived ethanol is the best option regarding ODP. This indicates that less fossil energy is used in the life cycle of sugarcane-ethanol. This result is in accordance with the one of ADP, where ethanol from sugarcane also leads to the

lowest impact. The ODP levels of fuel ethanol from other feedstocks do not differ significantly. Overall, the ODP score can be left out of account in decision making. Even a very high weight on this impact could not make it a relevant one.

Regarding POCP level, again sugarcane-derived ethanol shows the best performance, which is slightly lower than gasoline. POCP is mainly contributed by the emissions from the production and refining of oil and gas, and the volatile organic compounds in the gasoline and ethanol life cycle, respectively. Thus when shifting gasoline to ethanol fuels, the emissions from fossil resource extraction are reduced, however, the emissions from ethanol production and transport of chemicals are increased. In all ethanol life cycles except the one derived from sugarcane, the level of increase is higher than the one of reduction. Among all switchgrass-derived ethanol is the worst option due the large amount of acetaldehyde emitted from ethanol fermentation, which contributes 77% to its total POCP score (Bai et al., 2010). This finding indicates that, although the processes for ethanol product have all been optimized, possibilities for further optimization with better technology need to be investigated to reduce environmental impact.

In the category concerning HTP and ETP, ethanol fuels all have higher impact than gasoline. The main contributors of human and eco-toxicity are the production of chemicals and machineries used in agriculture. Among ethanol fuels from different feedstocks, ethanol from sugarcane and switchgrass perform worse. This does not mean their agriculture processes are more polluting. The reason for this is again the partitioning factors based on economic allocation in the agriculture of corn stover, flax shives and hemp hurds. Large amount of emissions in these three cases are allocated on the main crops – corn, flax and hemp.

The levels of AP increase slightly in all cases except flax shives-derived ethanol when replacing gasoline with ethanol fuels. This level is mainly contributed by the ammonia emitted in the agriculture, the nitrogen oxides (NO_x) emissions from the operation of lorries and FFV, and the sulphur dioxide (SO₂) from the oil refinery. Hence in the ethanol life cycles, although less SO₂ is emitted from the oil refinery, ammonia emissions are not negligible. This results in worse performance of most of ethanol fuels. For the adverse results from shives-derived ethanol, the same reasoning as the one for HTP and ETP can be applied. As shives shares only a very small part of environmental burdens in the agriculture, the level of AP is decreased.

With regards to EP the trend is similar to AP. The level of EP is mostly attributed to agriculture processes, especially the nitrate to ground water and nitrogen oxides (NO_x) to air from the application of nitrogen fertilizers. As flax shives has a much smaller allocation factor in the agriculture than other feedstocks, it gives the best performance, followed by gasoline, and then stover, switchgrass and sugarcane-derived ethanol. EP of hemp hurds-derived ethanol draws attention due to its significantly higher level compared to other fuel cycles. The main contributor of this is the large amount of nitrate leaching to fresh water.

It can be seen that different fuel options show better performance in different categories. The overall evaluation depends on the importance attached to each impact category. As weighting is not included in this study, it is impossible to draw conclusions on which fuel option is the best. However, as the results are normalized and are set to the same scale, it can be seen that GWP, ADP, HTP and ETP contribute relatively more to the world total, thus they deserve more attention when evaluating all the fuel options. POCP, AP and EP are of less importance, and ODP can definitely be left out of account.

3) Influence of methodology choice

In the studies on stover, shives, and hurds-derived ethanol, a sensitivity analysis on allocation methods was conducted. The results show that when allocations reflecting physically relationship (mass or energy content) are applied, GWP levels are significantly reduced. The reason for this outcome is that stover, shives and hurds are agricultural co-products which have low market prices when comparing to corn, flax and hemp. When economic allocation is applied, most of the CO₂ uptake is allocated to the crops due to their large partitioning factors; however, when mass or energy content based allocation is applied, the amount of CO₂ uptake allocated to stover, shives and hurds increases due to the large amount produced. For toxic effects of pesticide use, economic allocation similarly leads to a very low share, and allocation by mass would increase the already high human and eco-toxicity scores substantially. This allocation dependency of outcomes has been explained in more details in three of the studies (Luo et al., 2009a; González García et al., 2009a; González García et al., 2009b) Therefore allocation issues are of crucial importance in LCA studies applied to biofuels and should be discussed explicitly whenever it is concerned.

In most of the studies the usual allocation procedure is followed dealing with CO₂ uptake and CO₂ emissions – the uptake counts as an extraction from atmosphere, hence the emissions of the biogenic CO₂ at combustion are counted just the same as fossil

based CO₂. In the field of LCA on biofuels, there also is a ‘CO₂-neutral’ approach, which ignores both extractions and emissions of biogenic CO₂. In a straightforward system that does not require allocation the net result should be the same. However, when allocation is needed, this may no longer be the case. As the allocation method applied strongly influence the results of GWP scores, a comparative computation for the systems excluding biogenic CO₂ was made, and the results are give in Figure 6.2.

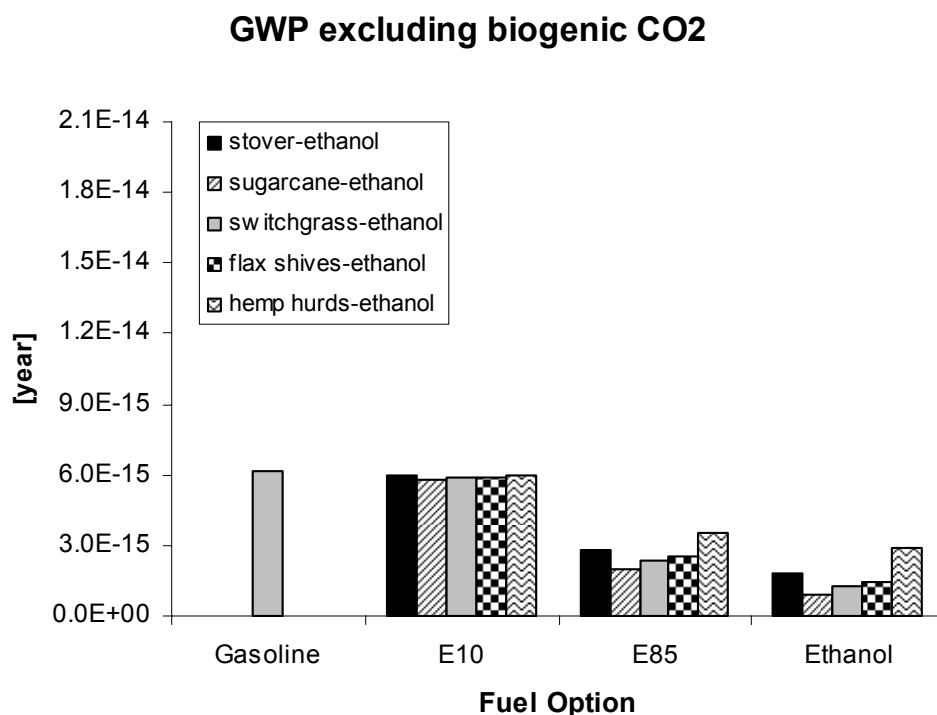


Figure 6.2 Results of GWP excluding biogenic CO₂ in all studies

When biogenic CO₂ is excluded, a reduction of GWP is achieved when replacing gasoline with ethanol fuels irrespective of the feedstocks used. As the switchgrass-ethanol system is relatively straightforward with only small amount of electricity co-generated, its GWP levels do not differ significantly in both approaches (allocation vs. CO₂-neutral). For the other four studies, as economic allocation plays an important role, the results turn to be very different in the ‘CO₂-neutral’ approach. In fact, what has happened here by excluding biogenic CO₂ is that CO₂ escapes the selected allocation method. Instead, CO₂ is allocated in all cases on the basis of carbon share of the products. Therefore, implicitly, another way of allocating is introduced in the carbon neutral approach and here then mixed with economic allocation.

The choice of allocation influences the impact category of global warming more significantly, as the other categories refer to more specific process in the chain and, more importantly, do not deal with negative emissions.

In order to have a clear overview, the environmental performances per impact category from the best to the worse fuel option are summarized in Table 6.4.

Table 6.4 Overall results of environmental performance of all fuel options in all studies

Impact category	Environmental performance					
	Best					Worst
GWP	Swi	Sug	Gas	Sto	Hur	Shi
GWP (CO ₂ -neutral)	Sug	Swi	Shi	Sto	Hur	Gas
ADP	Sug	Shi	Sto	Swi	Hur	Gas
ODP	Sug	Sto	Swi	Shi	Hur	Gas
POCP	Sug	Gas	Sto	Shi	Hur	Swi
HTP and ETP	Gas	Shi	Hur	Sto	Swi	Sug
AP	Shi	Gas	Sug	Swi	Sto	Hur
EP	Shi	Gas	Sto	Swi	Sug	Hur

* Abbreviations: Gas – gasoline; Sto – stover-derived ethanol; Sug – sugarcane-derived ethanol; Swi – switchgrass-derived ethanol; Shi – shives-derived ethanol; Hur – hurds-derived ethanol.

6.3 Energy Considerations

6.3.1 Methodology

The purpose of this section is to understand whether the second-generation bioethanol is more energy efficient compared to the first-generation. We have conducted two energy analyses on bioethanol from corn stover (Luo et al., 2009c) and sugarcane (Hadzhiyska et al., 2009). In both studies the energy inputs of all sub-processes are calculated and the resulting net energy values are compared with literature studies on the first-generation bioethanol from corn and sugarcane and the second-generation ethanol from switchgrass. In our sugarcane-ethanol system, as the data used are from the same source as the ones in LCA study, two scenarios are considered: base case – ethanol and sugar are produced from the juice sugar extracted from sugarcane, and bagasse is used for steam and electricity generation; future case – bagasse is also converted to ethanol, and heat and power are generated from the lignin residues and wastes.

All the relevant processes in biomass production and ethanol conversion are included in the system boundaries, as well as the capital goods production and wastes management.

No allocation is involved in the foreground processes, as all the energy used to produce all co-products is taken into account. Two types of NEV are estimated – with and without accounting for co-product energy values.

The outcomes of these two studies are compared with the six literature studies on corn-ethanol summarized by Farrell et al. (2006) (de Oliveira et al., 2005; Groboski, 2002; Patzek, 2004; Pimentel and Patzek, 2005; Shapouri and McAloon, 2002; Wang, 2001), one study on switchgrass-ethanol (Wang, 2001) and three studies on sugarcane ethanol (Macedo et al., 2004; de Oliveira et al., 2005; Pimentel and Patzek, 2007).

6.3.2 Results comparison and discussion

The net energy summaries excluding and including co-products compared to the literature values are presented in Tables 6.5 and 6.6, respectively.

When co-products are not included meaning that all the inputs and outputs are 100% allocated to stover, three studies on corn-ethanol result in negative net energy values due to their then seemingly more intensive agricultural practice. The other three studies on corn ethanol yield a very small positive NEV compared to the ones of ethanol from sugarcane and cellulosic feedstocks (stover and switchgrass). However, stover is not a promising feedstock due to its intensive agricultural production process. The reason why the energy use in agriculture per litre of ethanol in stover-ethanol case is the highest is that the yield of ethanol from stover is lower than the one from corn. In order to produce 1 litre of ethanol more stover is needed – the average ethanol yield of ethanol from corn is 0.4 litre/kg, while from stover it is only 0.3 litre/kg.

When the energy credits (taken as the energy content of the product) are taken into account for all the co-products, all studies yield a positive NEV. The highest NEV of stover-ethanol attributes to the co-product in the agriculture – corn. The resulting NEVs from corn-ethanol studies become comparable with those from ethanol derived from switchgrass and sugarcane. In the study conducted by Hadzhiyska et al. (2009) sugar is co-produced in the ethanol refinery in both the base and future case, the values of net energy are significantly higher than the those from other studies without sugar co-production. This indicates that outcomes of net energy calculations depend very much on whether or not taking the energy values of co-products into account.

Table 6.5 Net energy summary excluding co-products, no allocation

Energy use (MJ/L ^a)		Agriculture	Biorefinery	Total input	Ethanol ^b	Total output	Net energy value (NEV)
Feedstock							
Stover	Luo	10.0	0.5	10.5	21.2	21.2	10.7
Corn	Patzek	9.9	17.0	26.9	21.2	21.2	-5.7
	Pimentel	10.0	17.0	27.0	21.2	21.2	-5.8
	Shapouri	5.3	15.2	20.5	21.2	21.2	0.7
	Graboski	5.6	16.6	22.2	21.2	21.2	-1.0
	de Oliveira	6.3	14.1	20.4	21.2	21.2	0.8
	Wang	6.6	12.5	19.1	21.2	21.2	2.1
Switchgrass	Wang	2.4	1.0	3.4	21.2	21.2	17.8
Sugarcane	Hadzhiyska (base case)	6.5	0.1	6.6	21.2	21.2	14.6
	Hadzhiyska (future case)	2.7	0.5	3.2	21.2	21.2	18.0
	Pimentel	2.6	3.4	6.0	21.2	21.2	15.2
	de Oliveira	5.6	0.6	6.2	21.2	21.2	15.0
	Macedo	2.0	0.3	2.3	21.2	21.2	18.9

^a The unit of energy use is MJ per litre of ethanol produced from biorefinery

^b Normalized energy value for ethanol based on lower heating value (LHV).

Table 6.6 Net energy summary including co-products, no allocation

Energy use (MJ/L ^a)		Net energy summary including co-products, no allocation							
Feedstock		Agriculture	Biorefinery	Total input	Ethanol ^b	Co-products in agriculture ^c	Co-products in biorefinery ^d	Total output	Net energy value (NEV)
Stover	Luo	10.0	0.5	10.5	21.2	85.2	0.2	106.6	96.1
Corn	Patzek	9.9	17.0	26.9	21.2	25.9	4.1	51.2	24.3
	Pimentel	10.0	17.0	27.0	21.2	25.9	1.9	49.0	22.0
	Shapouri	5.3	15.2	20.5	21.2	24.0	7.3	52.5	32.0
	Graboski	5.6	16.6	22.2	21.2	24.6	4.1	49.9	27.7
	de Oliveira	6.3	14.1	20.4	21.2	24.6	4.1	49.9	29.5
	W'ang	6.6	12.5	19.1	21.2	24.6	4.0	49.8	30.7
Switchgrass	W'ang	2.4	1.0	3.4	21.2	0.0	4.8	26.0	22.6
Sugarcane	Hadzhiyska (base case)	6.5	0.1	6.6	21.2	0.0	32.7	53.9	47.3
	Hadzhiyska (future case)	2.7	0.5	3.2	21.2	0.0	12.6	33.8	30.6
	Pimentel	2.6	3.4	6.0	21.2	0.0	0.0	21.2	15.2
	de Oliveira	5.6	0.6	6.2	21.2	0.0	1.1	22.3	16.1
	Macedo	2.0	0.3	2.3	21.2	0.0	3.0	24.2	21.9

^a The unit of energy use is MJ per litre of ethanol produced from biorefinery^b Normalized energy value for ethanol based on lower heating value (LHV).^c In stover-ethanol study it refers to the corn as a co-product in the agriculture; in the other six studies on corn-ethanol it refers to the harvested stover (60%, dry mass basis) as a co-product, and the values are estimated in this study.^d In stover-ethanol and switchgrass-ethanol study it refers to electricity; in corn-ethanol studies it refers to a range of products from corn milling, such as dried distiller grains, corn gluten feed, corn oil, etc; in sugarcane-ethanol study it refers to electricity surplus or/and bagasse surplus, as well as sugar if it is co-produced.

As mentioned earlier, in our sugarcane-ethanol study, the base case demonstrates the current practice in Brazilian ethanol industries – ethanol and sugar are produced from sugar juice after cane milling, steam and electricity are generated from the combustion of bagasse; the future case presents the option that bagasse is also converted to ethanol, while heat and power are only generated from the lignin residues and wastes. In the base case 2.6 MJ/litre of surplus electricity is generated and sold to the grid, however, in the future case extra electricity needs to be purchased from the grid to supply the refinery. The results in Table 6.6 show that from an energy conservation perspective, it is better to use bagasse for electricity generation instead of ethanol production in such a refinery.

6.4 Conclusions and Recommendations

In the first part of this paper five studies on LCA of ethanol from lignocellulosic feedstocks are summarized. Seven impact categories are used for assessment and the results from different studies are compared per category. One interesting outcome is that ODP scores are quantitatively irrelevant in all cases, even if attributing a very high weight to this impact category. One limitation of the current method for life cycle impact assessment is that it does not reckon with the contribution of N₂O emissions to ODP, as recent findings show that N₂O now has become the major cause of depletion of ozone layer (Ravishankara et al., 2009).

In terms of GWP when economic allocation is applied, switchgrass is the best energy crop, followed by sugarcane. In both cases significant reductions of GHG emissions are achieved, which attributes to the CO₂ uptake in the agriculture. The electricity surplus generated in the switchgrass-ethanol refinery also helps reduce the GHG emissions in the life cycle of ethanol fuels. The application of ethanol fuels from stover, shives and hurds leads to worse performance than gasoline, due to the small partitioning factors based on economic allocation in the agriculture. When the ‘CO₂-netural’ approach is applied, reduction of GHG emissions is achieved by ethanol fuels from all feedstocks, compared to gasoline. Sugarcane, in this approach, becomes the most favourable feedstock, followed by switchgrass.

Sugarcane-derived ethanol turns out to be the best option in terms of ADP, ODP and POCP. Its less energy intensive agriculture and ethanol production process lead to less fossil resource extraction and related emissions which contributes POCP significantly. Ethanol derived from corn stover and flax shives shows modest performance, and hemp hurds and switchgrass are unfavourable feedstocks in these three categories.

In the category of HTP and ETP, AP and EP, flax shives-derived ethanol shows the best environmental performance among all the ethanol fuels. As the agricultural practices, especially the production machineries and the application of fertilizers, contribute most to these impacts, flax shives share only small part of environmental burdens due to its small allocation factor (0.042); thus it becomes the most promising feedstock.

In many impact categories (GWP, POCP, HTP and ETP, AP and EP) ethanol fuels as a whole does not show advantages over gasoline, which means that strong promotion of bioethanol as a transport fuel needs to be carefully (re)considered. More advanced technologies with optimization of energy use and emissions in both the agriculture and the ethanol refinery still need to be developed to reduce the current relatively high scores.

It is worth noting that in the sugarcane-ethanol study, ethanol is converted from both sugar and bagasse, as it is proposed to be the common practice in the future in Brazil. In the future research, in order to know whether bagasse is a promising lignocellulosic feedstock, environmental performance of ethanol fuels from bagasse shall be studied.

The choice of allocation methodology is essential for the outcomes especially related to GHG emissions. As this is an important issue and one of the main reasons for considering biofuels as a replacement of fossil fuels, it should be given special attention in life cycle based studies of biofuels. In order to support decision making, a sensitivity analysis shall always be conducted whenever more than one allocation methods can be applied. Furthermore, the results from the 'CO₂-neutral' approach seem to be more realistic, as GWP levels are highly affected by the allocation methods applied. It is important that LCA practitioners realize this and deal with it in an appropriate manner.

Although the LCA results from only five studies are compared, these five feedstocks can, to certain extent, represent other lignocelluloses. This paper gives an indication on the environmental performance of the second-generation bioethanol as a whole in comparison with gasoline; hence it contributes significantly to the current debate on the importance of biofuels in a future energy mix.

The second part of this paper summarizes the net energy values from ethanol-derived from stover and sugarcane and compares them with literature values. Two approaches are considered – excluding and including co-product energy credits. This is in fact similar to the allocation issue which has been extensively discussed in the stover-ethanol

study (Luo et al., 2009a). In order to prevent applying allocation procedure, here the ‘including co-product credits’ is similar to the ‘system expansion’ approach in LCA studies; while ‘excluding co-product credits’ means ‘cut-off of co-products and wastes’.

When co-products are not included, three studies on corn-ethanol results in a negative NEV. The others results in positive values with different degrees. Sugarcane and lignocellulosic feedstocks are more favourable due to their less energy intensive agriculture practice and refining process. The low energy inputs in these ethanol refining processes are due to the steam and electricity co-generation inside the refineries. This suggests that co-generation of heat and power from process wastes is an important way to increase energy efficiency in the cellulosic ethanol process.

When the energy credits of all co-products are taken into account, all studies yield positive net energy values with the highest from stover-ethanol case. Accounting for the energy values of co-products especially corn, stover and sugar produced in different cases affects strongly the performance of most cases from an energy perspective. This issue of co-product credits is in fact similar to the allocation issue in LCA studies, but is only solved here in a different manner.

The results of the sugarcane-ethanol cases conducted by us show that it is better to use bagasse for electricity generation instead of ethanol production in such a refinery. Here we assume the ‘grid’ as the average electricity mix from the Ecoinvent database. If the electricity supplied by the grid can be produced fully from renewable sources in the future, the outcomes would be different.

The changes occurred after taking all co-products into account are striking in the case of ethanol derived from corn, stover and sugarcane (Hadzhiyska et al., 2009) due to the large amount of stover (not using corn), corn (not using stover) and sugar co-produced. Literature studies on energy assessment are not conducted in a consistent way when co-product energy credits are concerned. For instance, Pimentel and Patzek (Patzek, 2004; Pimentel and Patzek, 2005; Pimentel and Patzek, 2007) conclude negative NEV without accounting for the energy value of the co-products which can be produced from the ethanol life cycle. Farrell et al. (2006) reckon with the co-products from corn-ethanol biorefinery for these studies, but not the stover produced from agriculture. Our study shows the importance and urgency of developing a consistent and relevant methodology for energy analysis in biofuel research.

As we account for total energy inputs and outputs, which mean, no allocation method is applied, taking all co-products into account becomes essential. To assess the energy flow of only one main product, an allocation based on energy content may be applied in some cases, i.e. between corn and stover, and between ethanol and electricity. Nevertheless, for the combined production of ethanol and sugar, it is difficult as the energy values of sugar and ethanol do not belong to the same category (food vs. energy product).

Although we compare the studies on only four feedstocks, they are the representative in the debate on energy analysis of the first- and second-generation bioethanol. Irrespective of the methodology used, switchgrass and sugarcane seem to be good feedstocks for ethanol production due to their low energy input in the agricultural production and good environmental performance.

**Biorefining of Lignocellulosic Feedstock –
Technical, Economic and Environmental Considerations**

* This chapter is published in Bioresource Technology; In press. Co-authors: Ester van der Voet and Gjalt Huppes

Abstract

Biorefinery, an example of a multiple products system, integrates biomass conversion processes and equipment to produce fuels, power and chemicals from biomass. This study focuses on technical design, economic and environmental analysis of a lignocellulosic feedstock (LCF) biorefinery producing ethanol, succinic acid, acetic acid and electricity. As the potential worldwide demand of succinic acid and its derivatives can reach 30 million tons per year, succinic acid is a promising high-value product if production cost and market price are substantially lowered. The results of the economic analysis show that the designed refinery has great potentials compared to the single-output ethanol plant; even when the price of succinic acid is lowered or the capital investment is doubled. In terms of eco-efficiency, the LCF biorefinery shows better environmental performances mainly in global warming potential due to the CO₂ fixation during acid fermentation. The overall evaluation of the eco-efficiency depends on the importance attached to each impact category.

7.1 Introduction

Crude oil refinery started with distillation and ended up combining it with sophisticated reaction engineering to develop complex material and energy networks making use of every ounce from a barrel of oil. Facing the threat of oil depletion and climate change, a shift to renewable resources is being made to ensure long-term supplies. A biorefinery is a facility that integrates biomass conversion processes and equipment to produce fuels, power, and chemicals from biomass. It stands ready for the transformation with recovery of sugars being combined with a variety of new fermentation and thermochemical processes. Careful management and utilization of materials, products and wastes are desirable, making biorefinery a clear example of industrial symbiosis – resource sharing and by-product (waste) exchange among nearby industries within the network. This type of network activity seems often to have both environmental and economic benefits, and it may include mechanisms for making industry more sustainable (Realf and Abbas, 2004). By producing multiple products and integrating waste treatment, biorefineries can maximize the values derived from biomass feedstocks and turn biomass processing into real opportunities.

Three types of biorefineries known as phase I, II and III have been described by Kamm and Kamm (2004) and van Dyne et al. (1999). The phase I and II biorefinery plants use grain as feedstocks such as corn and wheat. The difference is that phase I biorefinery has fixed processing capabilities and produces a fixed amount of ethanol and other feed products, while phase II biorefinery has the capability to produce various end products and has far more processing flexibility. Typical examples for phase I and II biorefinery are corn dry milling and corn wet milling, respectively. The latter one uses corn as the feedstock and produces multi-products such as gluten feed, high fructose corn syrup (HFCS), starch, glucose and dextrose, ethanol, gluten meal, and corn oil. A phase III refinery, the most promising to be developed, uses a mix of biomass feedstocks and yields an array of products by employing combination of technologies (Kamm and Kamm, 2004). It allows a mix of agriculture feedstocks, has the ability to use various types of processing methods, and has the capability to co-produce a mix of high-value chemicals in low volume while producing a bulk product like ethanol in high volume.

The phase III biorefineries may combine whole-crop, green and lignocellulosic feedstock (LCF) biorefineries. A whole-crop biorefinery consumes and processes the entire crop to obtain useful products. A green biorefinery is a multi-product system which handles natural wet feedstocks derived from untreated products such as grass, green plants or green crops as inputs. In an LCF biorefinery, cellulosic biomass or wastes is initially cleaned and degraded into three fractions (cellulose, hemicellulose and

lignin) via chemical digestion or enzymatic hydrolysis. The cellulose and hemicellulose are further processed to produce useful products such as fuels and chemicals, and the lignin has only limited uses, such as a fuel for direct combustion to generate steam and electricity.

The development and perspectives of LCF biorefineries have been extensively discussed in the literature studies. Kadam et al. presented a biorefinery converting corn stover into fuel ethanol, dissolving pulp and lignin for resin production (Kadam et al., 2008); Kaparaju et al. (2009) established a biorefinery framework producing bioethanol, biohydrogen and biogas from wheat straw; Laser et al. (2009a; 2009b) also proposed several scenarios in which fuels, power and animal feed protein are produced in one biorefinery. All these studies indicate that multiple products biorefineries are the future of biomass refining. Furthermore, several studies have focused on environmental assessment of a LCF biorefinery (Cherubini and Ulgiati, 2010; Uihlein and Schebek, 2009); Lynd and Wang (2004) developed a product-nonspecific framework to evaluate the potential of bio-based products to displace fossil fuels. Nevertheless, none has focused on a detailed technical design combining with economic and environmental analysis of a refinery converting LCF to fuel, power and high-value chemicals.

The present study involves designing a LCF biorefinery producing ethanol, succinic acid, acetic acid and electricity from corn stover, and next analyzing the refinery from an economic and environmental point of view. This study aims at optimizing the biorefinery in terms of technology, energy efficiency and environmental impact, bridging technical process design to system analysis, and providing indications on the sustainability of such a refinery.

7.2 Description of the Design

The focus of this study is the technical design and system analysis of a phase III biorefinery – LCF biorefinery. In this section product selection and process design are discussed.

7.2.1 Product selection criteria

For product selection a portfolio of candidates needs to be developed. A set of criteria was defined to select products to be included in the portfolio. Candidates were evaluated against the following criteria to decide their inclusion in the portfolio (Landucci et al., 1994):

- High theoretical product yield from substrate
- Market interest in the product as an end product or important intermediate
- High product volume (current or potential)
- Non-food use
- Ability to be biologically synthesized from the common sugars derived from various forms of biomass

7.2.2 Selection of products

The primary product in this study is chosen to be ethanol, which is produced in large volume in the refinery. The reason for this choice is the current strong promotion of bioethanol as a transport fuel in both Europe and the U.S.. Ethanol produced from a bioprocess instead of a traditional chemical process fulfils all the aforementioned criteria, and currently is the most competitive liquid fuel option compared to gasoline.

Based on the similar selection criteria mentioned above, Landucci et al. (1994) made a product portfolio which consists of 40 products. Fourteen of the 40 were classified as near-term opportunity, which are alginate, citric acid, fumaric acid, gluconic acid, itaconic acid, lactic acid, lysine, malic acid, protease, pullulan, rhaman gum, scleroglucan, succinic acid and xanthan gum. Succinic acid is selected here to be the main chemical produced from the refinery due to its FRF (Fraction of Revenue for Feedstock) value and the judgment from a number of industrial experts.

Succinic acid is a common intermediate in the metabolic pathway of several anaerobic and facultative microorganisms. All the succinic acid producing bacteria from mixed-acid fermentations produce varying amounts of succinate as well as other products, including ethanol, lactic acid, acetic acid and formic acid. For instance, *Escherichia coli* produces succinate as a minor fermentation product, typically 0.12 mol/mol glucose (Wood, 1961). On the other hand, *Anaerobiospirillum succiniciproducens* forms succinate up to 1.2 mol/mol glucose (Nghiem et al., 1997; Samuelov et al., 1991). A recent study on a *Corynebacterium glutamicum* strain (Δ ldhA-pCRA717) shows that succinic acid is efficiently produced at high-cell density under oxygen deprivation with intermittent addition of sodium bicarbonate and glucose. The yields of succinic acid and acetic acid from glucose are reported to be 1.4 mol/mol and 0.29 mol/mol, respectively (Okino et al., 2008).

In the biorefinery designed in this study, ethanol is produced as a main bulk fuel; succinic acid is the main chemical; acetic acid is produced simultaneously from the mixed-acid fermentation as a by-product; steam and electricity are generated from

process wastes. An important reason for combining ethanol with succinic acid production is that the CO₂ emerging from ethanol fermentation can be utilized in the acid fermentation without emissions. This is of crucial importance from an environmental point of view.

7.2.3 Design of the refinery

After the products are selected, the issues concerning the design of the biorefinery are presented in this section. For technical design and mass balance we used SuperPro Designer[®] from Intelligen, Inc.

1) Feedstock availability

Biomass availability is a critical issue. Global bio-based production should be based on decreasing competition with food and land use, thus low-value agricultural co-products and wastes are more favourable than conventional products like corn. Corn stover, the crop residue in the corn field, is produced at a rate of 1 dry kg per dry kg of corn grain. To avoid conflicts between food/feed uses and industrial uses of crops, the U.S. Department of Energy (DOE) is interested in utilizing part of the stover for ethanol production, competing with fodder only. Proponents of stover use claim that as much as 60% of the gross stover produced each year can be collected and converted to fuel ethanol (Sheehan et al., 2002) while maintaining soil productivity. Under this practice, 312 Tg of dry corn stover are globally available for further processing. The technology to produce ethanol from stover has already been studied by NREL (Aden et al., 2002). Lignin-rich fermentation residues are generated during corn stover-based processing to bioethanol (McAloon et al., 2000). These residues can be used for steam and electricity co-generation. In this study corn stover is selected as the feedstock. Other cellulosic feedstocks such as straw, sugarcane bagasse, switchgrass, and woodchip can also be utilized, but research on specific processing technologies is required.

2) Location and scale

The LCF biorefinery is assumed to be located in the middle of the Corn Belt farmland, State of Iowa, mid-west of the United States, to minimize transport distances. The stover is collected within an 80 km (50 miles) radius around the refinery (Aden et al., 2002). The harvested stover is transported by lorries. The capacity of the refinery and the prices of the feedstock and products are given in Table 7.1a.

Table 7.1a Production capacity of the biorefinery and price of the feedstock and products

Component	Amount	Price	Proceeds (million \$/yr)	Reference
Corn stover	1,581,203 tons/yr	0.033 \$/kg	52.18	Graham et al., 2007
Ethanol	170,729 tons/yr	0.357 \$/kg	60.95	Lynd et al., 2005
Succinic acid	294,819 tons/yr	1.000 \$/kg ^a	294.82	This study
Acetic acid	12,615 tons/yr	0.700 \$/kg	8.83	ISIC Pricing
Electricity	122,469,863 kWh/yr	0.110 \$/kWh	13.47 ^b	Saving Electricity, 2009

^a The current market price is 5.90 \$/kg (Lynd et al., 2005), the description of the assumption of 1.0 \$/kg is given in Section 7.3.1.

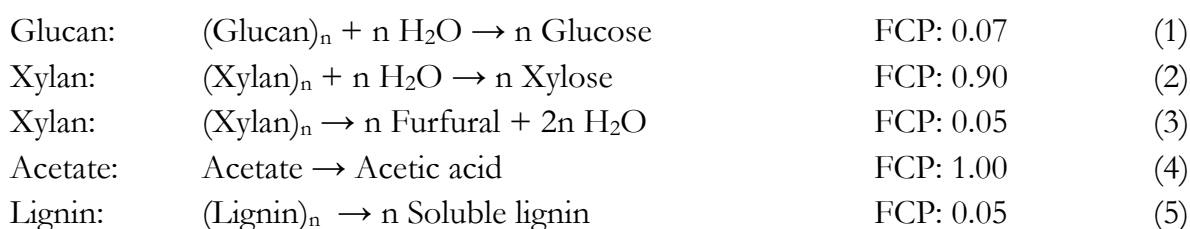
^b In case of the use of co-produced electricity in the plant itself, this represents avoided costs.

3) Process overview and design

The refinery is designed to operate 24 h per day, and 335 days (11 months) per year continuously. The remaining 1 month is for cleaning-up and restarting the operations. As crop residues are harvested and transported at different time of the year, long-term storage is required to provide feedstocks to the plant year-round. The life time of the refinery is assumed to be 20 years. The process overview is shown in Figure 7.1.

Feedstock handling and pretreatment

The aim of feedstock handling is feedstock washing and size reduction. Different pretreatment methods including physical, chemical, thermo-chemical and biological treatment have been reviewed by Sun and Cheng (2002). Dilute acid pre-hydrolysis is selected for the pretreatment of corn stover following the choice of Aden et al. (2002). The pretreatment step, in which dilute sulphuric acid and high temperature (190 °C) are engaged, converts most of the hemicellulose portion to soluble sugars – primarily xylose, arabinose, mannose and galactose. Glucan in the hemicellulose and a small portion of the cellulose are converted to glucose. The main reactions and the Fractions Converted to Product (FCP) in the pre-hydrolysis are given in Eqs. (1)–(5). The other hemicellulose carbohydrates (arabinan, mannan, and galactan) are assumed to have the same reactions and conversions as xylan.



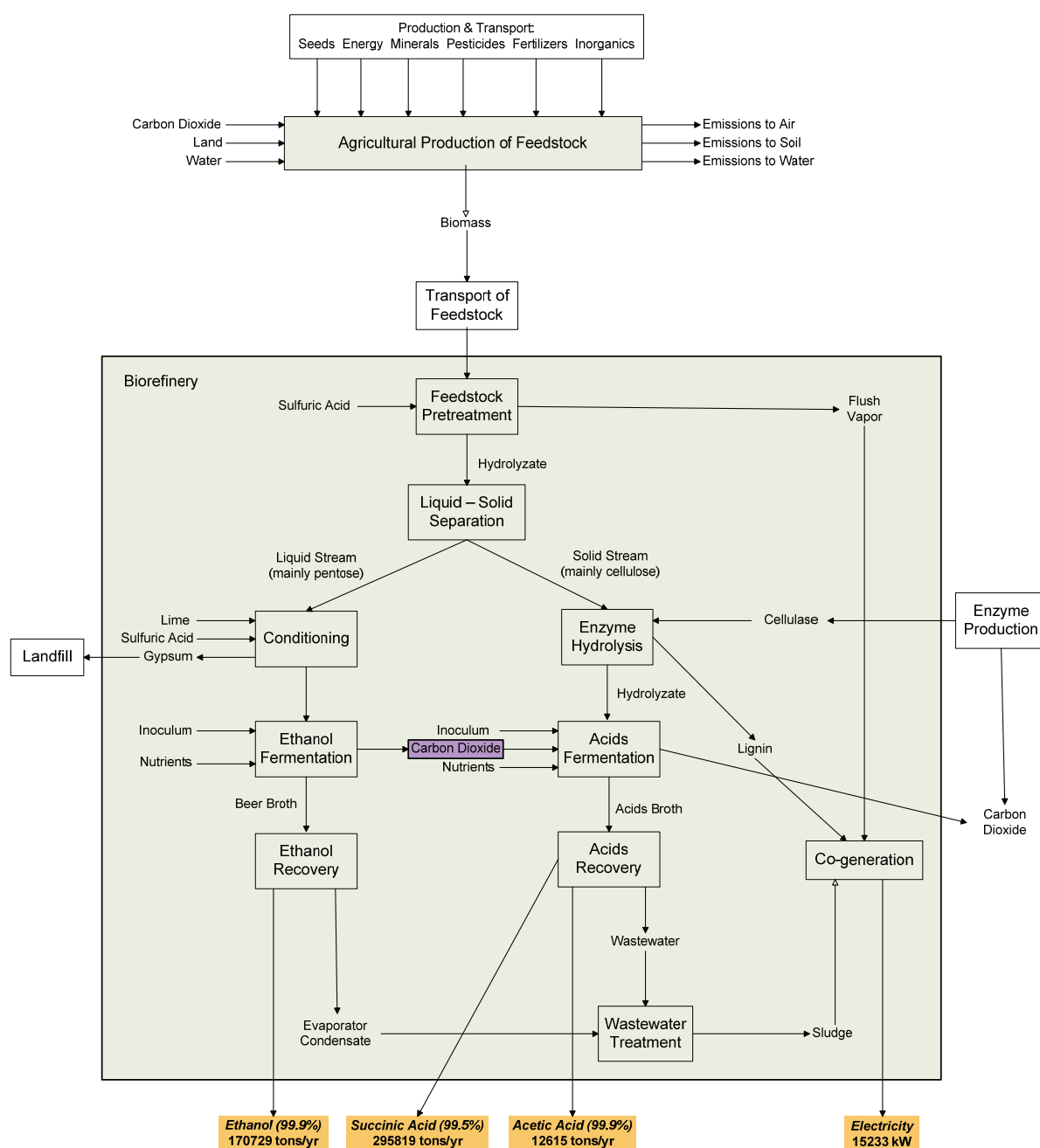


Figure 7.1 Process flow scheme of the LCF biorefinery

Bioconversion

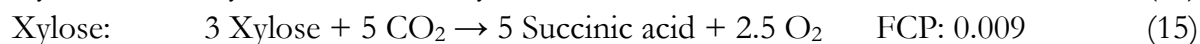
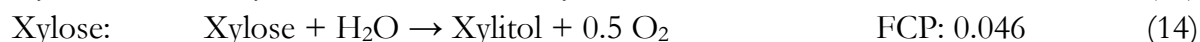
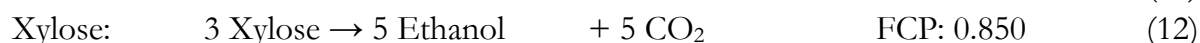
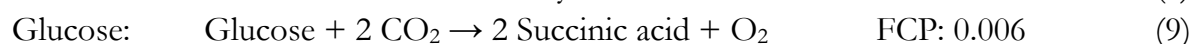
Following the pretreatment, a liquid-solids separation removes cellulose (solids) from the soluble sugars, which are then sent to fermentation for ethanol production. The cellulose is sent to saccharification, where cellulase enzyme is used to obtain mainly glucose. Cellulase enzyme is a collection of enzymes, which is comprised of endoglucanases for polymer size reduction, exoglucanases for crystalline cellulose

hydrolysis, and β -glucosidase for cellobiose hydrolysis to glucose. The most common organism used to produce cellulase industrially is *Trichoderma reesei*. The reaction and FCP in the enzyme hydrolysis are shown in Eq. (6).

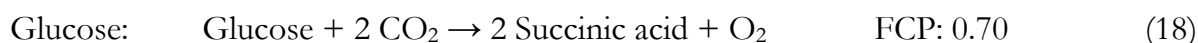


The glucose after enzyme hydrolysis is converted to succinic acid (main product) and acetic acid (co-product) by fermentation. The reason for this choice is that genetically modified strains have been developed to ferment both hexose and pentose sugars to ethanol; however, succinic acid production is still limited in using natural strains as biocatalysts, most of which can only utilize glucose. Depending on the market demand of succinic acid, the ratio of cellulose for the production of ethanol versus succinic acid can be determined.

There are various recombinant microorganisms that can utilize both pentose and hexose sugars. The main disadvantages of these organisms are their low productivities and stabilities. Recombinant *Zymomonas mobilis* is a promising bacterium for future ethanol production (Zhang et al., 1995), and it has been selected in this study for fermentation of pentose to ethanol. It is assumed that all the major pentose sugars (xylose and arabinose) are fermented together. The reactions and FCPs are given in Eqs. (7)-(17).



For the fermentation of glucose to succinic acid and acetic acid, recombinant *Corynebacterium glutamicum* is chosen as the biocatalyst because it forms succinic acid in a high concentration of about 146 g/l under anaerobic conditions in the presence of carbon dioxide (Okino et al., 2008). The reactions and FCPs are given in Eqs. (18)-(19).



Downstream processing

For the ethanol recovery, distillation and molecular sieve adsorption are used to produce 99.9% ethanol. Distillation is accomplished in two columns – the first, called the beer column, removes the dissolved CO₂ and most of the water, and the second concentrates the ethanol to a new azeotropic composition. All the water from the nearly azeotropic mixture is removed by vapour phase molecular sieve adsorption. The fermentation vent (containing mostly CO₂, but also some ethanol) and the beer column are scrubbed in a water scrubber, recovering nearly all of the ethanol. The vent from the scrubber (mostly CO₂) is compressed and sent to the fermenter for succinic acid production.

An emerging technology, which holds higher potential for commercialization and environmentally friendly processes for succinic acid purification, is simultaneous acidification by ion-exchange resins and a crystallization process (Zeikus, 1995). This technology is selected due to its cost-effectiveness and ease of scaling up to commercial use. Nevertheless, the major limitation of this process is that the membranes cannot handle divalent cations; therefore, the fermentation is neutralized with sodium hydroxide, forming soluble sodium succinate during the fermentation. The whole broth is filtered with a microfiltration unit to separate the cells and large insoluble particles from the succinate broth. The filtered sodium succinate is fed to a batch desalting electrodialysis unit, where the ionic species are separated from the non-ionic ones (sugars) and molecules with large molecular masses. The sodium succinate solution is then fed to a batch bipolar membrane electrodialysis unit where the ionic species are converted to their equivalent acid and base forms and separated. Sodium ions are transported across the cation membrane and associate with the hydroxyl ions to form sodium hydroxide, which is reused for fermenter neutralization. After succinic acid is purified (99.5%), a further distillation is engaged to purify acetic acid to 99.9%.

Part of the evaporator condensate, along with other wastewater from the plant is treated by anaerobic and aerobic digestion in the wastewater treatment section. The biogas (high methane concentration) from anaerobic digestion is sent to the combustor for energy recovery. The treated water is suitable for recycling and is returned to the process to use.

The solids containing lignin from the distillation, the concentrated syrups from the two production recovery systems, the biogas and the sludge from the wastewater treatment

are combusted in a fluidized bed combustor to produce high-pressure steam for electricity generation and process heat. Generally, the process produces excess steam that is converted to electricity for use in the plant and for sale to the grid.

4) Logistics

As mentioned previously, corn stover is transported by lorries. On-site short-term storage is provided equivalent to 72 h of production at an outside storage area. The stored material provides a short-term supply for weekends, holidays, and when normal direct delivery of material into the process is interrupted. The material will be rotated continuously, with a first-in, first-out inventory management strategy.

Except corn stover, other chemicals needed for the production are purchased from the closest production sites in order to shorten the transport distance. Only if the prices are comparatively high, longer distance transportation will be considered. In this study, we assume the electricity generated in the refinery is one co-product; while the electricity required is purchased from the grid. An alternative is, assuming that the produced electricity is used in the process and either the excess is sold to the grid, or the additionally required electricity is bought from the grid. Product and feed chemical storage section includes the storage of ethanol, succinic acid, acetic acid, chemicals needed for the plant, cellulose enzyme, and water for fire suppression.

The stored ethanol is transported to the nearby refinery to be blended into gasoline to produce biofuels. The acetic acid can be sold to the chemical industries. The succinic acid can be sold directly, or a flexible production section can be established in the biorefinery to produce other products from succinic acid according to the market demand. Whenever changes in the market occur, the production line can be switched easily from one to another.

7.2.4 Market analysis

As succinic acid is the main high-value chemical produced from the refinery with large quantity, market analysis of succinic acid is of crucial importance. Today, succinic acid is mainly produced by chemical process from *n*-butane/butadiene via maleic anhydride (Bechthold et al., 2008). There are four major existing markets for succinic acid: (1) as a surfactant/detergent; (2) as an ion chelator, where it is used in electroplating to prevent corrosion and pitting of metals; (3) food market, where it is used as an acidulant/pH modifier, as a flavouring agent, and as an anti-microbial agent; (4) the production of health-related agents, including pharmaceuticals, antibiotics, amino acid and vitamins (Zeikus, 1999). The current world market for succinic acid is negligibly small. At present

about 25,000 tons of succinic are produced worldwide; the market is growing by about 10% per year (BIOPRO). This is particularly due to the high conversion cost of maleic anhydride to succinic acid by the chemical process, which keeps the price high and limits the use of succinic acid for a wider range of applications.

However, beyond fossil-based chemistry, succinic acid can be used as a precursor of many industrially important chemicals including adipic acid, 1,4-butanediol, tetrahydrofuran, *N*-methyl pyrrolidinone, 2-pyrrolidinone, succinate salts and gamma-butyrolactone (Song and Lee, 2006). Furthermore, the increasing demand for succinic acid is expected and its use is extended to the synthesis of biodegradable polymers such as polybutyrate succinate (PBS) and polyamides (Nylon[®]x,4) (Willke and Vorlop, 2004) and various green solvents (Rudner et al., 2005). The market demand of several derivatives of succinic acid has been studied. The chemical industry produces about 900,000 tons petro-based 1,4-butanediol per year (BIOPRO, 2009); more than 230,000 tons of gamma-butyrolactone are produced worldwide (McKinlay et al., 2007); the estimated potential market size for the polymers polysuccinate esters and polyamides that can be synthesized from succinic acid is up to 27 million tons per year in 2001 (Baum and Engelmann, 2001). Therefore, the worldwide demand of succinic acid and its derivatives can reach 30 million tons per year, and probably will keep growing. The succinic acid produced from the refinery designed in this study is about 295,000 tons per year, which only accounts for about 1% of the potential worldwide demand. This suggests that the designed biorefinery has a reasonable scale in terms of the quantity of its outputs.

7.3 System Analysis

The system analysis in this study focuses on environmental and economic aspects. Social aspects are left out of research. In this section an economic analysis and eco-efficiency estimation are presented.

7.3.1 Economic analysis

First of all, bio-based products must be made at competitive costs, which means, the biorefinery has to be profitable. Otherwise, there will be no market for the products even though they are made from renewable resources.

In this study an economic analysis has been conducted to estimate the net present value (NPV) and internal rate of return (IRR), which is based on the capital investment, and on the variable and fixed operating costs of the refinery. The discount rate for this analysis was set at 10%, which was selected based on the recommendation by Short et al.

(1995). The construction period of the refinery is assumed to be 3 years. The first year expense is the engineering, construction and contingency costs. In the second year 80% of the total capital investment is assumed to be made and the investment is finished in the third year. It is assumed that the refinery starts to be operated at 75% capacity in the third year, and at full capacity (11 months per year) in the rest of the life time.

The current market price of succinic acid is found to be \$5.90/kg (Lynd et al., 2005). This high price is particularly due to the high conversion cost of maleic anhydride to succinic acid by the chemical process route. When adding substantially higher amounts of products to the market, the market price will collapse to a level where other applications can take up the large volumes. As succinic acid can be the precursor of several commodity chemicals which are produced in large quantity by chemical processes, the market price of succinic acid is expected to be drastically lowered to the level where it can take over the market. The price of 1,4-butanediol is \$2.76/kg in 2004 (McKinlay et al., 2007), and it can be produced from succinate in a two-step process (Paster et al., 2003). In order to assess whether the refinery would be competitive in a substantially extended market, we calculate with a price of \$1.00/kg, the price of succinic acid is substantially lower than the present price of 1,4-butanediol. In addition, we perform a sensitivity analysis for the price of succinic acid to assess its impact on the economic viability of the operation.

The results of the economic analysis were compared with the ones from the ethanol plant designed by Aden et al. from NREL (Aden et al., 2002). The production capacity of the ethanol plant and the prices of the feedstock and product are given in Table 7.1b. As our refinery aims at producing larger amount of high-value products (succinic acid), the market price of succinic acid will strongly affect the economic viability of the refinery. Moreover, the production costs of the refinery may have been underestimated, as novel designs tend to come out more expensive than originally planned. Hence, sensitivity analyses were conducted on the capital investment, the market price of both succinic acid and ethanol, and the purchase price of the feedstock corn stover.

Table 7.1b Production capacity of the ethanol plant and price of feedstock and product

Component	Amount (tons/yr)	Price (\$/kg)	Proceeds (million \$/yr)	Reference
Corn stover	821,183	0.033	27.10	Graham et al., 2007
Ethanol	206,770	0.357	73.82	Lynd et al., 2005

7.3.2 Environmental impact assessment

For the environmental performance of the refinery the full production system is assessed, ‘cradle-to-gate’. The following impact categories are taken into account, and the software package (CMLCA, 2009) is used for environmental analysis. This environmental impact assessment is performed to obtain a first idea of the benefits of biorefineries in that area.

- Abiotic resource depletion potential (ADP)
- Global warming potential (GWP)
- Ozone layer depletion potential (ODP)
- Photochemical oxidation potential (POCP)
- Human toxicity potential (HTP)
- Eco-toxicity potential (ETP)
- Acidification potential (AP)
- Eutrophication potential (EP)

7.3.3 Comparison of eco-efficiency

In this study eco-efficiency is defined as ‘emissions per unit of output’, as in line with the definition made by the World Business Council (Schmidheiny, 1992). This represents the environmental intensity of production, thus the lower the eco-efficiency number the better the performance. The total output is defined as the total of all values (summation of the market prices of all the products, expressed in dollar) derived from the refinery. As we account for the total production from the refinery, no allocation of emissions is needed among products. However, for the ‘cradle’ of the analysis, agricultural production, all inputs and emissions need to be allocated between corn and stover, and in this case economic allocation is applied, as is usual in managerial cost allocation as well.

A research question is raised as ‘How are the economic feasibility and environmental performance compared to a single product ethanol production plant?’ In order to project the environmental potential of such a refinery system, the results of eco-efficiency of the biorefinery were compared with the ones from the ethanol plant designed by Aden et al. from NREL (Aden et al., 2002). In the ethanol plant corn stover is converted to ethanol using advanced cellulosic technology, and the steam and electricity required is generated from lignin and wastes. There is no co-product or surplus of electricity; hence ethanol is the only product. In both the biorefinery designed in this study and the ethanol plant designed in NREL advanced technologies have been used and the processes have been optimized. As the capacity of the biorefinery in terms of feedstock handling is twice as high as for the ethanol plant, the capital investment

and operating cost of the biorefinery are much higher resulting in incomparable NPV. Nevertheless, the values of IRR from both systems are well comparable.

As blends of ethanol and gasoline with different percentage are already used in practice as transport fuels, it is important to also compare the eco-efficiency of biorefinery and ethanol plant with the gasoline refinery. The current market price of gasoline is around \$2.70/gallon including excises (EIA). In this comparative study the use phases of all the products are not taken into account.

7.4 Results

In this section the results of the system analysis are presented including economic analysis and its sensitivity analyses, environmental impact assessment, and the comparison of eco-efficiency of gasoline refinery, ethanol plant and biorefinery designed in this study.

7.4.1 Economic analysis

The basis for determining the breakdown of the production costs of the biorefinery is the method used by Aden et al. (2002). The description and the results including fixed capital investment, variable and fixed operating costs are given in Table 7.2.

The results of NPV and IRR in comparison with the ones from the ethanol production plant are given in Table 7.3.

The capital investment, variable and fixed operating costs of the ethanol plant were estimated in the NREL report (Aden et al., 2002). The internal rate of return (IRR) is the value of the discount rate for which the net present value is null. Generally speaking, the higher the IRR of the project, the more desirable it is to be undertaken. In the study by Aden et al. (2002), IRR is estimated to be 13%. In another study the IRR of an ethanol plant is reported as 20-30% (Efe et al., 2005), but assumptions may have been made differently, which is the reason why it is not used as a reference for comparison in our study. It can be seen that the biorefinery is economically much more viable than the ethanol plant as its high IRR (46%) shows. This is mainly due to the cost reduction of combined installations and the market price of high-value chemicals.

The results of sensitivity analysis on the capital investment, the market price of succinic acid and ethanol, and the purchase price of corn stover are given in Table 7.4.

Table 7.2 Cost breakdown of the biorefinery

Item	Description	Amount	Unit
Capital investment		388.75	million \$
Total installed cost	Cost of installed equipment, warehouse and site development	238.79	million \$
Prorateable costs	10% of total installed cost	23.88	million \$
Field expenses	10% of total installed cost	23.88	million \$
Home office and construction fee	25% of total installed cost	59.70	million \$
Project contingency	3% of total installed cost	7.16	million \$
Other costs	10% of the aforementioned costs	35.34	million \$
Variable operating costs		111.20	million \$/yr
Materials and chemicals	Feedstock and process chemicals	65.75	million \$/yr
Energy costs*	Mainly electricity (47,591 kW)	42.09	million \$/yr
Waste handling charges		3.36	million \$/yr
Fixed operating costs		14.78	million \$/yr
Total salaries		4.30	million \$/yr
General overhead	60% of total salaries	2.58	million \$/yr
Maintenance	2% of installed equipment cost	4.32	million \$/yr
Insurance and taxes	1.5% of total installed cost	3.58	million \$/yr

* Here it refers to the electricity purchased from the grid for the operation of the biorefinery. In case the co-produced energy is used within the plant, these costs would be \$13 million/year lower, and the proceeds would also be reduced with the same amount.

Table 7.3 Comparative results of the biorefinery and the ethanol plant from economic analysis

Items	Biorefinery	Ethanol plant
Capital investment (million \$)	388.75	197.40
Variable operating costs (million \$/yr)	111.20	41.50
Fixed operating costs (million \$/yr)	14.78	7.54
NPV (million \$)	1,695.48	59.72
IRR (%)	46	13

Table 7.4 Results of sensitivity analysis on (a) capital investment (b) price of succinic acid (c) price of ethanol (d) price of stover

(a)			
	Capital investment (million \$)	NPV (million \$)	IRR (%)
Present case	388.75	1,695.48	46
Scenarios I (2x)	777.50	1,276.87	26
Scenarios II (4x)	1,555.00	439.65	13
Ethanol plant	197.40	59.72	13

(b)			
	Price of succinic acid (\$/kg)	NPV (million \$)	IRR (%)
Present case	1.0	1,695.48	46
Scenarios I (0.5x)	0.5	474.00	23
Scenarios II (2x)	2.0	4,138.43	79
Ethanol plant	-	59.72	13

(c)			
	Price of ethanol (\$/kg)	NPV (million \$)	IRR (%)
Present case	0.357	1,695.48	46
Scenarios I (0.5x)	0.179	1,442.95	42
Scenarios II (2x)	0.714	2,200.53	54
Ethanol plant	0.357	59.72	13

(d)			
	Price of corn stover (\$/kg)	NPV (million \$)	IRR (%)
Present case	0.033	1,695.48	46
Scenarios I (1.5x)	0.050	1,514.66	43
Scenarios II (2x)	0.066	1,333.85	40
Ethanol plant	0.033	59.72	13

It can be seen that when the capital investment becomes twice as high as the current value, the refinery can still profit (IRR 26%) because the usual IRR is reported as 20-30%. However, when it becomes four times as high, the biorefinery does not show any advantage over the ethanol plant.

Increased market price of succinic acid brings more profit (IRR 79%), and even when the price decreases to half a dollar, the IRR is (23%) still much higher than the one of the ethanol plant. The fluctuations in ethanol price give less significant changes in NPV and IRR. In the future the price of the harvested stover is expected to increase; however,

this increase does not affect the profit significantly due to the high-value derived from the refinery, and affect the ethanol plant similarly.

7.4.2 Environmental impact assessment

The environmental performance of the biorefinery, ethanol plant and gasoline refinery per impact category is given in Table 7.5. These results cannot be directly compared due to the difference in products and plant capacity of the three systems. Nevertheless, they can act as basic information for the further estimation of the eco-efficiency of the biorefinery, as is done below in Section 7.4.3. Such an eco-efficiency analysis enables a comparison with other production systems as well.

Table 7.5 Environmental performance of the three refineries
(a) biorefinery (b) ethanol plant (c) gasoline refinery

(a)		
Impact category	Value	Unit ^a
ADP	4,596,025	kg antimony eq./yr
GWP	-260,771,475	kg CO ₂ eq./yr
ODP	46	kg CFC-11 eq./yr
POCP	386,974	kg ethylene eq./yr
HTP	165,470,547	kg 1,4-dichlorobenzene eq./yr
ETP	231,594,742	kg 1,4-dichlorobenzene eq./yr
AP	5,981,320	kg SO ₂ eq./yr
EP	987,018	kg PO ₄ --- eq./yr
(b)		
Impact category	Value ^b	Unit
ADP	3.25×10 ⁻³	kg antimony eq./kg ethanol
GWP	2.18	kg CO ₂ eq./kg ethanol
ODP	9.64×10 ⁻⁸	kg CFC-11 eq./kg ethanol
POCP	1.74×10 ⁻³	kg ethylene eq./kg ethanol
HTP	1.13×10 ⁻¹	kg 1,4-dichlorobenzene eq./kg ethanol
ETP	2.16×10 ⁻¹	kg 1,4-dichlorobenzene eq./kg ethanol
AP	6.88×10 ⁻³	kg SO ₂ eq./kg ethanol
EP	1.28×10 ⁻³	kg PO ₄ --- eq./kg ethanol

(c)

Impact category	Value ^c	Unit
ADP	2.62×10^{-2}	kg antimony eq./gasoline
GWP	7.00×10^{-1}	kg CO ₂ eq./ gasoline
ODP	4.72×10^{-7}	kg CFC-11 eq./ gasoline
POCP	1.78×10^{-3}	kg ethylene eq./ gasoline
HTP	1.89×10^{-1}	kg 1,4-dichlorobenzene eq./ gasoline
ETP	4.13×10^{-2}	kg 1,4-dichlorobenzene eq./ gasoline
AP	8.05×10^{-3}	kg SO ₂ eq./ gasoline
EP	6.65×10^{-4}	kg PO ₄ --- eq./ gasoline

^a As multiple products are produced in the refinery, the ‘environmental impact per year’ is used as unit.

^b Data obtained from Luo et al., 2009a.

^c Data obtained from the Ecoinvent database: <http://www.ecoinvent.org/>.

7.4.3 Comparison of eco-efficiency

The comparative results of the three aforementioned systems are shown in Figure 7.2. Internal normalization is performed by setting the results from gasoline refinery to 1 and the ones from biorefinery and ethanol plant can therefore be compared. As the eco-efficiency in this study is defined as ‘emissions per dollar of output’, lower eco-efficiency values represent better performance of the system.

The most striking result comes from GWP. In this category, the negative value for the biorefinery does not indicate a worse performance, but a substantially better one. In the biorefinery, a large fraction of the CO₂ emitted by the ethanol fermentation process is fixed by acid fermentation. Moreover, the use phase of the different products is not included in the study. This leads to negative GHG emissions, as can already be seen in Table 7.5¹. This shows that the combined production of ethanol and succinic acid is indeed a more promising option. The reason why the eco-efficiency of the ethanol plant is significantly worse than that of the gasoline refinery is twofold: (1) the contribution of agriculture related emissions to the total, which is significant and does not occur in the gasoline refinery², and (2) the market price of ethanol (\$0.36/kg) is much lower than

¹ In case the co-produced electricity is used on-site, the GHG emissions would be even more negative, as less fossil electricity would have to be obtained from the grid. The difference would be in the order of magnitude of 100,000 kg CO₂-eq. or 0.05% of the total.

² Due to the application of economic value based allocation between corn and stover in the agriculture, a small part of agricultural emissions are allocated to the corn stover. The effect of different allocation methods has been extensively studied in one of our previous papers (Luo et al., 2009a).

gasoline (\$0.98/kg), which however includes some excises. The price before excises is substantially lower, depending on state and country. Therefore, more value per kg of GHG emissions is created by gasoline refining.

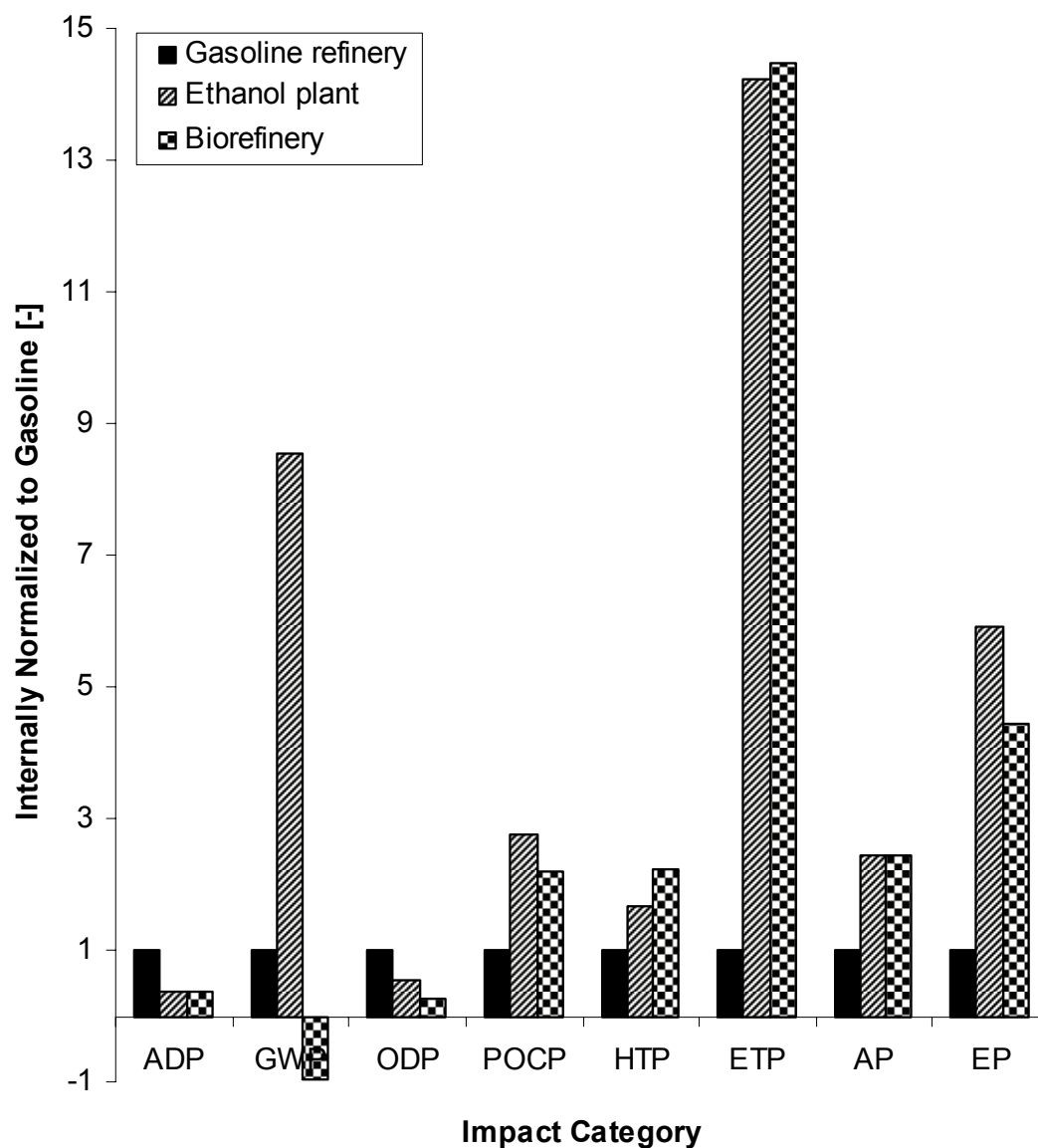


Figure 7.2 Comparative results eco-efficiency for the three production systems (lower values represent better results)

The eco-efficiencies of the biorefinery and the ethanol plant are better than the one of gasoline refinery in the category of ADP and ODP. This is obviously due to the replacement of fossil resources by renewables – corn stover in this case. Crude oil, natural gas, and coal are the main contributors to abiotic resource depletion, while the

ODP level is mainly contributed by the emissions from the crude oil production onshore.

In the rest of the impact categories, biorefining performs worse than gasoline refinery. In biorefinery and ethanol plant, although emissions causing POCP from natural gas production and oil exploitation decrease, the ones from ethanol production contribute even more to POCP level. Moreover, agriculture contributes largely to human and eco-toxicity, acidification, and eutrophication due to the use of agrochemicals; thus, gasoline is a better option in terms of these impacts.

In most of the impact categories the biorefinery has a better eco-efficiency than ethanol plant, which is attributed to the high-value of the succinic acid derived from such a refinery. In terms of human toxicity the result is opposite – the ethanol plant has slightly better eco-efficiency. The emissions of heavy metals to air and water from agriculture are the major contributor to human toxicity. As for both production systems corn stover is used as feedstock, the resulting difference might be due to the different emissions from the refining process.

The biorefinery designed in this study has clear advantages over the ethanol plant in terms of eco-efficiency. However, when comparing biorefining to gasoline refinery, the overall evaluation of the eco-efficiency depends on the importance attached to each impact category.

7.5 Discussion

In the present study the productions of low-value product ethanol and high-value product succinic acid are combined to maximize the values derived from biomass refining. Acetic acid is co-produced from succinic acid fermentation; hence it is also harvested as a co-product. Steam and electricity are generated from lignin residues and refinery wastes. Corn stover is selected as a lignocellulosic feedstock due to its high availability for non-food uses. From the feedstock handling and pretreatment till product purification, the refinery has been conceptually designed to provide technical process data for the environmental and economic analysis.

The systems analysis applied in this paper aims at estimating the net present value, internal rate of return and eco-efficiency of the biorefinery, compared to ethanol production and gasoline production. The economic model is based on discounted cash flow, which reflects a usual business approach. Sensitivity analyses provide indications on how profitable biorefining is.

No straightforward conclusion can be drawn with regard to the eco-efficiency analysis relative to gasoline. However, the GHG benefits of the biorefinery are remarkable compared to both the gasoline refinery and the ethanol plant. The eco-efficiencies of biorefinery and ethanol plant are better than the one of gasoline refinery in the category of ADP and ODP. For the rest of the impact categories, the gasoline refinery has the best performance. For all the impact categories except human toxicity and eutrophication, the biorefinery has a better eco-efficiency than the ethanol plant, which is attributed mainly to the high-values derived from such a refinery. The overall evaluation of the eco-efficiency thus depends on the importance attached to each impact category. A more substantial environmental analysis is needed to identify the hotspots in the chains, and therefore to suggest improvement options.

The price of gasoline used in this study includes excises; while for ethanol not excises but subsidies have been exerted. Therefore the outcomes are based on these assumptions. In the future if excises are exerted also on ethanol, the results of comparison will be much different.

From idea to operation of any new production is always time consuming due to a series of actions – innovation and research, technology transfer, business investment, conceptual process design, test in pilot scale, upscale and establishment of an operational plant. All these activities make the realization of such a biorefinery difficult but not impossible; ten years can be a good estimate to bring the products from our refinery into market.

The LCF biorefinery has been designed and optimized; process technologies and system analysis have been linked. However, due to the time limitation and scope of the study, some relevant issues have not been addressed, as follows:

- Corn stover is just one type of lignocellulosic feedstocks, but is produced with very high regional yields. The regional dependency of the feedstocks is of crucial importance, also outside the U.S.. Large amounts of the cellulosic biomass will have to be grown locally or cheap transport must be available, especially bulk water transport.
- The choice of the product combination is of crucial importance for biorefinery design. In this case ethanol and succinic acid are produced in the refinery together for one important environmental reason – CO₂ released by ethanol fermentation can be fixed by acid fermentation, which causes very substantial GHG benefits. This

should be an additional criterion in the list of product selection criteria mentioned in Section 7.2.1.

- The ratio of ethanol/succinic acid production selected in this study is only one choice. When the market changes, the shift from one product to the other is possible to full extent – one product line can be shut down completely or ready for the production of other fuels or chemicals, for instance, succinic acid can be replaced by the production of other dicarboxylic acids which can then be used in industrial polymerization processes. On the other hand, if 1,4-butanediol, polysuccinate esters or polyamides is produced from succinic acid in the refinery, more installations can be also added to serve the purpose. Moreover, acetic acid is one of the important bulk chemicals with already established market and reasonably high price (0.7 \$/kg) compared to ethanol, production of more acetic acid can always be profitable.
- The system analysis of the designed biorefinery firstly provides the absolute environmental and economic performance. Due to the difficulties in comparing these absolute values, an eco-efficiency indicator has been defined. The estimation and comparison of eco-efficiency give an indication on the relative performance of different production systems. In this type of study, in order to achieve better eco-efficiency one can increase profit of a refinery instead of reducing emissions to environment. This provokes the discussion on ‘strong sustainability’ and ‘weak sustainability’, a concept introduced by Daly (1990) and Dietz and Neumayer (2007), and is also recognized in the eco-efficiency field – see for example by Huppes and Ishikawa (2009). Methodology development for systems analysis of biorefining is still of crucial importance.
- Last but not least, two software packages are used separately – SuperPro Designer for technical process simulation and CMLCA for environmental assessment. The connection of these tools was made manually. In future studies, software development can help establish a linkage between process simulation and environmental assessment so that optimizations can be done in a more integrated way.

7.6 Conclusions

System analysis shows that the designed biorefinery has great potential in terms of profit compared to ethanol plant. Even when the price of the high-value succinic acid is lowered or the capital investment is doubled, the refinery is still highly profitable. Fluctuations in the price of ethanol and corn stover affect the profitability of the refinery less significantly. Eco-efficiency analysis shows a great reduction of greenhouse gas emissions due to the CO₂ fixation by acid fermentation, which indicates the

combined production of ethanol and succinic acid is indeed beneficial in a relative term (value created per unit of emissions).

General Discussion, Conclusions and Recommendations

8.1 General Discussion

The objective of this thesis is to address the role of biomass refining for sustainable development with a specific focus on environmental and economic analysis of refining of lignocellulosic biomass. To this end, three main research questions have been formulated:

- I. Is fuel ethanol from lignocelluloses better than gasoline, from an environmental point of view?
- II. How can bio-based production be optimized with regard to energy efficiency, environmental performance and economic feasibility?
- III. How can we design a methodology to achieve a more comprehensive sustainability assessment of biomass refining?

With regard to the first question, three chapters of this thesis are dedicated to comparative LCA with different focuses: *Chapter 2* addresses one of the most important methodological issues in LCA – allocation, using fuel ethanol from corn stover as a case study. *Chapter 3* compares the environmental performance and cost of sugarcane-derived fuel ethanol from two scenarios in Brazil: current practice – ethanol and sugar production from juice sugar, and electricity co-generation from the combustion of bagasse; future case – bagasse is also used for ethanol production, and electricity is generated from the combustion of lignin residues and plant wastes. *Chapter 4* focuses on LCA of another promising feedstock – switchgrass, and analyzes the changes in the environmental impact with regard to the choice of allocation, soil preparation and transport distance. *Chapter 6* summarizes and evaluates the results obtained from *Chapter 2, 3, 4* and two more studies with the same definition of system boundaries and using the same systematic allocation procedure.

The findings from these chapters present a clear case of problem shifting – solving one problem (oil depletion) at the expense of increasing others (mostly agriculture-related emissions). In most cases ethanol fuels perform better in terms of abiotic resource depletion and ozone depletion. However, gasoline shows advantages in the category of photochemical oxidation, acidification, eutrophication and toxicity aspects. The score on global warming depends very much on the type of feedstock used. The outcomes on different environmental themes, especially on global warming, furthermore depend on the allocation method applied. Nevertheless, it can be concluded that some feedstocks such as sugarcane and switchgrass are more promising for sustainable ethanol production than for example corn or corn stover. Improved agricultural practice and technology development of refining processes are of crucial importance for reducing

environmental impacts. For the real life choices on promoting biofuel against fossil gasoline an overall evaluation is required, which may be formalized based on setting weights for the different impacts. Without such weighting, it is impossible to conclude whether fuel ethanol from lignocelluloses is better than gasoline from an environmental point of view, and neither can clear statements be derived for a combined environmental and economic evaluation. It should be kept in mind as well that the analysis here concerns a direct systems analysis with an emphasis on pollution problems. Important impacts, such as land and water use, are not included. Moreover, indirect effects, as through induced shifts in staple markets for food and fodder have not been taken into account. These larger scale impacts require a larger scale analysis. In conclusion, there is no clear case for a strong promotion of even the second-generation bioethanol as a transport fuel, as this requires detailed value choices and depends on the method of analysis being used.

In relation to the second question on directions for optimization, first *Chapter 5* presents a detailed energy analysis on the corn stover-based ethanol system. The survey of energy inputs indicates the bottlenecks in the ethanol production chain – fertilizer production, tillage and harvesting in the agriculture, and pretreatment, enzyme production and product recovery in the biorefinery. The detailed investigation of the energy inputs in all the energy intensive processes provides the opportunity to optimize the system in terms of net energy gain. Also here, the set-up of the analysis, especially regarding system boundary choices and allocation methods, determines outcomes to a substantial degree.

Chapter 6 compares the net energy values (NEV) obtained from *Chapter 5* with the ones from selected literature studies on the same subject. The comparison of net energy values depends very much on whether or not the co-product energy credits are taken into account. The changes occurring after taking all the co-product energy credits into account are striking when the co-products have a large share in the total production. This is the case with ethanol derived from corn, stover and sugarcane due to the large amount of co-produced stover, co-produced corn and co-produced sugar, respectively. Literature studies on energy analysis are not conducted in a consistent way when co-product energy credits are concerned. For instance, Pimentel and Patzek (Patzek, 2004; Pimentel and Patzek, 2005; Pimentel and Patzek, 2007) conclude that the NEV of corn-based ethanol is negative, without reckoning with the energy value of the co-products which are produced in the ethanol life cycle. Farrell et al. (2006) do include the co-products from the corn-ethanol biorefinery for these studies, but not the stover co-produced from the agriculture. Our study shows the importance and urgency of developing a consistent methodology for energy analysis in biofuel research, at least

explicitly considering the methodological issues treated in the ISO14040-44 series (2006) for LCA.

Chapter 7 aims at designing a biorefinery producing fuel, chemicals and power in one plant and analyzing the environmental and economic potentials of such a refinery. For this analysis we partly left the domain of the strict LCA, by looking not at a functional unit (vehicle driving in all other studies) but at the total value created in the biorefinery. The value created then takes the role of the functional unit – one unit of function is one unit of value: one dollar (or a million dollars). In the conventional LCA, the outcomes are in terms of environmental effect per unit of function; here they are in terms of environmental effect per unit of value, often denoted as ‘eco-efficiency’. For the combined production in the biorefinery we chose succinic acid as one high-value product, combined with ethanol as the lower-value product in large volume. In environmental terms, the outcomes from the biorefinery analysis show considerable benefits with regard to greenhouse gas emissions, due to the carbon dioxide fixation by acid fermentation. The combined production of ethanol and succinic acid is indeed beneficial in terms of value created per unit of GHG emissions when compared to the alternative production routes. The potential impact score per dollar output of the biorefinery are also lower (indicating a better performance) than those of the gasoline refinery with regard to abiotic resource depletion and ozone layer depletion. For the rest of the impacts, biorefining performs worse than gasoline refinery. Compared to a single-output ethanol plant (Aden et al., 2002), the biorefinery has a better environmental performance per dollar of output for all impact categories except human toxicity, which is attributed to the high added value of the additional chemical production of such a refinery. The overall evaluation of the eco-efficiency depends on the importance attached to each impact category. To summarize, process optimization in terms of energy efficiency requires development of advanced technologies, however, such optimizations may bring side effects such as worse environmental performance, low profitability or unacceptable opinions from the society. Combined productions such as multi-output biorefining provide opportunities to reach a higher overall eco-efficiency combining energy, environment and economy. Such type of combined production refinery seems by far the most promising way towards successful future biomass refining.

Regarding the last question on methodology, this thesis starts with one widely used methodology in biofuel studies – life cycle assessment. *Chapter 2* investigates the influence of allocation methods on outcomes and indicates the limitations of LCA methodology. *Chapter 3* involves a cost analysis of fuel ethanol system by using a steady

state cost model (LCC). The results from these two chapters suggest that the development of methodologies beyond LCA is essential, especially for multi-product systems such as biorefineries. *Chapter 7* analyzes both the environmental and the economic feasibility of an exemplary lignocellulosic feedstock (LCF) biorefinery. The environmental performance is expressed 'per unit of value' as against 'per unit of function' in usual LCA. Moreover, the economic modelling we used reflects at least one market effect – the price change induced in succinic acid by large scale biorefinery. This market analysis is very crude, but determines very much the outcomes. It avoids the allocation issue at the stage of the refinery. The environmental performance is expressed as per unit of value created, or, in other words, eco-efficiency. The methodology developed for biorefinery systems analysis in this chapter builds on LCA but in these two respects, functional unit and market mechanism, expands beyond LCA.

The choice of an allocation method appears to be essential for the outcomes in traditional LCA. How should, for example, the pesticide use in corn agriculture be allocated to corn and to stover? This issue becomes even more important for carbon uptake, as a very substantial negative emission of CO₂: how shall these GHG benefits be allocated over corn and stover? Applying economic allocation, i.e. the share in total value of each of the co-products based on current prices, leads to a worse environmental performance for stover-based ethanol compared to gasoline. In contrast, a reduction of GHG emissions seems achieved when changing from gasoline to stover-ethanol when mass or energy content based allocation is applied. In the agricultural production, carbon dioxide is taken up for the growth of corn and stover, a negative emission, and positive GHG emissions are caused mainly by nitrous oxide (N₂O) released from the soil. When economic allocation is applied, both less credit (CO₂ uptake) and fewer penalties (N₂O emission) are allocated to stover compared to the case of mass or energy content based allocation. However, more CO₂ is taken up in the agriculture than N₂O (in kg CO₂ equivalent) is emitted, which results in a relative disadvantage for ethanol compared to gasoline when a smaller part of the agricultural emissions is allocated to ethanol. When biogenic CO₂ is altogether excluded from the system, as is customary in LCA type of studies of biofuels coming from the energy analysis field, a reduction of GHG emissions is achieved irrespective of the allocation method applied. However, it is important to notice that by doing this, in fact, a different allocation method has entered the stage implicitly - namely allocation based on carbon balance, which then is mixed with the other allocation methods for other environmental effects. If larger cellulosic ethanol markets can be established, resulting in a higher price for stover as a feedstock, the ratio of economic allocation will shift towards the one of mass or energy content based allocation. If this situation is reached, the replacement of

gasoline by ethanol will consistently show a reduction of global warming potential irrespective of the allocation method applied.

The results of LCC on ethanol derived from sugarcane indicate that driving with ethanol fuels is more economical than gasoline, and the future case is economically more attractive than the base case, which has probably been the driving force for the promotion of the advanced technologies converting bagasse to ethanol. Nevertheless, the outcomes depend very much on the assumed price for crude oil, which was considered already high in the year of 2005. In the year of 2008 the oil price was nearly doubled compared to 2005, which makes driving on ethanol fuels even more economical. As the aim of this analysis is to compare the cost of vehicle driving using ethanol and gasoline, the increased prices of food or fodder from biomass are out of the scope; therefore they are discussed only in the sensitivity analysis. Since LCA and LCC have their limitations in handling multi-output systems, such as in agriculture and complex biorefineries, broader approaches beyond LCA for the analysis of biorefinery systems may provide more robust indications on the sustainability of bio-based production. The eco-efficiency indicator defined in this study is an example of such an approach, which gives the relative performance based on the ratio of environmental impact and value created. In stead of applying allocation, the biorefinery system is analyzed as a whole, using the totals of the facilities and reckoning with all products. For the agricultural practice allocation was applied between corn and stover.

Much of the modelling work presented in this thesis follows the classical attributional LCA guidelines, in which indirect effects as through market mechanisms are not included. Therefore, consequences from direct and indirect land use change are not quantified. On the subject of land use change, there is yet no consensus on how to include this consistently in an LCA, both for the permanently required land area and for the one time effects of land use shifts, for example through deforestation. Reckoning adequately with such land use effects requires comprehensive modelling, which may be connected to LCA but requires substantial additional efforts.

The general and specific conclusions and some recommendations for further research are summarized in the following sections.

8.2 Conclusions

8.2.1 LCA

- 1) Production and utilization of ethanol as a transport fuel is a clear case of problem shifting – solving one problem (fossil resource depletion and GHG emissions) at the

- expense of others (mostly agriculture-related emissions).
- 2) The choice of the allocation method is essential for the environmental outcomes, especially related to GHG emissions. In the stover-ethanol system, the replacement of gasoline by ethanol increases GHG emissions when economic allocation is applied based on current prices. In contrast, a reduction of GHG emissions seems achieved when mass or energy content based allocation is applied.
 - 3) When biogenic CO₂ is altogether excluded from the system (in fact a quite specific type of allocation), a reduction of GHG emissions is achieved.
 - 4) The main GHG emitting processes in the ethanol life cycle are nitrous oxide emissions in the agriculture, and fermentation and electricity co-generation in the ethanol production. These processes should, therefore, receive most attention when focusing on improving the GHG performance of the chain.
 - 5) In terms of global warming, when economic allocation is applied, switchgrass is the best energy crop, followed by sugarcane. The application of ethanol fuels from corn stover, flex shives and hemp hurds leads to worse performance than gasoline, due to the small partitioning factors applied to the residues based on economic allocation in the agricultural production. This again shows that outcomes are highly dependent on the allocation method applied.
 - 6) Sugarcane-derived ethanol turns out to be the best in terms of ADP, ODP and POCP among all the fuel options (including gasoline). Its less energy intensive agriculture and ethanol production process lead to less fossil resource extraction and related emissions. As sugarcane is the only feedstock under study from which the first- and second-generation ethanol productions are combined, this finding indicates that the first-generation ethanol has clear advantages over the second-generation if the right feedstock is selected, not corn but sugar cane.
 - 7) One interesting outcome is that ODP scores are quantitatively irrelevant in all cases, even if attributing a very high weight to this impact category. One limitation of the current method for life cycle impact assessment is that it does not reckon with the contribution of nitrous oxide (N₂O) emissions to ODP, as recent findings show that N₂O now has become the major cause of ozone layer depletion.
 - 8) In many impact categories (POCP, HTP and ETP, AP and EP) ethanol fuels mostly do not show advantages over gasoline, which means that a strong promotion of bioethanol as a transport fuel needs to be carefully (re)considered. More advanced technologies with optimization of energy use and emissions in both agriculture and ethanol refinery still need to be developed.
 - 9) Although the LCA results from only five studies are compared, these five feedstocks (corn stover, sugarcane & bagasse, switchgrass, flax shives and hemp hurds) can, to a certain extent, represent a number of other lignocelluloses. The comparison

provides an indication on the environmental performance of the second-generation bioethanol as a whole in comparison with both the first-generation bioethanol and gasoline; hence it contributes significantly to the current debate on the importance of biofuels in a future energy mix.

- 10) The reason for the current promotion of the second-generation bioethanol is its less competition with food and agricultural land, and its better environmental performance compared to the first-generation ethanol. However, the present study suggests that it would be unfair to draw such a conclusion while the environmental performance of a sugar-based feedstock (sugarcane) can be much better than the one of lignocelluloses (corn stover, flax shives and hemp hurds).

8.2.2 LCC

- 11) Driving with ethanol fuels is more economical than with gasoline, and the future case (converting also bagasse to ethanol) is economically more attractive than the base case (combusting bagasse for heat and power generation), which has probably been the driving force for the promotion of advanced cellulosic technologies converting bagasse to ethanol.
- 12) In the LCC analysis a steady-state cost model was used and only the production costs were taken into account; taxes and subsidies are not included. Hence it can only provide a first indication on the economic feasibility of the process. In the real market the prices of fuels are very much dependent on taxes and subsidies, and discounting will be a serious issue.

8.2.3 Energy analysis

- 13) The survey of energy inputs indicates the bottlenecks in the ethanol life cycle – fertilizer production, tillage and harvesting in the agriculture, and pretreatment, enzyme production and product recovery in the biorefinery.
- 14) Sugarcane and most lignocellulosic feedstocks are more favourable than corn in terms of net energy gain due to their less energy intensive agricultural practice and refining processes. The low energy inputs in these ethanol refining processes are due to the steam and electricity co-generation inside the refineries. This suggests that co-generation of heat and power from lignin residues and wastes is an important way to increase the energy efficiency of the cellulosic ethanol process.
- 15) When the energy credits of all co-products are taken into account, all cases under comparison yield positive net energy values. The highest NEV is found in the stover-ethanol case, which shows that ethanol production from stover is more energy efficient than corn-based ethanol production.

- 16) Accounting for the energy values of co-products, illustrated by corn, stover and sugar produced in the different case studies of this thesis, strongly affects the performance from an energy perspective. This issue of co-product credits is in fact identical to the allocation issue in LCA studies, but is solved in a different manner.
- 17) If we specify the total energy inputs and outputs, which means no allocation method is applied; it becomes essential to also take all co-products into account. When analyzing energy flows related to only one main product, allocation is required. An allocation based on energy content might be applied in some cases, i.e. between corn and stover, or between fuel and electricity. However, for the combined production of ethanol and sugar, it is more questionable though it can be done technically, as the energy values of sugar and ethanol do not belong to the same category. Food is not an energy product and it has different value characteristics.

8.2.4 Biorefinery design and system analysis

- 18) The price assumed for the high-value succinic acid is \$1.0/kg, which is one sixth of the current market price. Sensitivity analysis shows that even when the price of the succinic acid is lowered further to \$0.5/kg, or the capital investment is doubled, the combined production refinery is still highly profitable. The fluctuations in the price of ethanol and corn stover do not affect the profitability of the refinery substantially.
- 19) GHG emissions of this biorefinery are very low due to the CO₂ fixation by acid fermentation, indicating that the combined production of ethanol and succinic acid is indeed beneficial. This is a profound finding and it could be one criterion for future biorefinery design and commercialization, which should focus on not only the technical and economic feasibility, but also the environmental impact.
- 20) The price of gasoline used in this study includes excises or similar payments to governments like royalties, while for bioethanol no excises but subsidies have been introduced. Therefore the outcomes are based on these assumptions. If the same excises are levied on ethanol, the results of the price comparison will be much different. This could be a serious risk for a single-output ethanol plant. The advantage of the biorefinery as designed in this thesis is that the high-value products (succinic acid in this case) can better ensure profits independent of political support.
- 21) The mass ratio of ethanol to succinic acid selected in this study is only one choice. When the market changes, the shift from one product to the other is possible to full extent – one product line can be shut down completely or be made ready for the production of other fuels or chemicals.

8.3 Recommendations

8.3.1 Methodological issues

The LCA type of outcomes are highly sensitive to the allocation method applied, especially with regard to global warming – one of the main reasons to consider biofuels as one renewable energy source. In the domain of energy analysis studies the situation is even worse. Here, the awareness of the need for explicit allocation has just begun to dawn. This is unacceptable from a societal point of view and a challenge from a scientific point of view. Nevertheless, this has not yet raised the awareness of many decision makers who use energy analysis or LCA as a support tool. In the stover-ethanol case, this was solved by showing and explaining the differences in the outcomes by performing a sensitivity analysis using several allocation assumptions. In many other cases on LCA of cellulosic ethanol this may also be the best way forward. It is relevant to notice that the uncontested practice of ignoring biogenic CO₂ in the chain is, in fact, another allocation choice – allocation based on carbon balance, using different modes of allocation for other environmental impacts. It is important that LCA practitioners realize this and deal with it in an explicit and most appropriate manner. Mixing allocation methods in one case study is not advisable, as then the effects of allocation choices become very difficult to analyze, and inconsistency may easily occur.

In most of the LCA and energy analysis studies, the systems under study are incomplete. For instance, in several studies the ethanol refining system is incomplete by not including the production of cellulase enzyme which is used to degrade the cellulosic feedstocks, and hence leaving out the associated environmental impacts. Moreover, co-products are often neglected, such as stover in the case of ethanol production from corn. In the field of LCA this would have been identified as a situation requiring allocation. This should raise the awareness of especially the energy analysis community – results obtained from systems excluding co-product energy credits can be misleading and are unacceptable. There is still an urgent need in performing LCA and energy analysis in a consistent way in order to obtain at least comparable results from this type of technology focused analyses.

LCA as it stands cannot capture all the relevant effects, neither in terms of the mechanism included in modelling as explained earlier, nor in the practical sense regarding data. Issues related to indirect effects of land use change, such as market effects leading to competition with food products, do not fit well into the present (attributional) LCA framework. Reckoning adequately with effects of land use shifts requires more comprehensive modelling, which may be connected to LCA by shifting from attributional to consequential LCA. How to link such consequences to the

functional unit level is one main question, as in market mechanisms the volumes of many products change. On the specific subject of land use change, there is yet no consensus on how to include this consistently in an LCA. One idea is to specify what land use changes occur exactly where in the world as the result of changing the of the land area required to produce an additional amount of fuel. Another is, to specify such changes at the global level and then scale them down to the LCA micro-level, translating them into standard impact factors. Both options have apparent drawbacks.

Another question is whether the functional unit approach is relevant for decisions on multi-output systems, such as complex biorefineries. Biofuels are just one of their products, perhaps not even the most important one. Broader approaches beyond LCA for the analysis of biorefinery systems with regard to energy conservation, environmental impact, and costs and benefits are needed to provide general indications on the sustainability of bio-based productions.

The systems analysis of the designed biorefinery firstly provides figures on the environmental and economic performance of the total system, including all (co-) products. Instead of comparing systems in terms of environmental impact per functional unit, we compared them on the basis of environmental impact per unit of value created, which is in terms of their eco-efficiency. This is an example of the aforementioned ‘broader approach’. The estimation and comparison of the eco-efficiencies give an indication on the relative performance of different production systems, even if they have a different overall size. In this type of study, in order to achieve a better eco-efficiency one can increase the value created by the refinery instead of reducing emissions to the environment which is the only option when using a functional unit. This links to the discussion on ‘strong sustainability’ and ‘weak sustainability’. In order to achieve ‘strong sustainability’, one should improve the eco-efficiency, but with a higher percentage than the increase in the production which also are occurring, in the form of economic growth. LCA cannot link to this broader societal development and hence cannot contribute to this sustainability discussion.

8.3.2 Perspectives and outlook

Technology improvement is a key to reducing energy consumption and GHG emissions, as well as to reducing the cost of the fuel ethanol productions. However, new energy technologies may have unwanted side effects such as a worse overall environmental performance, a low profitability or a low acceptability in society. Therefore, it is crucial to develop a model for optimization with a complete set of criteria, among which a

reduced energy requirement and a better energy generation technology can be important ones.

The systems analysis required now focuses on LCA. With better integration of production processes in an industrial ecology vein, co-products become increasingly important, with outcomes of the analysis increasingly depending on the choices of allocation. As these choices do hardly reflect reality, this is a situation to overcome. Using value creation is one key step towards this more integrated analysis. We have made this step exemplary and for part of the life cycle only. The problems encountered have been indicated and need further consideration for improving the life cycle system analysis.

We have touched upon indirect effects of choices regarding biofuels, such as through their influence on market prices for staple foods and fodders. For choices regarding large scale introduction of biofuels, such indirect effects should certainly be analyzed as well, next to LCA and eco-efficiency analysis, and in the longer term possibly integrating such mechanisms.

The route from idea to operation of any new production facility is always time consuming due to a series of actions required in the process – innovation and research, technology transfer, business investment, conceptual process design, test in pilot scale, upscale and establishment of an operational plant. All these activities make the realization and commercialization of a biorefinery difficult but not impossible; ten years can be a good estimate to bring the products from our designed refinery into the market.

Two software packages now have been used separately – SuperPro Designer for the technical process design and CMLCA for the environmental assessment. The connection of these tools was made manually. Further integrated software development can help establish a linkage between process simulation and environmental assessment so that optimization becomes a more straightforward activity.

Social aspects have not been treated in this study. These may firstly be analyzed in the same system analysis as used for environmental and economic analysis. However, large scale biomass refining raises a number of societal concerns through more indirect mechanisms remaining uncovered now. An example is the well known dilemma “fuel for the rich or food for the poor”, which has been extensively discussed in some literature studies going beyond LCA. These concerns should be on the mind of every responsible leader in government, business and civil society, and in the mind of producers and consumers. On a global scale, dialogues among nations help to better

understand regional problems and needs; exchanging information and sharing technologies create opportunities for the economic growth in the developing nations; new initiatives create incentives for local and global sustainable development to take place simultaneously. More importantly, these concerns should also be on the mind of every citizen – collective sustainability is an individual responsibility.

Summary

The increasing world energy demand, depletion and unequal distribution of fossil resources, and the dangers caused by climate change are the driving forces for the development of alternative energy sources. In view of the GHG emission reduction target agreed upon in the Kyoto protocol, a shift from fossil fuels to renewable resources is ongoing to secure the long-term energy supply at both national and international level.

Renewable energy is generated from natural resources such as sunlight, wind, waves and geothermal heat. In 2006, about 18% of global energy consumption came from renewables, 13% of which was from traditional biomass such as wood combustion. Hydroelectricity was the second largest renewable source, providing 3% of global energy consumption. To keep up with the growing energy demand, many nations have established new regimes on renewable energy. For instance, the European Commission decided in 2007 on a 20% target for the overall share of energy from renewable sources and a 10% target for energy from renewable sources in transport by 2020.

At least for the foreseeable future, low-carbon fuels in liquid form are required for use in existing internal combustion engines in transportation. Biofuels are potential low-carbon energy sources, and can provide energy for the transport sector. With the available conversion technologies they may contribute substantially to achieving the renewable energy targets in the near future.

Biomass, with its abundance and renewable nature, is available as a feedstock for the production of fuels. Examples of biomass that can be used to produce fuels include conventional crops (corn, wheat, rice, sorghum, sugarcane, sugar beet, cassava, palm oil, rapeseed, etc.), agricultural residues (corn stover, wheat and rice straw, sugarcane bagasse etc.) and dedicated cellulosic plants (poplar, switchgrass and miscanthus, for example).

Against the background of the ongoing debate on biofuels and biorefining, the objective of this thesis is to indicate possible directions for biomass refining for sustainable development, focusing on environmental and economic analyses of the refining of lignocellulosic biomass. To this end, three main research questions have been formulated:

- I. Is fuel ethanol from lignocelluloses better than gasoline, from an environmental point of view?
- II. How can bio-based production be optimized with regard to energy efficiency, environmental performance and economic feasibility?
- III. How can we design a methodology to achieve a more comprehensive sustainability assessment of biomass refining?

With regard to the first question, life cycle assessment (LCA) was chosen as an analysis tool, as it is capable of handling fuel systems on a life cycle basis. Three chapters of this thesis are dedicated to comparative life cycle assessment (LCA), with different focuses: *Chapter 2* addresses one of the most important methodological issues in LCA – allocation, using fuel ethanol from corn stover as a case study. It concludes that the comparison of fossil fuels with biofuels is highly sensitive to the choice of allocation method.

Chapter 3 compares the environmental performance and cost of fuel ethanol for two scenarios in Brazil: current practice – ethanol and sugar production from juice sugar, and electricity co-generation from combustion of bagasse – and the future case, in which ethanol and sugar are produced from juice sugar and bagasse is also used to produce ethanol, while electricity is generated from the combustion of lignin residues and wastes. It is concluded that the system using bagasse to produce electricity has a better environmental performance than the system in which ethanol is produced from it.

Chapter 4 focuses on LCA for another promising feedstock, switchgrass, and analyzes the changes in environmental impact relating to the choice of allocation, soil preparation and transport distance. Compared to the stover- and sugarcane-ethanol systems, this is a relatively simpler chain, because switchgrass is a dedicated energy crop for ethanol production, without agricultural co-products. Moreover, only a small amount of surplus electricity is co-generated in the ethanol production process, which makes the choice of allocation easier – no allocation is needed in agricultural production. Switchgrass-ethanol seems to have a much better environmental performance than gasoline.

In order to compare and evaluate the environmental performance of bioethanol from lignocelluloses with that of gasoline, *Chapter 6* summarizes the results reported in *Chapters 2, 3 and 4*, and two more studies on ethanol production from flax shives and hemp hurds. In all these studies, the same technologies were used to convert cellulose and hemicellulose to ethanol and to generate heat and power from lignin and wastes; the same system boundaries were defined; and the same allocation procedures were

followed. A comprehensive set of environmental impacts is addressed, ranging from abiotic resource depletion and GHG emissions to acidification, eutrophication and toxicity aspects.

The findings from these four chapters present a clear example of problem shifting – solving the problems of oil depletion and ozone depletion at the expense of increasing agriculture-related emissions, which contribute significantly to eutrophication and toxicity aspects, as well as to global warming via N₂O emissions. Moreover, the outcomes of LCA especially in terms of global warming greatly depend on the choice of allocation method. If agricultural co-products are utilized for ethanol production, the GHG performance greatly depends on the amount of carbon dioxide uptake that is allocated to the lignocellulosic co-products. These two issues make it difficult to conclude whether, from an environmental point of view, fuel ethanol from lignocelluloses is better than gasoline. However, bioethanol certainly has potential in terms of reducing fossil resource use, as well as in GHG emissions, if more promising feedstocks like switchgrass and sugarcane are used. The limitations lie in the agricultural production of biomass. Savings can be offset by poor management, for instance due to the loss of soil organic matter, or high emissions of nitrous oxide (N₂O) if too much nitrogen fertilizer is used. Technology development, improved agricultural practice and reduction of land use are crucial to reducing the environmental impact.

In relation to the second question, *Chapter 5* presents a detailed energy analysis of the corn stover-based ethanol system, and the resulting energy inputs in sub-processes point out directions for process optimization in terms of energy efficiency. The estimated net energy values are compared with the literature values on first-generation bioethanol to assess more accurately whether second-generation ethanol is more energy efficient.

Chapter 6 compares the net energy values obtained from *Chapter 5* with those from selected literature studies on the same subject. These studies have mainly focused on corn-, stover-, switchgrass- and sugarcane-derived ethanol systems. Two types of accounting are used – including and excluding co-products and energy credits.

A single-product (ethanol) system can be optimized only to a certain extent, due to the fixed process options and relatively low price of ethanol. Full optimization in terms of energy efficiency, environment and economy should focus on an integrated production system – multi-product biorefinery. *Chapter 7* reports on the design of a lignocellulosic feedstock biorefinery producing fuel, chemicals and power in one plant, and analyzes the environmental and economic potential of such a refinery. In this case, the selected

production combination is ethanol (low value) and succinic acid (high value), together with acetic acid and electricity as co-products.

The outcomes reported in *Chapter 5* and *Chapter 6* indicate that the energy-intensive processes in the ethanol life cycle are fertilizer production, tillage and harvesting in agriculture, and pre-treatment, product recovery and enzyme production in the ethanol production. These findings suggest options for optimization in terms of process technology and energy efficiency. Moreover, when the energy credits of all co-products are taken into account, ethanol production from cellulosic feedstocks is much more energy efficient than corn-based ethanol. With regard to environmental performance, improvements can be achieved by selecting feedstocks which require less intensive agricultural practices. *Chapter 7* demonstrates that multi-product biorefining can indeed be more feasible technically, economically as well as environmentally than single-output productions such as an ethanol plant, especially when an appropriate product combination is chosen. Essential in the refinery design in this thesis is the fact that the CO₂ generated is not emitted, but used in the process of succinic acid production. Although the refinery in this thesis was designed with highly optimized technology, further development and improvements could be made. However, we should keep in mind that optimization in terms of process technology and energy efficiency may bring side-effects – not just poorer environmental performance, but also lower profitability or a lower acceptability to society.

Regarding the last research question, this thesis starts with a methodology widely used in biofuel studies – life cycle assessment. *Chapter 2* investigates the influence of allocation methods on outcomes and indicates the limitations of LCA methodology. Three allocation methods are discussed – mass/energy-based allocation, economic value-based allocation and system expansion. These are combined with a sensitivity analysis for the treatment of biogenic carbon: leaving biogenic carbon out of the analysis, as is usual in many biofuel studies, or accounting for both extractions and emissions of CO₂, as is standard LCA practice. These issues appear to be essential in a biofuel-fossil fuel comparison.

Chapter 3 involves life cycle costing (LCC) of the fuel ethanol system using a steady state cost model, in which only production costs are taken into account. This can give an indication of the economic feasibility but does not reflect the dynamic effect in the real market. The results of both LCA and LCC are compared with those of the gasoline system.

The results reported in these two chapters suggest that the development of methodologies beyond LCA is essential, especially for multi-product systems such as biorefineries. *Chapter 7* assesses the economic feasibility of a newly designed biorefinery using economic modelling that reflects market effects. It further develops an eco-efficiency indicator (emissions per unit of value derived) to analyze the environmental impact of the refinery without applying an allocation procedure. Although the methodology developed for system analysis in this chapter is based on LCA, it is expanded beyond LCA.

Although LCA is a tool developed for decision-making in sustainable development, it is innately prone to discrepancies, being heavily reliant on methodological choices and assumptions made. *Chapter 2* concludes that LCA as it stands has a number of limitations. First of all, outcomes are greatly dependent on the allocation method applied; secondly, important impacts such as land and water use are not yet included in standard LCA databases; thirdly, issues related to indirect land use changes and competition with food products do not fit well into the LCA framework; and finally, LCA is also limited in terms of handling multi-output systems, such as complex biorefineries. The results of LCC on ethanol derived from sugarcane indicate that driving on ethanol fuels is more economical than on gasoline, and that the future case is economically more attractive than the base case, which has probably been the driving force for the promotion of advanced technologies converting bagasse to ethanol. Due to the steady-state cost model used in LCC, the results can only provide a preliminary indication of the economic feasibility of the process. In the real market, the prices of fuels are very much dependent on taxes and subsidies.

The findings reported in these two chapters urge us to develop a broader approach to analyze the environmental performance and profitability of a multi-product biorefinery system. The eco-efficiency indicator used in *Chapter 7* presents one example of such an approach, which is based on a ‘cradle-to-gate’ LCA methodology. The difference between this approach and the methodology of LCA and LCC lies in accounting for the environmental impact of the whole system and the values derived from it. Since this avoids allocation, it is considered a methodology based on LCA but going beyond LCA.

Sustainability has implied the integration of the economic, social and environmental spheres to meet the needs of the present generation without compromising the ability of future generations to meet theirs. This thesis has addressed the directions and perspectives of biomass refining, especially to produce fuels and chemicals, for sustainable development. Methodologies for this critical analysis and assessment have

been developed and applied. Although social aspects were beyond the scope of this study, they have been extensively discussed in some literature studies, including the dilemma “fuel for the rich or food for the poor” caused by the biofuels regime. Such concerns should be on the mind of every responsible leader in government, business and civil society. On a global scale, dialogues among nations help to better understand regional problems and needs. Exchanging information and sharing technologies create opportunities for the developing nations, whilst new initiatives create incentives for simultaneous local and global sustainable development. More importantly, these matters should be a concern for every citizen, because collective sustainability is also an individual responsibility.

Samenvatting

De toenemende energievraag in de wereld, de uitputting en ongelijke verdeling van fossiele brandstoffen en de gevaren van klimaatverandering vormen de drijvende kracht achter de ontwikkeling van alternatieve energiebronnen. Naar aanleiding van de in het Kyoto Protocol afgesproken doelstelling voor reductie van de uitstoot van broeikasgassen, is momenteel een verschuiving aan de gang van fossiele brandstoffen naar duurzame energiebronnen, met het doel de energievoorziening op zowel nationaal als internationaal niveau veilig te stellen.

Duurzame energie wordt opgewekt met behulp van natuurlijke hulpbronnen als zonlicht, wind, golfenergie en geothermische warmte. In 2006 was ca. 18% van het mondiale energieverbruik afkomstig van duurzame bronnen, waarvan 13% uit traditionele biomassa zoals stookhout. Waterkracht is de op één na grootste duurzame energiebron, met 3% van het wereldenergieverbruik. Om te kunnen voldoen aan de groeiende vraag naar energie hebben vele landen nieuwe doelstellingen voor duurzame energie vastgesteld. Zo heeft de Europese Commissie in 2007 als nieuwe doelstelling voor 2020 ingevoerd dat 20% van het totale energieverbruik, en 10% van het energieverbruik door vervoermiddelen afkomstig moet zijn uit duurzame bronnen.

Voor de afzienbare toekomst zijn vloeibare koolstofarme brandstoffen nodig voor de in vervoermiddelen gebruikte verbrandingsmotoren. Biobrandstoffen voldoen aan deze omschrijving, en kunnen potentieel worden gebruikt voor de energievoorziening in de transportsector. Met de momenteel beschikbare conversietechnieken kunnen biobrandstoffen in de nabije toekomst een aanzienlijke bijdrage leveren aan het halen van de doelstellingen voor duurzame energie.

Biomassa is in grote hoeveelheden voorhanden en is een vernieuwbare grondstof die kan worden gebruikt voor de productie van brandstoffen. Tot de voorbeelden van biomassa die voor dit doel kunnen worden gebruikt behoren traditionele gewassen (zoals maïs, tarwe, rijst, sorghum, suikerriet, suikerbiet, cassave, palmolie en raapzaad), 'afval' en landbouwresiduen (maïsstro, tarwe- en rijststro, bagasse van suikerriet, enz.) en speciaal voor dit doel verbouwde cellulosehoudende gewassen (b.v. populier, vingergras en olifantsgras).

Tegen de achtergrond van het voortgaande debat over biobrandstoffen en bioraffinage is het doel van dit proefschrift om richtingen aan te geven voor de raffinage van biomassa ten behoeve van duurzame ontwikkeling, met bijzondere aandacht voor

milieutechnische en economische analyses van de raffinage van lignocellulose-biomassa. Hiertoe werden drie onderzoeksvragen geformuleerd:

- I. Is vanuit milieutechnisch oogpunt gezien ethanol uit lignocellulose als brandstof beter dan benzine?
- II. Hoe kan de productie op basis van biomassa worden geoptimaliseerd voor wat betreft energie-efficiëntie, milieuprestaties en economische haalbaarheid?
- III. Hoe kunnen we een methodiek ontwikkelen voor een meer volledige beoordeling van de duurzaamheid van biomassa-raffinage?

Ter beantwoording van de eerste vraag is gekozen voor het gebruik van levenscyclusanalyse (LCA) als analytisch instrument, aangezien hiermee brandstofsysteem kunnen worden bestudeerd op basis van hun levenscyclus. Drie van de hoofdstukken van dit proefschrift zijn gewijd aan vergelijkende levenscyclusanalyse (LCA), elk met een eigen focus. In *Hoofdstuk 2* wordt een van de belangrijkste methodologische problemen bij LCA, dat van allocatie, onderzocht aan de hand van het gebruik van ethanol uit maïsstro als casestudy. Geconcludeerd wordt dat de vergelijking tussen fossiele brandstoffen en biobrandstoffen zeer gevoelig is voor de gebruikte allocatiemethode.

In *Hoofdstuk 3* worden de milieuprestaties en kosten van ethanol als brandstof vergeleken voor twee scenario's in Brazilië: de huidige praktijk (productie van ethanol en suiker uit suikersap en cogeneratie van elektriciteit door verbranding van bagasse) tegenover een toekomstscenario waarbij naast de productie van ethanol en suiker uit suikersap ook de bagasse wordt gebruikt voor de productie van ethanol, terwijl elektriciteit wordt opgewekt door verbranding van lignine-residu en afval. Geconcludeerd wordt dat het systeem waarbij de bagasse wordt gebruikt voor de elektriciteitsopwekking, betere milieuprestaties levert dan wanneer deze wordt gebruikt voor de productie van ethanol.

In *Hoofdstuk 4* wordt ingegaan op het gebruik van LCA ter beoordeling van een ander veelbelovend uitgangsmateriaal, vingergras, en wordt geanalyseerd hoe de milieueffecten veranderen met de gekozen allocatiemethode, bodembewerking en transportafstand. Vergeleken met het systeem maïsstro/ethanol en het systeem suikerriet/ethanol is hier sprake van een relatief eenvoudige keten, aangezien het vingergras uitsluitend wordt verbouwd als energiegewas ten behoeve van de ethanolproductie, zonder agrarische nevenproducten. Daarnaast wordt in dit systeem bij de ethanolproductie slechts een gering surplus aan elektriciteit opgewekt, hetgeen de allocatie-keuzes eenvoudiger maakt:

er hoeft geen allocatie naar landbouwproductie plaats te vinden. Het lijkt erop dat ethanolproductie uit vingergras leidt tot veel betere milieuprestaties dan benzine.

In *Hoofdstuk 6* worden de resultaten uit *Hoofdstuk 2, 3 en 4*, alsmede van twee andere studies over de productie van ethanol uit afvalvlas- en hennepvezels, samengevat. De milieuprestaties van bioethanol uit deze lignocellulose-grondstoffen wordt vergeleken en getoetst aan de milieuprestatie van benzine uit aardolie. Bij al deze onderzoeken werden dezelfde technieken gebruikt om cellulose en hemicellulose om te zetten in ethanol en om warmte en elektriciteit te genereren uit lignine en afval, werden dezelfde systeemgrenzen gehanteerd en werden dezelfde allocatieprocedures gevolgd. De resultaten zijn daarom goed vergelijkbaar. De analyse is gebaseerd op een uitgebreide reeks milieueffecten, uiteenlopend van uitputting van abiotische grondstoffen en emissies van broeikasgassen tot aspecten van verzuring, eutrofiëring en toxiciteit.

De in deze vier hoofdstukken gerapporteerde resultaten laten duidelijk zien dat er sprake is van probleemafwenteling: het oplossen van het probleem van het opraken van olie gaat ten koste van een stijging van emissies van eutrofiërende en toxische stoffen in de landbouw. De reductie van CO₂-emissies gaat gepaard met een toename van emissies van het broeikasgas N₂O. Voorts blijkt het resultaat van de LCA, vooral voor wat betreft het broeikaseffect, sterk afhankelijk van de gekozen allocatiemethode. Bij het gebruik van bijproducten van de landbouw voor het produceren van ethanol hangt de berekende uitstoot van broeikasgassen bovendien sterk af van de manier waarop de opname van CO₂ is meegenomen in de analyse (biogeen CO₂). Door deze twee problemen wordt het moeilijk te beoordelen of het gebruik van ethanol uit lignocellulose uit milieu-oogpunt beter is dan dat van benzine. Toch heeft bioethanol zeker potentieel als het gaat om het verminderen van het gebruik van fossiele brandstoffen, en ook als het gaat om het terugdringen van de uitstoot van broeikasgassen, mits gebruik wordt gemaakt van veelbelovende gewassen als vingergras en suikerriet. De beperkingen liggen op het gebied van de productie van biomassa door de landbouw. De besparingen kunnen worden tenietgedaan door het gebruik van verkeerde landbouwmethoden, zoals door verlies van organische stof uit de bodem, of door hoge N₂O-uitstoot door gebruik van teveel stikstofbemesting. Cruciale factoren voor het verminderen van de milieueffecten zijn technologische ontwikkelingen, verbeterde landbouwmethoden en beperking van het landgebruik.

Ter beantwoording van de tweede onderzoeksvraag wordt in *Hoofdstuk 5* een gedetailleerde energie-analyse gepresenteerd van het systeem van ethanolproductie uit maïsstro. De daaruit resulterende energie-invoer in deelprocessen geeft richtingen aan

voor het optimaliseren van de energie-efficiëntie van de betrokken processen. De geschatte netto energiewaarden worden vergeleken met de in de literatuur gemelde waarden voor eerste-generatie bioethanol, teneinde beter te kunnen inschatten of tweede-generatie ethanol een hogere energie-efficiëntie kent.

In *Hoofdstuk 6* worden de in *Hoofdstuk 5* afgeleide netto energiewaarden vergeleken met de waarden die worden genoemd in een aantal literatuurstudies over dit onderwerp. Deze studies gingen voornamelijk over systemen waarin maïs of maïsstro, vingergras en suikerriet worden gebruikt voor ethanolproductie. Hierbij worden twee opties gebruikt, respectievelijk met en zonder energy credits voor nevenproducten.

Een systeem met één enkel product (ethanol) kan maar tot op zekere hoogte worden geoptimaliseerd, omdat de procesopties vastliggen, en vanwege de relatief lage prijs van ethanol. Een hogere graad van optimalisatie voor wat betreft energie-efficiëntie, milieueffecten en economische aspecten kan worden verkregen door gebruik van geïntegreerde productiesystemen, dwz. bioraffinage met meerdere producten. In *Hoofdstuk 7* is getracht een systeem te ontwerpen voor bioraffinage van lignocellulose waarbij in één installatie brandstof, chemicaliën en energie worden geproduceerd, en wordt het milieutechnische en economische potentieel van een dergelijk systeem geanalyseerd. In het beschreven systeem is gekozen voor de productie van ethanol (met een lage economische waarde) en barnsteenzuur (met hoge economische waarde), met azijnzuur en elektriciteit als nevenproducten.

De in *Hoofdstuk 5* en *Hoofdstuk 6* beschreven resultaten geven aan dat de meest energie-intensieve processen in de levenscyclus van ethanol te vinden zijn bij de productie van kunstmest, de grondbewerking en oogstmethoden in de landbouw, en bij de voorbehandeling, de productafscheiding en de enzymproductie voor de ethanolproductie. Deze resultaten bieden mogelijk aanknopingspunten voor optimalisatie op het gebied van procestechnologie en energie-efficiëntie. Bovendien blijkt dat wanneer de energy credits van alle nevenproducten in aanmerking worden genomen, de productie van ethanol uit cellulose-grondstoffen een veel hogere energie-efficiëntie kent dan de productie van ethanol uit maïs. Wat betreft de milieuprestaties kunnen verbeteringen worden gerealiseerd door te kiezen voor grondstoffen die minder intensieve landbouwmethoden vergen. Uit *Hoofdstuk 7* blijkt dat bioraffinage met meerdere producten technisch, economisch en milieutechnisch gezien meer haalbaar kan zijn dan systemen met maar één product, zoals een ethanolfabriek, vooral wanneer een geschikte combinatie van producten wordt gekozen. Een essentieel aspect van het hier gepresenteerde ontwerp voor een dergelijk raffinagesysteem is dat de

geproduceerde CO₂ niet wordt uitgestoten, maar wordt gebruikt voor de productie van barnsteenzuur. Hoewel voor het ontwerp van deze raffinaderij gebruik is gemaakt van sterk geoptimaliseerde technologie, zijn nog verdere ontwikkelingen en verbeteringen denkbaar. Daarbij dient echter te worden bedacht dat optimalisatie van de procestechniek en de energie-efficiëntie tot ongewenste nevenverschijnselen kan leiden, niet alleen in de vorm van minder goede milieuprestaties maar ook in de vorm van lagere winstgevendheid of geringere maatschappelijke aanvaardbaarheid.

Ter beantwoording van de derde en laatste onderzoeksvraag is in dit proefschrift in eerste instantie uitgegaan van een methodiek die veel wordt gebruikt bij onderzoek op het gebied van biobrandstoffen, namelijk levenscyclusanalyse (LCA). In *Hoofdstuk 2* wordt de invloed van allocatiemethoden op de analyseresultaten bestudeerd, alsmede de beperkingen van de LCA-methode. Daarbij worden drie allocatiemethoden beoordeeld: allocatie op basis van massa/energie, allocatie op basis van economische waarde en systeemuitbreiding. Dit wordt gecombineerd met een gevoeligheidsanalyse betreffende de manier waarop biogene koolstof in de analyse wordt behandeld, hetzij door deze buiten beschouwing te laten, zoals in veel onderzoek over biobrandstof wordt gedaan, hetzij door zowel extractie als emissie van CO₂ mee te nemen, zoals standaard wordt gedaan bij LCA. Het lijkt erop dat deze aspecten cruciaal zijn bij vergelijkingen tussen biobrandstoffen en fossiele brandstoffen.

In *Hoofdstuk 3* gaat het om life cycle costing (LCC) van het systeem voor ethanol als brandstof, op basis van een steady state kostenmodel waarin alleen de productiekosten in aanmerking worden genomen. Hierdoor kan een indicatie worden verkregen van de economische haalbaarheid, maar wordt geen rekening gehouden met het dynamische effect op de werkelijke markt. De resultaten van zowel LCA als LCC worden vergeleken met die voor een op benzine gebaseerd systeem.

De resultaten van deze twee hoofdstukken geven aan dat het van essentieel belang is om methodieken te ontwikkelen die verder gaan dan LCA, met name voor systemen met meerdere producten zoals bioraffinaderijen. In *Hoofdstuk 7* wordt de economische haalbaarheid van een ontwerp voor een bioraffinaderij geanalyseerd met behulp van een economisch model dat rekening houdt met de markteffecten. Ook wordt hier een indicator voor eco-efficiëntie (emissies per eenheid van waarde van de geproduceerde producten) ontwikkeld waarmee de milieueffecten van de raffinage kunnen worden geanalyseerd zonder dat een allocatieprocedure wordt toegepast. De hier ontwikkelde methodiek voor systeemanalyse is gebaseerd op LCA, maar gaat verder dan LCA.

Hoewel LCA is ontwikkeld als instrument voor de besluitvorming op het gebied van duurzame ontwikkeling, kan het inherent aanleiding geven tot discrepanties, aangezien het sterk leunt op bepaalde methodologische keuzes en aannames. In *Hoofdstuk 2* wordt geconcludeerd dat LCA in zijn huidige vorm een aantal beperkingen kent. Om te beginnen zijn de resultaten sterk afhankelijk van de gebruikte allocatiemethode. Ten tweede zijn bepaalde belangrijke effecten, zoals die op het gebruik van land en water, nog niet opgenomen in de standaard LCA-databases. Ten derde passen aspecten die samenhangen met indirecte veranderingen in landgebruik en concurrentie met voedselgewassen niet goed binnen het LCA-kader. En ten slotte is LCA maar beperkt in staat om systemen met meerdere producten, zoals complexe bioraffinaderijen, te analyseren. Uit de met LCC verkregen resultaten met betrekking tot de productie van ethanol uit suikerriet blijkt dat het rijden op ethanol goedkoper is dan op benzine, en dat het toekomstscenario economisch aantrekkelijker is dan de huidige praktijk. Dit vormt waarschijnlijk de drijvende kracht voor de stimulering van geavanceerde technieken voor het omzetten van bagasse in ethanol. Vanwege het in de LCC gebruikte steady-state model kunnen de gevonden resultaten slechts een eerste indicatie geven van de economische haalbaarheid van dit proces. In de werkelijke markt zijn de brandstofprijzen sterk afhankelijk van belastingen en subsidies.

De in deze twee hoofdstukken beschreven resultaten geven de noodzaak aan van het ontwikkelen van een bredere aanpak voor de analyse van milieuprestaties en de winstgevendheid van een bioraffinagesysteem met meerdere producten. De in *Hoofdstuk 7* beschreven eco-efficiëntie indicator is een voorbeeld van een dergelijke benadering, gebaseerd op een 'cradle-to-gate' LCA-methodiek. Het verschil tussen deze benadering en de bij LCA en LCC gebruikte methodiek ligt daarin dat rekening wordt gehouden met de milieueffecten van het gehele systeem en de waarde van alle producten ervan. Aangezien hiermee allocatie wordt vermeden, kan deze benadering worden beschouwd als zijnde gebaseerd op LCA maar tegelijkertijd verder gaand dan LCA.

Duurzaamheid kan alleen worden gerealiseerd door integratie van economische, sociale en milieutechnische aspecten, met het doel om de behoeften van de huidige generatie te kunnen vervullen zonder dat de mogelijkheden voor komende generaties om in de hunne te voorzien worden aangetast. In dit proefschrift is gezocht naar ontwikkelingsrichtingen en perspectieven voor de raffinage van biomassa, met name voor de productie van brandstoffen en chemicaliën voor duurzame ontwikkeling. Voor deze kritische analyse en beoordeling zijn diverse methodieken ontwikkeld en toegepast. De sociale aspecten zijn in deze studie buiten beschouwing gelaten, maar deze zijn uitgebreid besproken in literatuurstudies. Dit geldt bijvoorbeeld voor het door het

toenemend gebruik van biobrandstoffen veroorzaakte dilemma “brandstof voor de rijken of voedsel voor de armen”. Verantwoordelijke leiders in regeringen, de zakenwereld en de burgermaatschappij dienen zich terdege bewust te zijn van deze problemen. Op wereldschaal is dialoog tussen de verschillende naties een middel om beter begrip te kweken voor de problemen en behoeften in diverse regio’s. Door informatie uit te wisselen en technologieën te delen kunnen nieuwe mogelijkheden worden geschapen voor de ontwikkelingslanden en voor de gelijktijdige stimulering van lokale en mondiale duurzame ontwikkeling. Elke burger zou zich hiervoor medeverantwoordelijk moeten voelen, aangezien collectieve duurzaamheid ook een individuele verantwoordelijkheid is.

References

- Aden A., Ruth M., Ibsen K., Jechura J., Neeves K., Sheenhan J., et al. (2002). Lignocellulosic biomass to ethanol process design and economics utilizing co-current dilute acid prehydrolysis and enzymatic hydrolysis for corn stover. NREL/TP-510-32438.
- Anex R and Lifset R. (2009). Assessing corn ethanol – Relevance and responsibility. *Journal of Industrial Ecology* 13(4): 479-482.
- Arrouays D., Balesdent J., Germon J.C., Jayet P.A., Soussana J.F., Stengel P. (2002). Contribution of à la lutte contre l'effet de serre. Stocker du carbone dans les sols agricoles de France? Expertise Scientifique Collective. Rapport d'expertise réalisé par INRA à la demande du Ministère de l'Ecologie et du Développement Durable. INRA, Paris, France.
- Audsley E., Alber S., Clift R., Cowell S., Crettaz P., Gaillard G., et al. (1997). Harmonization of environmental life cycle assessment for agriculture. Concerted Action AIR3-CT94-2028. European Commission. DG VI Agriculture. SRI, Silsoe, United Kingdom.
- Bai Y., Luo L., van der Voet E. (2010). Life cycle assessment of switchgrass-derived ethanol as transport fuel. *International Journal of Life Cycle Assessment*. Accepted for publication.
- Baum P., Engelmann J. (2001). Applied macromolecular chemistry. *Nachr Chemie* 49: 368-373.
- Bechthold I., Bretz K., Kabasci S., Kopitzky R., Springer A. (2008). Succinic acid: a new platform chemical for biobased polymers from renewable resources. *Chemical Engineering Technology* 31(5): 647-654.
- Beer T., Grant T. (2007). Life-cycle analysis of emissions from fuel ethanol and blends in Australian heavy and light vehicles. *Journal of Cleaner Production* 15: 833-837.
- BIOPRO:
<http://www.biopro.eu/magazin/wirtschaft/index.html?lang=en&artikelid=/artikel/03558/index.html>.
- Botha T., von Blottnitz H. (2006). A comparison of the environmental benefits of bagasse-derived electricity and fuel ethanol on a life-cycle basis. *Energy Policy* 34: 2654-2661.
- Bullard M. and Metcalfe P. (2001). Estimating the energy requirement and CO₂ emissions from production of the perennial grasses miscanthus, switchgrass and reed canary grass. ETSU B/U1/00645/REP.

- Cardona Alzate C.A., Sánchez Toro O.J. (2006). Energy consumption analysis of integrated flowsheets for production of fuel ethanol from lignocellulosic biomass. *Energy* 31: 2447-2459.
- Cherubini F., Ulgiati S. (2010). Crop residues as raw materials for biorefinery systems – A LCA case study. *Applied Energy* 87: 47-57.
- Curran M.A. (2007). Studying the effect on system preference by varying coproduct allocation in creating life-cycle inventory. *Environmental Science and Technology* 41: 7145-7151.
- Daly H.E. (1990). Sustainable development: from concept and theory to operational principles. *Population and development review*, Vol. 16. Supplement: Resources, environment and population: Present knowledge, future Options, pp. 25-43.
- de Oliveira M.E.D., Vaughan B.E., and Rykiel E.J. (2005). Ethanol as fuel: energy, carbon dioxide balances, and ecological footprint. *Bioscience* 55: 593-602.
- Dietz S. and Neumayer E. (2007). Weak and strong sustainability in the SEEA: concepts and measurement. *Ecological Economics* 61(4): 617–626.
- Directive 2009/28/EC (2009) of the European Parliament and of the Council of 23 April 2009 on the promotion of the use of energy from renewable sources and amending and subsequently repealing Directives 2001/77/EC and 2003/30/EC.
- DOE/EIA-0383 (2008). Annual Energy Outlook 2008 with Projections to 2030. U.S. Energy Information Administration. Washington D.C.
- Efe Ç., Straathof A.J.J., van der Wielen L.A.M. (2005). Technical and economical feasibility of production of ethanol from sugarcane and sugarcane Bagasse. In: B-Basic Internal Report. ISBN: 978-90-809691-6-2.
- Energy Information Administration. International Energy Outlook. Available online: <http://www.eia.doe.gov/>. U.S. Department of Energy, Washington, D.C.
- Ethanol market: <http://www.ethanolmarket.com/industrialethanol.html>.
- Faaij A.P.C. (2006). Bio-energy in Europe: changing technology choices. *Energy Policy* 34: 322-342.
- Fargione J., Hill J., Tilman D., Polasky S., Hawthorne P. (2008). Land clearing and the biofuel carbon debt. *Science* 319: 1235-1238.
- Farrell A.E., Plevin R.J., Turner B.T., Jones A.D., O'Hare M., Kammen D.M. (2006). Ethanol can contribute to energy and environmental goals. *Science* 311: 506-508.
- Fernando S., Adhikari S., Chandrapal C., and Nurali N. (2006). Biorefineries: current status, challenges, and future direction. *Energy & Fuels* 20: 1727-1737.
- Fu G.Z., Chan A.W., Minns D.E. (2003). Life cycle assessment of bio-ethanol derived from cellulose. *International Journal of Life Cycle Assessment* 8(3): 137-141.

- Gabrielle B., Gagnaire N. (2008). Life-cycle assessment of straw use in bio-ethanol production: a case study based on biophysical modelling. *Biomass and Bioenergy* 32: 431-441.
- Gnansounou E., Dauriat A., Panichelli L., Villegas J. (2008). Energy and greenhouse gas balances of biofuels: Biases induced by LCA modeling choices. *Journal of Scientific & Industrial Research* 67: 885-897.
- Gnansounou E., Dauriat A., Villegas J., Panichelli L. (2009). Life cycle assessment of biofuels: energy and greenhouse gas balances. *Bioresource Technology* 100: 4919-4930.
- González García S., Luo L., Moreira M.T., Feijoo G., Huppes G. (2009a). Life cycle assessment of flax shives derived second-generation ethanol fuelled automobiles in Spain. *Renewable and Sustainable Energy Reviews* 13(8): 1922-1933.
- González García S., Luo L., Moreira M.T., Feijoo G., Huppes G. (2009b). Fuel ethanol from hemp hurds: environmental performance. Submitted.
- Graboski M. (2002). Fossil energy use in the manufacture of corn ethanol. National Corn Growers Association, Washington D.C.
- Graham R.L., Nelson R., Sheehan J., Perlack R.D., and Wright L.L. (2007). Current and potential U.S. corn stover supplies. *Agronomy Journal* 99: 1-11.
- Guerra Miguez, O., Siva Siddharthan, D., Suárez Zuluaga, D.A. (2009). Technical and economical feasibility of production of ethanol from switchgrass. In: B-Basic internal report. Delft University of Technology, The Netherlands.
- Guinée J.B. et al. (2002). Handbook on life cycle assessment – operational guide to the ISO standard. ISBN 1-4020-0228-9. Kluwer Academic Publishers.
- Guinée J.B., Heijungs R., and Huppes G. (2004). Economic allocation: examples and derived decision tree. *International Journal of Life Cycle Assessment* 9(1): 23-33.
- Hadzhiyska D., Luo L., van der Voet E. (2009). An energy analysis of ethanol from sugar cane, CML report, Leiden, The Netherlands.
- Halleux H., Lassaux S., Renzoni R. and Germain A. (2008). Comparative life cycle assessment of two biofuels ethanol from sugar beet and rapeseed methyl ester. *International Journal of Life Cycle Assessment* 13(3): 184-189.
- Hauschild M.Z. (2000). Estimating pesticide emissions for LCA of agricultural products. In: Weidema, B.P., Meeusen, M.J.G., editors. *Agricultural data for life cycle assessments*. Vol 2. The Hague, The Netherlands. LCANet Food: 64-79.
- Heijungs R. (2009). Chain Management by Life Cycle Assessment (CMLCA) software package version 5.1. Institute of Environmental Sciences (CML), Leiden University. Free online: <http://cml.leiden.edu/software/software-cmlca.html>.
- Homewood B. (1993). Will Brazil's cars go on the Wagon? *New Scientist* 137: 22-24.

- Hu Z., Pu G., Fang F., Wang C. (2004a). Economics, environment, and energy life cycle assessment of automobiles fueled by bio-ethanol blends in China. *Renewable Energy* 29: 2183-2192.
- Hu Z., Fang F., Ben D., Pu G., Wang C. (2004b). Net energy, CO₂ emission, and life-cycle cost assessment of cassava-based ethanol as an alternative automotive fuel in China. *Applied Energy* 78: 247-256.
- Huppes G. (1993). *Macro-environmental policy: principles and design*. Elsevier, Amsterdam.
- Huppes G. and Ishikawa M. (2009). Eco-efficiency guiding micro-level actions towards sustainability: Ten basic steps for analysis. *Ecological Economics* 68: 1687–1700.
- IEA (2006). *Key world energy statistics 2006*. International Energy Agency, Energy statistic division. Paris, France. p.82.
- IPCC (2007). *Climate change 2007: the physical science basis*. Contribution of working group I to the fourth assessment. International Panel on Climate Change. Geneva, Switzerland.
- ISIC pricing: http://www.icispricing.com/il_shared/Samples/SubPage167.asp.
- ISO Norm 14040 (2006). *Environmental management – life cycle assessment – principles and framework*. International Organization for Standardization.
- ISO Norm 14044 (2006). *Environmental management – life cycle assessment – principles and framework*. International Organization for Standardization.
- Jungbluth N., Bauer C., Dones R., Frischknecht R. (2005). Life cycle assessment for emerging technologies: case studies for photovoltaic and wind power. *International Journal of Life Cycle Assessment* 10(1): 24-34.
- Kadam K.L. (2002). Environmental benefits on a life cycle basis of using bagasse-derived ethanol as a gasoline oxygenate in India. *Energy Policy* 30: 371-384.
- Kadam K.L., Chin C.Y., Brown L.W. (2008). Flexible biorefinery for producing fermentation sugars, lignin and pulp from corn stover. *Journal of Industrial Microbiology and Biotechnology* 35: 331-341.
- Kamm B. and Kamm M. (2004). Principles of biorefinery. *Applied Microbiology and Biotechnology* 64: 137-145.
- Kaparaju P., Serrano M., Thomsen A.B., Kongjan P., Angelidaki I. (2009). Bioethanol, biohydrogen and biogas production from wheat straw in a biorefinery concept. *Bioresource Technology* 100: 2562-2568.
- Keller J.L. (1984). Ethanol and methanol as fuel. in *Encyclopedia of Chemical Processing and Design*, 4th edition, New York, Dekker M., 20: 11-39.
- Kelly K.J., Bailey B.K., Coburn T.C., Clark W., Lissiuk P. (1996). Federal test procedure emissions test results from ethanol variable-fuel vehicle Chevrolet Lumina. Society

- for Automotive Engineers, International Spring Fuels and Lubricants Meeting, Dearborn, MI.
- Kemppainen A.J. and Shonnard D.R. (2005). Comparative life-cycle assessments for biomass-to-ethanol production from different regional feedstocks. *Biotechnology Progress* 21: 1075-1084.
- Kim S. and Dale B.E. (2002). Allocation procedure in ethanol production system from corn grain I. system expansion. *International Journal of Life Cycle Assessment* 7(4): 237-243.
- Kim S. and Dale B.E. (2005a). Environmental aspects of ethanol derived from no-tilled corn grain: nonrenewable energy consumption and green house gas emissions. *Biomass and Bioenergy* 28: 475-489.
- Kim S. and Dale B.E. (2005b). Life cycle assessment of various cropping systems utilized for producing biofuels: Bioethanol and biodiesel. *Biomass and Bioenergy* 29: 426-439.
- Kim S. and Dale B.E. (2006a). Ethanol fuels: E10 or E85 – life cycle perspectives. *International Journal of Life Cycle Assessment* 11(2): 117-121s.
- Kim S. and Dale B.E. (2006b). Global potential bioethanol production from wasted crops and crop residues. *Biomass and Bioenergy* 26: 361-375.
- Kim S., Dale B.E., Jenkins R. (2009). Life cycle assessment of corn grain and corn stover in the United States. *International Journal of Life Cycle Assessment* 14: 160-174.
- Lal R. (2005). World crop residues production and implications of its use as a biofuel. *Environmental International* 31: 575-84.
- Landucci R., Goodman B., Wyman C. (1994). Methodology for evaluating the economics of biologically producing chemicals and materials from alternative feedstocks. *Applied Biochemistry and Biotechnology* 45/46: 677-696.
- Laser M., Jin H., Jayawardhana K., Dale B.E., Lynd L.R.. (2009a). Projected mature technology scenarios for conversion of cellulosic biomass to ethanol with coproduction thermo-chemical fuels, power, and/or animal feed protein. *Biofuels Bioproducts & Biorefining* 3: 231-246.
- Laser M., Larson E., Dale B.E., Wang M., Greene N., Lynd L.E. (2009b). Comparative analysis of efficiency, environmental impact, and process economics for mature biomass refining scenarios. *Biofuels Bioproducts & Biorefining* 3: 247-270.
- Lavigne A., Powers S.E. (2007). Evaluating fuel ethanol feedstocks from energy policy perspectives: A comparative energy assessment of corn and corn stover. *Energy Policy* 35: 5918-5930.

- Leng R., Wang C., Zhang C., Dai D., Pu G. (2008). Life cycle inventory and energy analysis of cassava-based fuel ethanol in China. *Journal of Cleaner Production* 16: 374-384.
- Liska A.J., Yang H.S., Bremer V.R., Klopfenstein T.J., Walters D.T., Erickson G.E. and Cassman K.G. (2009). Improvements in life cycle energy efficiency and greenhouse gas emissions of corn-ethanol. *Journal of Industrial Ecology* 13(1): 58-74.
- Luo L., van der Voet E., Huppes G., Udo de Haes H.A. (2009a). Allocation issues in LCA methodology: A case study of corn stover-based fuel ethanol. *International Journal of Life Cycle Assessment* 14: 529-539.
- Luo L., van der Voet E., Huppes G. (2009b). Life cycle assessment and life cycle costing of bioethanol from sugarcane in Brazil. *Renewable and Sustainable Energy Reviews* 13(6-7): 1613-1619.
- Luo L., van der Voet E., Huppes G. (2009c). An energy analysis of ethanol from cellulosic feedstock – corn stover. *Renewable and Sustainable Energy Reviews* 13(8): 2003-2011.
- Lynd L.R., Wang M.Q. (2004). A product nonspecific framework for evaluating the potential of biomass-based products to displace fossil fuels. *Journal of Industrial Ecology* 7(3-4): 17-32.
- Lynd L.R., Wyman C., Laser M., Johnson D., Landucci R. (2005). Strategic biorefinery analysis: analysis of biorefineries. NREL/SR-510-35578, NREL.
- Macedo I.C. (1998). Greenhouse gas emissions and energy balances in bio-ethanol production and utilization in Brazil (1996). *Biomass and Bioenergy* 14(1): 77-81.
- Macedo I.C., Leal M.R.L.V., Silva J.E.A.R. (2004). Assessment of greenhouse gas emissions in the production and use of fuel ethanol in Brazil.
- Macedo I.C., Seabra J.E.A., Silva J.E.A.R. (2008). Greenhouse gases emissions in the production and use of ethanol from sugarcane in Brazil: The 2005/2006 averages and a prediction for 2020. *Biomass and Bioenergy* 32: 582-595.
- Malça J., Freire F. (2006). Renewability and life-cycle energy efficiency of bioethanol and bio-ethyl tertiary butyl ether (bioETBE): assessing the implications of allocation. *Energy* 31: 3362-3380.
- McAloon A., Taylor F., Yee W., Ibsen K., Wooley R. (2000). Determining the cost of producing ethanol from corn starch and lignocellulosic feedstocks. NREL/TP-580-28893, NREL.
- McKinlay J.B., Vieille C., Zeikus J.G. (2007). Prospects for a bio-based succinate industry. *Applied Microbiology and Biotechnology* 76: 727-740.
- Mitchell R., Vogel K.P. and Sarath G. (2008). Managing and enhancing switchgrass as bioenergy feedstock. *Biofuels, Bioproducts & Biorefining* 2: 530-539.

- Nemecek T., Heil A., Huguenin O., Meier S., Erzinger S., et al. (2004). Life cycle inventories of agricultural production systems. Ecoinvent report No. 15. Swiss Centre for Life Cycle Inventories, Dübendorf, Switzerland.
- Nemecek T. and Kägi T. (2007). Life cycle inventories of Swiss and European agricultural production systems. Ecoinvent Report No. 15. Swiss Centre for Life Cycle Inventories, Zurich and Dübendorf, Switzerland.
- Nghiem N.P., Davison B.H., Suttle B.E., Richardson G.R. (1997). Production of succinic acid by *Anaerobiospirillum succiniciproducens*. *Applied Biochemistry and Biotechnology* 63-65: 565-576.
- Nguyen T.L.T. and Gheewala S.H. (2008a). Fossil energy, environmental and cost performance of ethanol in Thailand. *Journal of Cleaner Production* 16: 1814-1821.
- Nguyen T.L.T. and Gheewala S.H. (2008b). Life cycle assessment of fuel ethanol from cane molasses in Thailand. *International Journal of Life Cycle Assessment* 13: 301-311.
- NREL Biomass Research: <http://www.nrel.gov/biomass/biorefinery.html>.
- OECD/IEA (2007). World energy outlook 2007. International Energy Agency, Organisation for economic co-operation and development. Paris, France.
- OECD/IEA (2008). World energy outlook 2008. International Energy Agency, Organisation for economic co-operation and development. Paris, France. p.578.
- Okino S., Noburyu R., Suda M., Jojima T., Inui M., Yukawa H. (2008). An efficient succinic acid production process in a metabolically engineered *Corynebacterium glutamicum* strain. *Applied Microbiology and Biotechnology* 81: 459-464.
- Ometto A.R., Hauschild M.Z., Roma W.N.L. (2009). Lifecycle assessment of fuel ethanol from sugarcane in Brazil. *International Journal of Life Cycle Assessment* 14: 236-247.
- Organic Facts: <http://www.organicfacts.net/nutrition-facts/cereals/nutritional-value-of-corn-and-rice.html>.
- Paster M., Pellegrino J.L., Carole T.M. (2003). Industrial bio-products: today and tomorrow. Energetics, Incorporated, Columbia, MD.
- Patyk A., Reinhardt G.A. (2002). LCA of bioethanol and ETBE. Internal report. Institute for Energy and Environmental Research (IFEU).
- Patzek T.W. (2004). Thermodynamics of the corn-ethanol biofuel cycle. *Critical Review of Plant Science* 23: 519-567.
- Pimentel D. (2003). Ethanol fuels: energy balance, economics, and environmental impacts are negative. *Natural Resources Research* 12(2): 127-134.
- Pimentel D. and Patzek T.W. (2005). Ethanol production using corn, switchgrass, and wood; biodiesel production using soybean and sunflower. *Natural Resources Research* 14: 65-76.

- Pimentel D. and Patzek T.W. (2007). Ethanol production: energy and economic issues related to U.S. and Brazilian sugarcane. *Natural Resources Research* 16: 235-241.
- Pordesimo L.O., Hames B.R., Sokhansanj S., Edens W.C. (2005). Variation in corn stover composition and energy content with crop maturity. *Biomass and Bioenergy* 28: 366-374.
- Ravishankara A.R., Daniel J.S., Portmann R.W. (2009). Nitrous Oxide (N₂O): The dominant ozone-depleting substance emitted in the 21st century. *Science* 326: 123-125.
- Reading A.H., Norris J.O.W., Feest E.A., Payne E.L. (2002). Ethanol emissions testing. AEAT unclassified, E&E/DDSE/02/021, Issue 3.
- Realff M.J. and Abbas C. (2004). Industrial Symbiosis – Refining the Biorefinery. *Journal of Industrial Ecology* 7 (3-4): 5-9.
- Reinhardt G., Uihlein A. (2002). Bioethanol and ETBE versus other biofuels for transportation in Europe: an ecological comparison. In: The 114th international symposium on alcohol fuels (ISAF XIV).
- Renewable Energy Road Map – Renewable energies in the 21st century: building a more sustainable future. 2007. COM (2006) 848 final.
- Renouf M.A., Wegener M.K., Nielsen L.K. (2008). An environmental life cycle assessment comparing Australian sugarcane with US corn and UK sugar beet as producers of sugars for fermentation. *Biomass and Bioenergy* 32(12):1144-1155.
- Rosegrant M.W., Paisner M.S., Meijer S. and Witcover J. (2001). 2020 global food outlook: trends, alternatives, and choices. International Food Policy Research Institute, Washington, D.C.
- Rudner M.S., Jeremic S., Petterson K.A., Kent D.R., Brown K.A., Drake M.D., et al. (2005). Intramolecular hydrogen bonding in disubstituted ethanes. A comparison of NH · · · O– and OH · · · O– hydrogen bonding through conformational analysis of 4-amino-4-oxobutanoate (succinamate) and monohydrogen 1,4-butanoate (monohydrogen succinate) anions. *Journal of Physical Chemistry A*. 109: 9076–82.
- Samuelov, N.S., Lamed, R., Lowe, S., Zeikus, J.G. (1991). Influence of CO₂-HCO₃⁻ levels and pH on growth, succinate production, and enzyme activities of *Anaerobiospirillum succiniciproducens*. *Applied Environmental Microbiology* 57: 3013-3019.
- Saving Electricity: <http://michaelbluejay.com/electricity/cost.html>.
- Schmer M.R., Vogel K.P., Mitchell R.B., and Perrin R.K. (2008). Net energy of cellulosic ethanol from switchgrass. *PNAS* 105(2): 464-469.
- Schmidheiny S. (1992). *Changing Course: A global business perspective on development and the environment*. ISBN: 0-262-69153-1.

- Searchinger T., Heimlich R., Houghton R.A., Dong F., Elobeid A., Fabiosa J., Tokgoz S., Hayes D., Yu T. (2008). Use of U.S. croplands for biofuels increases greenhouse gases through emissions from land-use change. *Science* 319: 1238-1240.
- Searcy E., Flynn P.C. (2008). Processing of straw/corn stover: comparison of life cycle emissions. *International Journal of Green Energy* 5: 423-437.
- Shapouri H., McAloon A. (2002). The 2001 net energy balance of corn-ethanol. U.S. Department of Agriculture, Washington D.C.
- Sheehan J., Aden A., Paustian K., Killian K., Brenner J. Walsh M. et al. (2004). Energy and environmental aspects of using corn stover for fuel ethanol. *Journal of Industrial Ecology* 7(3-4): 117-146.
- Sheehan J., Aden A., Riley C., Paustian K., Brenner J., Lightle D., et al. (2002). Is ethanol from corn stover sustainable? Adventures in cyber-farming: a life cycle assessment of the production of ethanol from corn stover for use in a flex fuel vehicle. Draft report for peer review, NREL, Colorado.
- Shell Report (2008). Shell energy scenarios to 2050.
- Short W., Packey D.J., Holt T. (1995). A manual for economic evaluation and energy efficiency and renewable energy technologies. NREL/TP-462-5173, NREL, Golden, CO.
- Silalertruksa T., Gheewala S.H. (2009). Environmental sustainability assessment of bio-ethanol production in Thailand. *Energy* 34(11): 1933-1946.
- Sokhansanj S., Mani S., Turhollow A., Kumar A., Bransby A., Lynd L. et al. (2009). Large-scale production, harvest and logistics of switchgrass (*Panicum virgatum* L.) – current technology and envisioning a mature technology. *Biofuels, Bioproducts & Biorefining* 3: 124-141.
- Song H., Lee S.Y. (2006). Production of succinic acid by bacterial fermentation. *Enzyme and Microbial Technology* 29: 352-261.
- Spatari S., Zhang Y. and Maclean H.L. (2005). Life cycle assessment of switchgrass- and corn stover-derived ethanol-fueled automobiles. *Environmental Science and Technology* 39: 9750-9758.
- Spielmann M., Kägi T., Stadler P., Tietje O. (2004). Life cycle inventories of transport services. Ecoinvent report No. 14. Swiss Centre for Life Cycle Inventories, Dübendorf, Switzerland.
- Styles D., Jones M.B. (2008). Life-cycle environmental and economic impacts of energy-crop fuel-chains: an integrated assessment of potential GHG avoidance in Ireland. *Environmental Science & Policy* II: 294-306.
- Sun Y., Cheng J. (2002). Hydrolysis of lignocellulosic materials for ethanol production: a review. *Biosource Technology* 83: 1-11.

- Swiss Centre of Life Cycle Inventories. Ecoinvent database. Available online: <http://www.ecoinvent.org/>.
- Tan R.R. and Culuba A.B. (2002). A life cycle assessment of conventional and alternative fuels for road vehicles. In: InLCA.
- Tukker A., Huppes G., Guinée J.B., Heijungs R., de Koning A., van Oers L., et al. (2006). Environmental impact of products (EIPRO) – analysis of the life cycle environmental impacts related to the final consumption of the EU-25.
- Uihlein A., Schebek L. (2009). Environmental impacts of a lignocellulose feedstock biorefinery system: An assessment. *Biomass and Bioenergy* 33: 793-802.
- UN (2005). Millennium ecosystem assessment report: ecosystems and human well-being. Millennium ecosystem assessment working groups.
- UNPD (2006). World population prospects: the 2006 vision. United Nations Population Division. New York.
- U.S. Life-Cycle Inventory Database: <http://www.nrel.gov/lci/>.
- van Dyne D.L., Blase M.G., Clements L.D. (1999). A strategy for returning agriculture and rural America to long-term full employment using biomass refineries. *Perspectives on New Crops and New Uses*. Janick J. Ed; ASHS Press, Alexandria, VA.
- von Blottnitz H. and Curran M.A. (2007). A review of assessments conducted on bio-ethanol as a transportation fuel from a net energy, greenhouse gas, and environmental life cycle perspective. *Journal of Cleaner Production* 15: 607-619.
- Wang M. (2001). Developing and use of GREET 1.6 fuel-cycle model for transportation fuels and vehicle technologies. Tech. Rep. ANL/ESD/TM-163. Argonne National Laboratory, Argonne, IL.
- Willke Th, Vorlop K-D. (2004). Industrial bioconversion of renewable resources as an alternative to conventional chemistry. *Applied Microbiology and Biotechnology* 66: 131-142.
- Wood W.A. (1961). Fermentation of carbohydrates and related compounds. In: Gunsalus IC, Stanier RY (eds) *The bacteria*. Academic Press, volume 2: 59-149.
- Wooley R., Ruth M., Sheehan J., Ibsen K., Majdeski H., Galvez A. (1999). Lignocellulosic biomass to ethanol process design and economics utilizing co-current dilute acid prehydrolysis current and futuristic scenarios. NREL/TP-580-26157.
- Wu M., Wu Y., Wang M. (2006a). Energy and emission benefits of alternative transportation liquid fuels derived from switchgrass: a fuel life cycle assessment. *Biotechnology Progress* 22: 1012-1024.

- Wu M., Wang M., and Huo H. (2006b). Fuel-cycle assessment of selected bioethanol production pathways in the United States. Energy System Division, Argonne National Laboratory.
- WWI (2006). Biofuel for transportation: global potential and implications for sustainable agriculture and energy in the 21st century. The Worldwatch Institute. EarthScan Publications Ltd, London, United Kingdom. p.480.
- Zah R., Böni H., Gauch M., Hischer R., Lehmann M., Wäger P. (2007). Life cycle assessment of energy products: environmental impact assessment of biofuels. Empa, Technology and Society Lab.
- Zeikus J.G. (1995). Chemical and fuel production by anaerobic bacteria. Annual Review of Microbiology 34: 423-64.
- Zeikus J.G., Jain, M.K., Elankovan, P. (1999). Biotechnology of succinic acid production and markets for derived industrial products. Applied Microbiology Biotechnology 51: 545-552.
- Zhang M., Eddy C., Deanda K., Finkelstein M., Picataggio S. (1995). Metabolic engineering of a pentose metabolism pathway in *Zymomonas mobilis*. Science 267: 240-243.

List of Publications

- Luo L., van der Voet E., Huppes G., Udo de Haes H.A. (2009). Allocation issues in LCA methodology: A case study of corn stover-based fuel ethanol. *International Journal of Life Cycle Assessment* 14: 529-539.
- Luo L., van der Voet E., Huppes G. (2009). Life cycle assessment and life cycle costing of bioethanol from sugarcane in Brazil. *Renewable and Sustainable Energy Reviews* 13(6-7): 1613-1619.
- Luo L., van der Voet E., Huppes G. (2009). An energy analysis of ethanol from cellulosic feedstock – Corn stover. *Renewable and Sustainable Energy Reviews* 13(8): 2003-2011.
- Luo L., van der Voet E., Huppes G. (2010). Biorefining of lignocellulosic feedstock – Technical, economic and environmental considerations. *Bioresource Technology*. In press.
- Luo L., van der Voet E., Huppes G. (2010). Energy consideration and environmental performance of bioethanol production from lignocelluloses. Special Issue “Bioprocess Development for Biofuels and Bioproducts” in *International Journal of Chemical Engineering*. Submitted for publication.
- Bai Y., Luo L., van der Voet E. (2010). Environmental and economic life cycle impacts of switchgrass-derived ethanol as transport fuel. *International Journal of Life Cycle Assessment*. Accepted for publication.
- González García S., Luo L., Moreira M.T., Feijoo G., Huppes G. (2009). Life cycle assessment of flax shives derived second generation ethanol fuelled automobiles in Spain. *Renewable and Sustainable Energy Reviews* 13(8): 1922-1933.
- González García S., Luo L., Moreira M.T., Feijoo G., Huppes G. (2009). Fuel ethanol from hemp hurds: Environmental performance. *Biomass and Bioenergy*. Submitted for publication.
- van der Voet E., Lifset R., Luo L. (2010). Life cycle assessment of biofuels, convergence and divergence. *Biofuels*. Submitted for publication.
- Luo L., van der Voet E., Huppes G. (2008). Life cycle assessment of fuel ethanol from different regional feedstocks. *Proceedings Venice 2008, Second International Symposium on Energy from Biomass and Waste*. ISBN 978-88-6265-004-5.
- Luo L., van der Voet E., Huppes G. (2008). Energy analysis of bioethanol production from biomass. *Proceedings Venice 2008, Second International Symposium on Energy from Biomass and Waste*. ISBN 978-88-6265-004-5.

Curriculum Vitae



Lin Luo was born on 15th of August 1978 in Beijing, China. From 1997 to 2001 she studied Biotechnology in Beijing Union University, and received her Bachelor degree with honours.

In 2001 she was awarded a scholarship to continue her graduate study in Chemical/Biochemical Engineering in Delft University of Technology, the Netherlands. Her graduation research was conducted in the Department of Process and Energy in the field of reactive crystallization, and in August 2003 she received her Master degree.

After her graduation she started a special postgraduate programme (TwAIO) in Bioprocess Design, and in November 2005 she obtained Professional Doctorate in Engineering (PDEng) with a research project “Miniaturized self-interaction chromatography for predictive protein crystallization”.

In December 2005, she joined the Department of Industrial Ecology, Institute of Environmental Sciences (CML), Faculty of Science, University of Leiden to work towards a PhD. Her key research is “Analysis and directions of biomass refining for sustainable development”.

Since December 2009 she has been employed as post-doctoral researcher at CML.

