Sustainability assessment of second generation bioethanol production

Model-based life cycle assessment of various biochemical conversion paths

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Abstract

Lignocellulosic biomass is of increasing importance for the bio-economy in providing feedstock for sustainable energy carriers and chemicals. Second generation bioethanol is currently one of the most developed processes based on lignocellulosic biomass as feedstock and the findings from latest research offer valuable insights for the further development of the bio-economy. Main challenge is the recalcitrant behavior of lignocellulosic biomass that requires pretreatment before subsequent hydrolysis and fermentation. Obtaining sugars from lignocellulosic biomass is also important for the production of second generation fuels and chemicals other than bioethanol. Pretreatment can be performed in numerous ways, each especially suitable for certain types of biomass and coming with distinct advantages and disadvantages.

In order to determine the environmental performance of second generation bioethanol, the production chain was studied using life cycle assessment (LCA). The bioethanol production process was modeled using a recent NREL model on the biochemical conversion of lignocellulosic biomass. The LCA was especially focused on the pretreatment part of the production chain. The non-renewable energy use (NREU) needed to produce 1 kg of ethanol from corn stover was 8.4 MJ in case of the system expansion approach and 9.5 MJ in case of allocation based on energy content. The corresponding greenhouse gas emissions (GHG) were -1.1 kg CO_2 eq. and -1.0 kg CO_2 eq.

The LCA results were found to be especially sensitive to the pretreatment temperature, acid loading, hydrolysis enzyme loading and conversion efficiencies in the system expansion approach; and toward the pretreatment acid loading, hydrolysis enzyme loading and conversion efficiencies in the energy allocation approach. Further adaptations in the NREL model were made to represent experimental pretreatment results for corn stover and switchgrass, found in literature. These adapted cases show in general lower performance than the calculations based on the original NREL model as result of lower solids loading, lower conversion efficiencies and increased requirements of chemical or higher temperature. However, when increased demand of electricity or decreased electricity production result in the purchase of additional electricity, the environmental impact increases drastically.

Comparison of the LCA results based on the NREL model with the available LCA studies on second generation bioethanol showed average environmental performance. Comparison of the results of second generation bioethanol production show better performance compared to usage of first generation ethanol or gasoline as fuel.

Acknowledgements

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List of Acronyms

AFEX	Ammonia Fiber Explosion pretreatment
ARP	Ammonia Recycle Percolation
CBP	Consolidated Bioprocessing
CAFI	Biomass Refining Consortium for Applied Fundamentals and Innovation
CSL	Corn Steep Liquor
DA	Dilute Acid pretreatment
DAP	Diammonium Phosphate
GHG	Greenhouse Gas emissions
GREET	Greenhouse gases, Regulated Emissions and Energy use in Transportation model
HHV	Higher Heating Value
HMF	Hydroxymethylfurfural
ILs	Ionic Liquids pretreatment
INL	Idaho National Laboratory
LCA	Life Cycle Assessment
LCI	Life Cycle Inventory
LCIA	Life Cycle Impact Assessment
LHV	Lower Heating Value
LHW	Liquid Hot Water pretreatment
NREL	National Renewable Energy Laboratory
NREU	Non-Renewable Energy Use
REU	Renewable Energy Use
SE	Steam Explosion pretreatment
SHF	Separate (or sequential) Hydrolysis and Fermentation
SSCF	Simultaneous Saccharification and Co-Fermentation
SSF	Simultaneous Saccharification and Fermentation
TSDA	Two-Stage Dilute Acid pretreatment

1. Introduction

Rising prices of fossil fuels and the increasing need for greenhouse gas reduction in order to avoid climate change has strengthened the importance of producing clean, low carbon and secure energy carriers and chemicals. The concept of the bio-based economy provides attractive ideas to produce energy carriers and chemicals based on non-fossil resources and with reduced environmental impact. However, this strategy will fail unless the supply of feedstock and the subsequent processing steps are sustainable.

Production of bioethanol in the European Union has increased from only 292 million L in 2000 to 4,393 million L in 2011 (Biofuels Platform 2012; ePURE 2012) (Figure 1-1). At the moment, the largest part is produced from first generation feedstocks: sugars and vegetable oils found in arable crops, like wheat, corn and sugar cane. First generation bioethanol generally shows a net benefit in greenhouse gas emissions and energy balance (de Vries et al. 2010); however, there are several concerns, with the most important being that first generation bioethanol (Sims et al. 2009):

- offers only limited greenhouse gas emission reduction at relatively high costs in terms of €/tonne of carbon dioxide avoided;
- is accelerating deforestation (with other potentially indirect land use effects also to be accounted for);
- potentially has a negative impact on biodiversity;
- competes for scarce water resources in some regions; and
- potentially contributes to higher food prices due to competition with food crops.
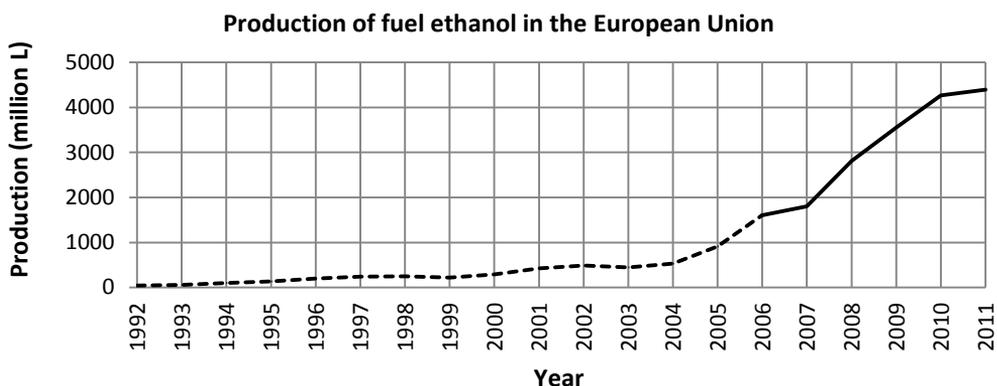
Figure 1-1: Production of fuel ethanol in the European Union (EU-27) from 1992 to 2011.
Source: 1992-2006 (Biofuels Platform 2012), 2006-2011 (ePURE 2012).

As result of these concerns, first generation bioethanol may not meet its claimed environmental benefits. In contrast, second generation feedstocks are based on lignocellulosic biomass from non-food crops or agricultural and forestry residues[1], generally showing better performance with respect to the concerns described above (Sims et al. 2009).

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[1] 'Lignocellulosic' bioethanol and 'second generation' bioethanol are used interchangeably in this report.

As an example, Cherubini et al. (2009) describe the life cycle performance of ethanol from sugar cane compared to ethanol from lignocelluloses. For the use of bioethanol as fuels in cars, the cumulative energy requirement for bioethanol from sugarcane is 12-13 MJ/km, whereas the requirement for bioethanol from lignocelluloses is only 6.1-9.3 MJ/km. In addition, greenhouse gas emissions are 50-75 g CO_2-eq/km for sugar cane based ethanol and 25-50 g CO_2-eq/km for lignocellulosic ethanol.

At the moment, several technologies are in development with the objective to use second generation feedstocks for the production of bioethanol. The production of second generation bioethanol is expected to increase drastically in the coming years (Figure 1-2).

To promote the development of second generation biofuels and avoid the negative impacts from first generation biofuels, the European Commission recently presented a proposal for an amendment to the renewable energy directive that limits the contribution of biofuels from food crops to a maximum of 5% (European Commission 2012). Second generation biofuels are counted two- or even four-fold with respect to their energy content in reaching the share of renewable energy. However, requirements for greenhouse gas reduction of both first and second generation biofuels are also more stringent: installations starting operation after July 1, 2014 have to reach at least 60% reduction, while installations that were in operation before July 1, 2014 have to achieve 35% reduction until December 31, 2017 and 50% reduction from January 1, 2018.
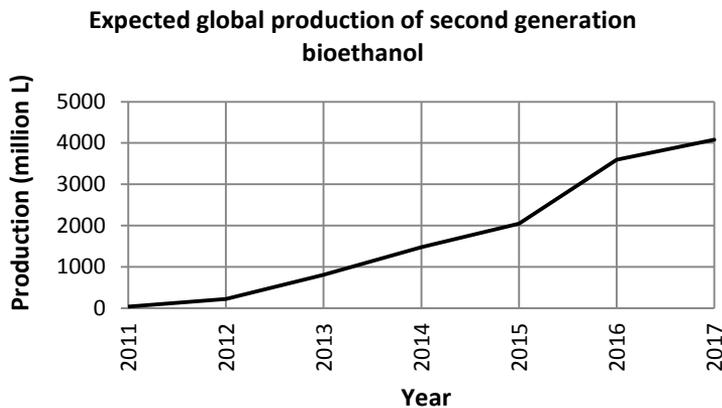
Figure 1-2: Expected production of second generation bioethanol in the world from 2011-2017 (BiofuelsDigest 2012).

Compared to first generation feedstocks, lignocellulosic materials are rather difficult to process, due to the more woody character of those materials. The main components of lignocellulosic biomass are cellulose, hemicellulose and lignin. Cellulose ($C_6H_{10}O_5$)$_n$ is a polymer of glucose and many properties depend on the degree of polymerization, which varies between 800 and 10000 units. The possibility of hydrogen bond formation results in a parallel arrangement of cellulose chains. Cellulose is found in crystalline and non-crystalline structures. Hemicellulose represents a family of polysaccharides, like xylan, glucomannan and various other molecules, and forms highly branched structures. Lignin is also an amorphous three-dimensional polymer, with coumaryl, coniferyl and sinapyl alcohol as general building blocks (Harmsen et al. 2010). The

properties of the main components of lignocellulosic biomass and their role in the recalcitrant behaviour are further described by Pu et al. (2013) and Harmsen et al. (2010).

Depending on the source and the composition the biomass can be divided in several categories, with the most important being: agricultural residues (including agro-industrial waste), hardwood, softwood, herbaceous biomass, next to cellulosic waste and municipal solid waste (Cardona, Sánchez, and Gutiérrez 2009). According Menon and Rao (2012) biomass in general consists of 40-50% cellulose, 25-30% hemicellulose and 15-20% lignin. In Table 1-1 the composition and category of different types of lignocellulosic biomass is given. While the composition varies both within a category and between different sources of one type of biomass, some differences can be observed. Softwood and hardwood contain more cellulose, while the hemicellulose content of agricultural residues and herbaceous biomass is higher. In addition, wood in general contains more lignin than the other categories. Finally, the lignin percentage of softwood is higher compared to hardwood.

Conversion of biomass into biofuels is achieved by thermochemical conversion, like pyrolysis and gasification, or biochemical conversion. In case of thermochemical conversion, the pyrolysis process is used in most cases, resulting in products like charcoal, tars and gasses including methane, hydrogen, carbon monoxide and carbon dioxide (Bhaskar et al. 2011). Production of ethanol from syngas originating from the gasification of biomass is in development and can be achieved by catalytic conversion (Subramani and Gangwal 2008) or microbial fermentation (Mohammadi et al. 2011). The biochemical conversion route comprises conversion of biomass using enzymes.

The biochemical production of lignocellulosic bioethanol consists of various processing steps. The main steps are biomass pretreatment, hydrolysis, fermentation and product recovery (Figure 1-3). During pretreatment the recalcitrant properties of lignocellulosic biomass are reduced, in order to obtain an enhanced hydrolysis and fermentation. During the hydrolysis, the polymers are converted to monomeric sugars, which can then be fermented in order to obtain ethanol. While reduction of recalcitrant properties and the hydrolysis reaction are strictly spoken separate processes, many pretreatment processes result in (partial) glucose or hemicellulose hydrolysis, mainly promoted by acids that are either added or formed during the process. Hydrolysis and fermentation by enzymes can be performed sequentially in Separate (or Sequential) Hydrolysis and Fermentation (SHF) or concurrently in Simultaneous Saccharification and Fermentation (SSF). In addition, when both fermentation of pentose (originating from hemicellulose) and hexose (originating from cellulose) occur, this is called co-fermentation (SSCF). Currently, the Consolidated Bioprocessing (CBP) production is in development, where ethanol and all required enzymes are produced in a single reactor. CPB implies lower capital and operational cost for enzyme production, but requires hydrolysis and fermentation enzymes to have optimal performance at similar temperatures (Hamelinck, Van Hooijdonk, and Faaij 2005).

The pretreatment is one of the first large steps in the bioethanol production chain; it has therefore a large impact on the performance of further processing. Efficient pretreatment with respect to yields and energy performance is therefore crucial for the economic viability of lignocellulosic bioethanol.

Table 1-1: Composition (%) of lignocelluloses in several feedstocks on dry basis.

Lignocellulosic material	Cellulose	Hemi-cellulose	Lignin	Ash	Acids	Extrac-tives	Reference
Agricultural residues							
Corn stover	36.1	29.2	17.2	7.1			Wyman et al. (2005)
Sugarcane bagasse	40	25	25				Ekman (2012)
Wheat straw	30-38	41-50	20-25				Ekman (2012)
Wheat straw	30	50	15				Sun and Cheng (2002)
Hardwood							
Birch	38.2	19.7	22.8				Jørgensens et al. (2007)
Black locust	41.6	17.66	26.7	2.15	4.57	7.31	Hamelinck et al. (2005)
Eucalyptus	49.5	13.07	27.71	1.26	4.19	4.27	Hamelinck et al. (2005)
Poplar	43.8-45.1	20.4-21.5	21.4-29.1	0.8-1.1		3.4-3.6	Wyman et al. (2009)
Stems	40-55	24-40	18-25				Menon and Rao (2012)
Willow	43	29.3	24.2				Jørgensens et al. (2007)
Softwood							
Douglas fir	35-48	20-22	15-21				Menon and Rao (2012)
Pine	44.55	21.9	27.67	0.31	2.67	2.88	Hamelinck et al. (2005)
Pine	46.4	22.9	29.4				Jørgensens et al. (2007)
Spruce	43.4	18	28.1				Jørgensens et al. (2007)
Spruce wood	49	22	29				Ekman (2012)
Stems	45-50	24-40	18-25				Menon and Rao (2012)
Stems	45-50	25-35	25-35				Sun and Cheng (2002)
Herbaceous biomass							
Bermuda grass	25	35.7	6.4				Sun and Cheng (2002)
Grasses	25-40	25-50	10-30				Menon and Rao (2012)
Switchgrass	31-45	25-30	12-18				Ekman (2012)
Switchgrass	33-36	22	21-23	3-5	1-6	1-9	Wyman et al. (2011)
Switchgrass	45	31.4	12				Sun and Cheng (2002)
Others							
Cardboard	49.56	15.77	14.86			2.4	Wang et al. (2012a)
Leaves	15-20	80-85	0				Sun and Cheng (2002)
Magazine	34.35	13.56	14.19			3.3	Wang et al. (2012a)
Newspaper	43.78	16.86	16.82			3.65	Wang et al. (2012a)
Office paper	55.69	13.91	5.78			1.87	Wang et al. (2012a)
Paper	85-99	0	0-15				Sun and Cheng (2002)

Figure 1-3: Simplified lignocellulosic ethanol production chain.

1.1   Problem definition

Second generation bioethanol production technologies are of increasing importance for the bio-economy to provide sustainable energy carriers and chemicals. However, the literature on the environmental assessment of the feedstock-technology combinations is scattered, partly dated, partly confidential and written for different types of audiences. In order to facilitate further research and strategic decisions regarding second generation bioethanol production, the available information needs to be compiled and analysed in a consistent way. Since different types of crops and plant materials require specific types of pretreatment, a range of combinations can be studied. The objective is to prepare a generic comparative assessment. The following main question is defined in order to specify the aim of this research project:

> Main question: What is the environmental performance of second generation bioethanol production?

The main question is split in three sub-questions, focused on both technologies and environmental performance:

> Sub-question 1: What is the environmental performance of first generation bioethanol production?

> Sub-question 2: What are the state-of-the-art production processes for bioethanol from second generation feedstocks?

> Sub-question 3: What is the environmental performance of various second generation bioethanol production processes?

1.2   Outline

This report start with a description of the characteristics of pretreatment technologies and the available experimental and process data in chapter 2 (sub-question 2). The methodology, including a description of the process models used and the life cycle assessment performed, is given in chapter 3. The chapter on the results consists of the life cycle assessment results from the process model in section 4.1 (sub-question 3) and a review of existing life cycle assessment studies in section 4.2 (sub-question 1 and 3). The research is discussed and concluded in chapter 5 and 6.

2. Pretreatment process descriptions

2.1 Introduction

The literature with respect to the pretreatment of lignocellulosic biomass can be divided in four categories: review articles; lab-scale experiments; techno-economic models and environmental assessment studies.

Review articles

Review articles provide the background information on the pretreatment techniques, typically describing general process conditions with references to lab-scale experiments. Review articles are used for a general description of the technique and as starting point for further research.

Lab-scale experiments

Articles dealing with lab-scale experiments contain specific process conditions (loading, temperature, pressure, time and added chemicals) and the corresponding yields, mainly for only one type of crop. During the last decade, the Biomass Refining Consortium for Applied Fundamentals and Innovation (CAFI) published lab-scale pretreatment data for various technologies and biomass crops (corn stover (Wyman et al. 2005), poplar (Wyman et al. 2009) and switchgrass (Wyman et al. 2011)). Various experiments are performed by various partners, but the experiments have been carried out using a uniform procedure, making the results comparable.

Techno-economic models

In techno-economic models, the production of ethanol using lignocellulosic biomass is modelled. Process parameters used for the calculation are partly based on dedicated experiments and partly on model predictions ('n[th] plant'[2]). Since 1999, the National Renewable Energy Laboratory (NREL) has been working on the process design and economics for the biochemical conversion of lignocellulosic biomass to ethanol. They developed a process model in Aspen Plus (Aspen Tech 2010), which is continuously improved (Humbird et al. 2011). Based on this model also other techno-economic analyses have been performed for various pretreatment techniques (e.g. Littlewood, Murphy, and Wang 2013).

Environmental assessment studies

Several life cycle assessment (LCA) studies have been performed on lignocellulosic ethanol; however, the explicit analysis of pretreatment technologies is very scarce. Kumar and Murthy recently published an article where they compare four pretreatment technologies based on a techno-economic model (Kumar and Murthy 2011). Other LCA studies in the field of lignocellulosic biomass are more case specific, focusing on crops, locations and type of hydrolysis and fermentation.

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[2] "Industrial facilities that have overcome cost and performance penalties of the first-of-a-kind (pioneer) facilities." (Spatari, Bagley, and MacLean 2010)

In this section the various types of technologies are described. The first part deals with the general description of pretreatment technologies and their advantages and disadvantages (section 2.2), followed by an overview of some lab-scale experiments, including process conditions and yields (section 2.3). Finally, an overview of techno-economic models is given (section 2.4). A review of LCA studies for both first and second generation bioethanol is covered in the results (section 4.2).

2.2   Technologies

The recalcitrant properties of lignocellulosic biomass require pretreatment prior to hydrolysis and subsequent fermentation. The aim of pretreatment is to alter the structure of the lignocellulosic biomass to enhance the enzyme accessibility during the hydrolysis step (Mosier et al. 2005). According to Kumar et al. (2009) the goals of pretreatment are the removal of lignin and hemicelluloses, the reduction of the crystallinity of cellulose and the increase in porosity of the lignocellulosic material (Figure 2-1).
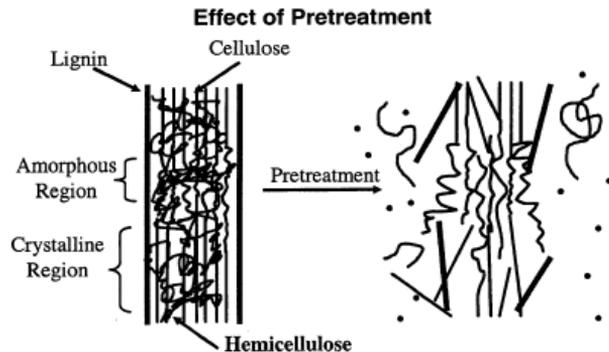
Figure 2-1: Schematic presentation of pretreatment effects on lignocellulosic biomass (Mosier et al. 2005).

In order to facilitate effective and efficient hydrolysis and fermentation, pretreatment technologies have to fulfil additional requirements (Alvira et al. 2010; Kumar et al. 2009); they need to:
- avoid biomass size reduction prior to pretreatment;
- improve the formation of sugars or the ability to subsequently form sugars by hydrolysis;
- give high yields for multiple crops, sites, ages and harvesting times;
- come with no significant sugar degradation;
- minimize the formation of toxic compounds;
- be effective at low moisture content;
- result in high sugar concentrations;
- minimize heat and power requirements; and
- be cost effective.

Pretreatment technologies can be divided in four categories: physical, chemical, physicochemical and biological pretreatment. In physical pretreatment no chemicals are used and pretreatment is mainly performed by mechanical forces. In chemical pretreatment various

chemicals are used to catalyse the degradation of the lignocellulosic biomass. Pretreatment that combines both chemical and physical processes is called physicochemical pretreatment. In biological pretreatment microorganisms or enzymes are used for the degradation celluloses and lignin.

The pretreatment technologies are described in several review articles, e.g. by Tomás-Pejó et al. (2011), Harmsen et al. (2010), Alvira et al. (2010), Hendriks and Zeeman (2009), Carvalheiro et al. (2008) and Taherzadeh and Karimi (2008). Examples of physical, chemical, physicochemical and biological pretreatment technologies are given in Table 2-1.

Table 2-1: Overview of pretreatment technologies.

Physical	Chemical	Physicochemical	Biological
Mechanical comminution	Acid pretreatment	Steam explosion	Fungal
	Alkaline pretreatment	Liquid hot water	
	Organosolv	Ammonia fiber explosion	
	Ionic liquids	Supercritical CO_2	
	Liquid hot water	explosion	

Short descriptions of the various pretreatment technologies are given below. An overview of the advantages and disadvantages is given in *Appendix I: Advantages and disadvantages of pretreatment technologies* on page 65.

2.2.1 Physical pretreatment

Mechanical comminution

Mechanical communition is performed to obtain small particle size biomass and to reduce the cellulose crystallinity. It can be used as single pretreatment, but can also be needed prior to or in combination with other pretreatment technologies (e.g. acid-assisted twin screw-driven reactor pretreatment (Kim, Choi, and Oh 2013)). The size after chipping is generally 10-30 mm and can improve further pretreatment processes. After milling the size is 0.2-2 mm. With decreasing particle size, the energy consumption increases drastically, even above the energy content of the biomass (Kumar et al. 2009). Zhu and Pan (2010) report an energy use of 0.18 MJ/kg wood for chipping and up to 2.88 MJ/kg wood for milling. In general, the energy requirement can be predicted by the Kick's law ($E \sim \ln[L_i/L_f]$) or Rittinger's law ($E \sim [1/L_f - 1/L_i]$), where L_i is the diameter of the feed particle and L_f is the diameter of the product particle (De Meester et al. 2011). Both laws show that for $L_f \ll L_i$ the energy use increases drastically with lower particle size.

Also combinations of mechanical comminution are in development. Yan and Modigell (2012) recently developed a method where comminution with a cutting mill to a particle size of 6 mm is followed by treatment with a screw press, requiring only 0.44 MJ/kg, but resulting in adsorption characteristics compared to 2.2 mm particles. However, mechanical comminution generally is time-consuming, energy-intensive and expensive. Furthermore it is generally less effective compared to other pretreatment techniques (Zheng, Pan, and Zhang 2009).

2.2.2   *Chemical pretreatment*

Acid pretreatment

Pretreatment of lignocellulosic biomass with acids results in the solubilization of the hemicellulosic fraction (Alvira et al. 2010). Solubilization is caused by the hydrolysis of especially xylan, as glucomannan is relatively acid stable (Hendriks and Zeeman 2009). Acid treatment can be either performed with concentrated or dilute acids (Taherzadeh and Karimi 2008).

Concentrated acid pretreatment is performed with e.g. 30-70% sulfuric acid or 41% hydrochloric acid at low temperatures (e.g. 40 °C) (Taherzadeh and Karimi 2008). The pretreatment comes with high hydrolysis rate, providing flexibility in feedstock choice, high monomeric sugar yields and mild temperature conditions (Harmsen et al. 2010). However, it also results in the formation of inhibiting compounds, like furfural and HMF.[3] The acidic environment requires suitable equipment (due to corrosion) and additional acid neutralization and recycling too, resulting in high investment, operation and maintenance costs (Alvira et al. 2010; Harmsen et al. 2010; Carvalheiro, Duarte, and Gírio 2008).

Dilute acid (DA) pretreatment is the one of the most common and effective pretreatment technologies (Harmsen et al. 2010) and is extensively studied, both on laboratory scale, but also with models and on pilot scale. Acid concentrations up to 2% are used to promote solubilization of hemicelluloses and convert them to fermentable sugars (Alvira et al. 2010). The most commonly used acid is sulfuric acid (H_2SO_4), but also hydrochloric acid, phosphoric acid, nitric acid and various organic acids can be used. Dilute acid pretreatment is used at a high temperature for a short time or at a low temperature for a longer time (Taherzadeh and Karimi 2008).

Dilute acid pretreatment performs well on most biomass materials (Kumar et al. 2009; Zheng, Pan, and Zhang 2009). However, as with concentrated acid pretreatment, sugar degradation takes places, affecting enzymatic processes (Alvira et al. 2010). With increasing temperature both the risk of sugar degradation and the formation of volatile degradation products increases, resulting in the loss of carbon for ethanol production (Hendriks and Zeeman 2009). Similar to concentrated acid pretreatment, dilute acid pretreatment comes also with equipment and neutralization requirements. To reduce the formation of inhibitors, dilute acid pretreatment can be performed in two stages. Two-stage dilute acid (TSDA) consist of a stage in which the hemicelluloses is solubilised at lower acid concentrations, while in the second stage a higher concentration of acid is used to induce hydrolysis of cellulose and hemicelluloses (Kabir Kazi et al. 2010). Chen et al. (2012) describe the combination of alkaline deacetylation, followed by acid impregnation, acid pretreatment and subsequent mechanical refining to avoid formation of furfural in the acid pretreatment step. They report ethanol yields up to 90%.

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[3] More information about inhibitors and the possibilities of detoxification can be found in the review article by Jönsson, Alriksson and Nilvebrant (2013).

Alkaline pretreatment

During pretreatment with alkaline chemicals swelling and saphonication takes place, increasing the accessibility for hydrolysis and fermentation (Quintero 2011). Where most pretreatment technologies mainly convert cellulose and hemicellulose, alkaline pretreatment is especially effective for lignin solubilization (Alvira et al. 2010; Carvalheiro, Duarte, and Gírio 2008). However, lignin solubilization by alkaline pretreatment is only suitable using biomass with low lignin content. According to Kumar et al. (2009) lignin solubilization is only effective with biomass with <26% lignin content, so generally, alkaline pretreatment is more effective on agricultural residues than on woody materials (Taherzadeh and Karimi 2007).

Alkaline pretreatment can be divided in two major groups: pretreatment using sodium, potassium or calcium hydroxide (lime) and pretreatment using ammonia like ammonia fibre explosion (AFEX) (section 2.2.3) and ammonia recycle percolation (ARP) (Carvalheiro, Duarte, and Gírio 2008). Alkaline pretreatment is performed at lower temperatures and low pressures compared to acid pretreatment, however, pretreatment times are in the order of hours to days as opposed to minutes in the case of acid pretreatment.

Various combinations of alkaline pretreatment with other technologies have been studied, e.g. the addition of an oxidant agent (Alvira et al. 2010; Carvalheiro, Duarte, and Gírio 2008), steam explosion followed by an alkaline peroxide post-treatment, mild alkaline pretreatment followed by an alkaline/oxidative pretreatment (Taherzadeh and Karimi 2007) and pretreatment with alkali and white rot fungus (Liong et al. 2012).

Organosolv

The organosolv pretreatment process makes use of an organic solvent or a mixture of organic solvents with water in order to solubilise the lignin (Harmsen et al. 2010). In addition, hydrolysis of hemicellulose bond occurs resulting in improved accessibility of the cellulosic fraction. Organosolv pretreatment can be done using numerous of organic and aqueous solvent mixtures, including methanol, ethanol, acetone, ethylene glycol, tetrahydrofurfuryl alcohol, often combined with an acid catalyst to increase hemicellulose hydrolysis (Alvira et al. 2010; Zhao, Cheng, and Liu 2009).

Organosolv pretreatment results in relatively pure lignin as by-product, which might facilitate higher-value application of lignin (Harmsen et al. 2010; Zhao, Cheng, and Liu 2009). However, solvent cost is high and recycling of solvents is necessary (Alvira et al. 2010), resulting in a more complicated process compared to other pretreatment techniques. The recovery requirements favour the alcohols with low boiling points over alcohols with higher boiling points (e.g. ethylene glycol and tetrahydrofurfuryl alcohol) (Taherzadeh and Karimi 2007).

Ionic liquids

The development of ionic liquids (ILs) as pretreatment agent is still in its infancy, but shows promise as efficient and green cellulose solvents (Liu et al. 2012). The pretreatment results in a high dissolution of cellulose at mild conditions. Also the feasibility of nearly 100% recovery makes ionic liquids attractive (Zheng, Pan, and Zhang 2009).

Ionic liquids are salts, typically composed of large organic cations and small inorganic anions, which are in liquid form at relatively low temperatures (Alvira et al. 2010). Examples are NMMO, BMIMCl, AMIMCl and BDTACl (Zheng, Pan, and Zhang 2009). The combination of an anion with a cation results in a broad selection of different chemicals. The ionic liquids exhibit low hydrophobicity, low viscosity, both electrochemical and thermal stability, high reaction rates and low volatility. However, costs are currently high, resulting in regeneration requirements. Currently, there is also a lack of knowledge about reaction characteristics, toxicity and inhibitor generation (Zheng, Pan, and Zhang 2009).

2.2.3 Physicochemical pretreatment

Steam explosion

In addition to dilute acid pretreatment, steam explosion (SE) is one of the most commonly used pretreatment technologies. During steam explosion, lignocellulosic biomass is heated with high-pressure steam. The biomass is held in this condition for some time resulting in hemicellulose hydrolysis, followed by a sudden release of pressure causing the decomposition of the material. Steam explosion pretreatment can be done at high temperatures and short times (e.g. 270 degrees, 1 min) or at lower temperatures for a longer time (e.g. 190 degrees, 10 min) (Kumar et al. 2009).

Steam explosion can be improved with the addition of an acid or alkali catalyst (Harmsen et al. 2010) to improve hemicellulose solubilization, to lower the optimal pretreatment temperature and to partially hydrolyze cellulose (Alvira et al. 2010).

The advantages of steam explosion over other physicochemical pretreatment technologies are the low use of chemicals and the limited energy consumption (Harmsen et al. 2010). In addition, the capital costs are lower and one can use a high chip size, which is especially favourable for woody biomass (Alvira et al. 2010). However, the use of high temperatures, water and acids can result in the formation of degradation products inhibiting hydrolysis and fermentation (Harmsen et al. 2010) and partial degradation of hemicellulose (Alvira et al. 2010).

Liquid hot water

Another thermal pretreatment technology is liquid hot water (LHW) pretreatment. In this technology, water at high temperatures and pressures is used to solubilize hemicelluloses in order to make the cellulose more accessible (Harmsen et al. 2010; Alvira et al. 2010). During liquid hot water pretreatment, also lignin is partly depolymerised and solubilized, however, complete delignification is not possible due to recondensation of the soluble lignin components (Alvira et al. 2010). In order to keep the water in the liquid phase pretreatment operates at high pressures. Temperatures up to 240 °C and pressures up to 11 bar are used. Liquid hot water pretreatment results in a high cellulose content solid fraction and a high hemicelluloses content liquid fraction (Alvira et al. 2010).

For liquid hot water pretreatment no catalysts or other chemicals are needed, resulting in less equipment requirements. Pretreatment occurs at low biomass loadings resulting in a high water consumption and low concentrations of products, but also reduced formation of inhibitors (Alvira et al. 2010).

Ammonia fiber explosion

Ammonia fiber explosion (AFEX) pretreatment can be compared to steam explosion pretreatment, but in this case liquid ammonia at high temperature and pressure is used instead of steam. After a period of time (typically for 30 minutes) the pressure is suddenly released and the ammonia is evaporated (Chiaramonti et al. 2012). Ammonia fiber explosion pretreatment results in biomass swelling, physical disruption of the biomass fibers and partial decrystallization of cellulose (Alvira et al. 2010; Harmsen et al. 2010). Generally, ammonia fiber explosion pretreatment is performed with liquid ammonia around 90 °C up to 20 bar. Output of the pretreatment is not a slurry containing a liquid and solid phase, but only pretreated solid biomass (Alvira et al. 2010)

AFEX pretreatment results in high hydrolysis yields, however it is only effective on agricultural residues and herbaceous crops, biomass with low lignin content (Alvira et al., 2010). The use of ammonia requires efficient recycling to reduce cost. Ammonia is volatile and recovery is feasible, but the recovery and recycle process is complex (Harmsen et al. 2010; Eggeman and Elander 2005).

Supercritical CO_2 pretreatment

A more novel technique is the utilization of supercritical CO_2 (> 31.1 °C and >73.8 bar) to remove lignin. CO_2 molecules are small and can therefore easily penetrate into the small pores of lignocellulose (Alvira et al. 2010). During pretreatment, CO_2 forms carbonic acids, favouring hydrolysis. Supercritical CO_2 pretreatment operates at low temperatures, preventing degradation. While less inhibitory compounds are formed compared to steam explosion, yields are low (Alvira et al. 2010).

2.2.4 Biological pretreatment

In case of biological pretreatment, microorganisms are used instead of chemicals. White-, brown- and soft-rot fungi, and some bacteria are capable of degrading lignocellulosic biomass (Wan and Li 2012). Brown-rot fungi mostly attack the cellulose, while white- and soft-rot fungi attack both cellulose and lignin (Cardona, Sánchez, and Gutiérrez 2009). Degradation by white-rot fungi is most effective (Alvira et al. 2010). Also the use of enzymes for direct treatment of lignocellulose has been studied. The advantage of enzymatic treatment is that this pretreatment only take several hours to days, where fungal pretreatment can require weeks. However, the costs of enzyme production are high.

Biological pretreatment with fungi is a simple technique with low energy requirements, reduced output of waste streams and little inhibitor formation (Wan and Li 2012). The environmental conditions are mild (Cardona, Sánchez, and Gutiérrez 2009) and the capital cost are low (Alvira et al. 2010). However, pretreatment is very slow and there is substantial loss of cellulose and hemicelluloses (Wan and Li 2012). Combined use of fungal pretreatment with other pretreatment can reduce chemical and physical requirements.

2.2.5 Overview

In Table 2-2 an overview of the process conditions of the pretreatment technologies is given. The discussed pretreatment technologies show large variability in process conditions, chemical usage and required time, resulting in distinct advantages and disadvantages. In Table 2-3 some novel and less studied pretreatment technologies, which are not further studied, are listed.

Table 2-2: Process conditions of pretreatment technologies.

Pretreatment technology	Biomass	Temperature	Pressure	Time	Chemicals
Mechanical comminution	wood	–	–	–	–
Concentrated acid	various	40 °C	moderate	minutes	e.g. 30-70% H_2SO_4
Dilute acid	various	130-210 °C	moderate	minutes-hours	< 2% H_2SO_4
Alkaline	agricultural residues; lignin < 26%	various	low	hours-days	e.g. lime or ammonia
Organosolv	–	various	low	hours	organic solvent
Ionic liquids	–	–	–	–	ionic liquids
Steam explosion	wood	160-230 °C	up to 22 bar	minutes	none or catalyst
Liquid hot water	–	< 240 °C	e.g. 11 bar	minutes	–
Ammonia fibre explosion	agricultural residues; low lignin content	90 °C	up to 20 bar	5-30 minutes	ammonia
Supercritical CO_2 explosion	–	>31.1 °C	>73.8 bar	–	CO_2
Biological	–	ambient	ambient	days	microorganism

Table 2-3: Novel or less studied pretreatment technologies.

Physical	Chemical	Physicochemical	Biological
Extrusion High energy radiation	Ozonolysis Wet oxidation (WO)	Ammonia recycle percolation (ARP) Soaking in aqueous ammonia (SAA) Sulfite pretreatment to overcome recalcitrance of lignocellulose (SPORL) Oxidative delignification	Enzymes

2.3   Experimental data

The main part of the literature about pretreatment of lignocellulosic biomass is related to lab-scale experiments of various pretreatment technologies. Experiments are performed under various conditions, like temperature, pressure, time, chemicals and for various feedstocks. Due to the large amount of parameters that can be changed, the results of the lab scale experiments show a wide range and are difficult to compare. In Table 2-5 and Table 2-6 the process conditions and yields for various lab scale experiments are given. In Table 2-7 and Table 2-8 an overview of the data used in models is given.

2.4   Process data

As the development of second generation bioethanol is in its infancy there is little data on pilot processes available. In order to assess the techno-economic performance of lignocellulosic ethanol plants, several techno-economic models have been developed. These models are partly based on lab-scale experimental data and partly on pilot data. In Table 2-9 an overview of techno-economic studies is given.

The National Renewable Energy Laboratory (NREL) has been working on models of lignocellulosic ethanol plants for years. Wooley et al. (1999) and Aden et al. (2002) published Aspen Plus based models of a lignocellulosic biomass to ethanol process design using dilute acid pretreatment, that has served as basis for several other studies. The most recent model was published by NREL in 2011 (Humbird et al. 2011) and is available online. Kazi et al. (2010) adapted the NREL model in order to analyze dilute acid pretreatment, ammonia fibre explosion pretreatment, liquid hot water pretreatment and two-stage dilute acid pretreatment. Kumar and Murthy (2011) developed a model in SuperPro designer, partly based on the NREL model, for dilute acid pretreatment, steam explosion, alkali pretreatment and liquid hot water pretreatment. In addition to that, they also performed an LCA study with their models (Kumar and Murthy 2012). Recently, Littlewood et al. (2013) adapted the NREL model in order to model dilute acid pretreatment, steam explosion (without or with catalyst), liquid hot water pretreatment and wet oxidation pretreatment.

2.5   Pilot plants

At the moment various companies are starting with the production of second generation ethanol. There are generally three types of plants: pilot plants, demo plants and commercial plants (Table 2-4). The ethanol production capacity is expected to grow from 1331 million L in 2012 to 5474 million L in 2015 (see Figure 1-2). Approximately 17 companies are expected to start with production in the next three years. In addition, companies are increasing their production capacity: commercial facilities producing more than 1 million L per year are expected to increase from 37 to 64 and large commercial facilities, producing more than 100 million L per year will increase from 6 to 14. An overview of the plants planned or in operation can be found various databases (BiofuelsDigest 2012; Task39 2012).

Table 2-4: Description of types of plants. Adapted from: http://demoplants.bioenergy2020.eu/ (Task39 2012).

Type	Description
Pilot facility	- Facility, which does not operate continuously - Facility not embedded into a supply chain - Only the feasibility of selected technological steps is demonstrated - The product might not be marketed
Demonstration facility	- Facility demonstrating the capability of the technology for on-going production - Facility covers entire production process or is embedded into a supply chain - The product is being marketed - Facility may not be operated under economical objectives
Commercial facility	- Facility operated continuously with high level of availability - Facility operated under economical objectives - The product is being marketed

Table 2-5: Overview of experimental data (part 1).

Reference	Pretreatment method	Biomass	Loading	Temperature (°C)	Pressure	Time	Additives
Yat et al. (2008)	Dilute acid	various	50 g of dry biomass/L	160-190			0.25-1.0% H_2SO_4
Wyman et al. (2011)	Dilute acid	switchgrass	10%	140		40 min	1.0 wt% H_2SO_4 solution
Elander et al. (2009)	Dilute acid	corn stover	10-40%	130-200	3-15 atm	2-30 min	0.5-3.0% H_2SO_4
Murnen et al. (2007)	Ammonia fiber explosion	miscanthus		160		5 min	2:1 w/w ammonia-to biomass loading, 2.3 g water per gram of biomass
Wyman et al. (2011)	Ammonia fiber explosion	switchgrass		140		30 min	1.5:1.0 NH_3
Elander et al. (2009)	Ammonia fiber explosion	corn stover	60-90%	70-90	15-20 atm	<5 min	100% (1 g ammonia per 1 g dry biomass) anhydrous ammonia
Kurakake et al. (2007)	Bacterial pretreatment	office paper					various bacteria
Wan and Li (2012)	Fungal pretreatment	various		25-39		up to 120 days	various fungi
Ruiz et al. (2008)	Steam explosion	sunflower stalks		220		5 min	
Zimbardi et al. (2007)	Catalyzed steam explosion	corn stover		190		5 min	1.5% H_2SO_4
Cara et al. (2008)	Catalyzed steam explosion	olive tree biomass		190-240			1.0 or 2.0% H_2SO_4
Wyman et al. (2011)	Catalyzed steam explosion	switchgrass	10%	180		10 min	0.05 g SO_2 per g biomass
Elander et al. (2009)	Catalyzed steam explosion	corn stover	20-40%	170-210	8-18 atm	5-10 min	0.5-3.0% SO_2
Wyman et al. (2011)	Lime	switchgrass		120		240 min	1 g $Ca(OH)_2$ per g biomass + 100 psi O_2
Hu and Wen (2008)	Alkali + microwave	switchgrass					0.1 g NaOH/g
Zhao et al. (2008)	Alkali	spruce	20%	up to 60		2-24 h	1-12% NaOH | 1-7%/12% NaOH/Urea
Elander et al. (2009)	Lime	corn stover	5-20%	70-130	1-6 atm	1-6 h	0.05-0.15 g $Ca(OH)_2$/g biomass
Wyman et al. (2009)	Ammonia recycle percolation	poplar wood		185		27.5 min	15% ammonium hydroxide

Reference	Pretreatment method	Biomass	Loading	Temperature (°C)	Pressure	Time	Additives
Elander et al. (2009)	Ammonia recycle percolation	corn stover	2-12%	150-170	9-17 atm	10-20 min	10-15 wt% ammonia
Li et al. (2010)	Ionic Liquids	corn cops					[MMIM]DMP
Binder and Raines (2010)	Ionic Liquids	corn stover					[EMIM]Cl
Mosier et al. (2005)	Liquid hot water–flow through			180-220	350-400 psig		
Wyman et al. (2011)	Liquid hot water	switchgrass	15%	200		10 min	
Zhang et al. (2007)	Organosolv	corn stover		50	1 atm	0.5-1 h	H_3PO_4/acetone
O'Connor et al. (2009)	Organosolv	corn stover		170		0.5 h	ethanol and H_2SO_4 as catalyst, 6%w/w
Sun et al. (2007)	Organosolv	wheat straw		240	1 atm	4 h	glycerol
Narayanaswamy et al. (2011)	Super critical CO_2 explosion	corn stover		150	241 bar	1 h	CO_2

Table 2-6: Overview of experimental data (part 2).

Reference	Pretreatment method	Biomass	Pretreatment yield (%)[a]				Hydrolysis yield (%)[a]				Ethanol yield (%)
			Glucose	Xylose	Sugar	Lignin sol.	Glucose	Xylose	Sugar	Lignin sol.	
Yat et al. (2008)	Dilute acid	various	10.6-13.6	70-94							
Wyman et al. (2011)	Dilute acid	switchgrass	7.1	74.4	33.6		76.7	82.7	79.2		
Elander et al. (2009)	Dilute acid	corn stover	8.6	79.2	37.1		92.1	82.2	88.1		
Murnen et al. (2007)	Ammonia fiber explosion	miscanthus					96	81			
Wyman et al. (2011)	Ammonia fiber explosion	switchgrass	6.8	65.7	30.0		84.8	79.4	82.6		
Elander et al. (2009)	Ammonia fiber explosion	corn stover					102.7[b]	79.2	94.1		
Kurakake et al. (2007)	Bacterial pretreatment	office paper							94		
Wan and Li (2012)	Fungal pretreatment	*various*					< 66		< 66.4		< 57.8
Ruiz et al. (2008)	Steam explosion	sunflower stalks							72		
Zimbardi et al. (2007)	Catalyzed steam explosion	olive tree					20.8-69.9				23.1-68.3
Cara et al. (2008)	Catalyzed steam explosion	corn stover					65.9	63.1			
Wyman et al. (2011)	Catalyzed steam explosion	switchgrass	5.0	72.8	31.7		84.8	81.0	83.2		
Elander et al. (2009)	Catalyzed steam explosion	corn stover	3.9	37.1	17.3		95.0	91.8	93.7		
Wyman et al. (2011)	Lime	switchgrass	1.3	28.2	11.9		79.0	93.1	84.6		
Hu and Wen (2008)	Alkali + microwave	switchgrass							90%		
Zhao et al. (2008)	Alkali	spruce	91			19					
Elander et al. (2009)	Lime	corn stover	1.5	22.8	10.1		97.5	71.0	86.8		
Wyman et al. (2009)	Ammonia recycle percolation	poplar wood	0.5	37.2	10.0		49.3	68.6	54.5		
Elander et al. (2009)	Ammonia recycle percolation	corn stover	1.3	47.0	19.8		90.1	84.4	87.8		
Li et al. (2010)	Ionic Liquids	corn cops							>70		
Binder and Raines (2010)	Ionic Liquids	corn stover	90								

Reference	Method	Feedstock						
Mosier et al. (2005)	Liquid hot water–flow through								96
Wyman et al. (2011)	Liquid hot water	switchgrass	1.5	34.5	14.5		90.6	91.4	90.9
Zhang et al. (2007)	Organosolv	corn stover	95	79		50			
O'Connor et al. (2009)	Organosolv	corn stover	92	91		85			
Sun et al. (2007)	Organosolv	wheat straw							>90
Narayanaswamy et al. (2011)	Super critical CO_2 explosion	corn stover					75		

[a] Yields after pretreatment and hydrolysis are based on the maximum available yields, calculated by *yield = component concentration / maximum component concentration*.

[b] The yield is calculated by *yield = reported yield / maximum yield · 100% = 61.2/59.6· 100 % = 102.7%*. The reference does not discuss why this yield is higher than 100%.

Table 2-7: Overview of the data used in various techno-economic models (part 1).

Reference	Pretreatment method	Biomass	Loading (%wt solid)	Temperature (°C)	Pressure	Time	Additives
Humbird et al. (2011)	Dilute acid	corn stover	30	158	5.5 atm	5 min	18 mg H_2SO_4 per g dry biomass
Littlewood et al. (2013)	Dilute acid	wheat straw		121		90 min	2% w/v H_2SO_4
Laser et al. (2009)	Ammonia fiber explosion	switchgrass	50	90			0.3 NH_3:dry biomass
Kumar and Murthy (2011)	Steam explosion	tall fescue	30	180	11 bar	15 min	
Littlewood et al. (2013)	Steam explosion	wheat straw		180		10 min	
Littlewood et al. (2013)	Catalyzed steam explosion	wheat straw		180		10 min	0.9% w/w H_2SO_4
Kumar and Murthy (2011)	Dilute alkali	tall fescue	20	180	11 bar	15 min	1% alkali concentration
Eggeman and Elander (2005)	Lime	corn stover		55			lime = 0.08 g as CaO/g stover
Eggeman and Elander (2005)	Ammonia recycle percolation	corn stover		170			liquid loadings = 3.185 g/g stover
Kumar and Murthy (2011)	Hot water	tall fescue	20	180	11 bar	15 min	
Littlewood et al. (2013)	Liquid hot water	wheat straw		188		40 min	
Littlewood et al. (2013)	Wet oxidation	wheat straw		180		15 min	O_2 at 12 bar

Table 2-8: Overview of the data used in various techno-economic models (part 2).

Reference	Pretreatment method	Biomass	Pretreatment yields					Hydrolysis yields		Fermentation yields	
			Glucose	Xylose	Lignin sol.	Furfural	HMF	Glucose	Xylose	Ethanol (glucose)	Ethanol (xylose)
Humbird et al. (2011)	Dilute acid	corn stover	9.9	90	5	5	0.3				
Littlewood et al. (2013)	Dilute acid	wheat straw	12	85	16	0.2	2.7	62.2	73.9		
Laser et al. (2009)	Ammonia fiber explosion	switchgrass	0	0	0.33	0	0	95		90	95
Kumar and Murthy (2011)	Steam explosion	tall fescue	5	70	5	15	15	70	80	95	70
Littlewood et al. (2013)	Steam explosion	wheat straw	10	95	18	0.85	1.5	60			
Littlewood et al. (2013)	Catalyzed steam explosion	wheat straw	10	82	31	0.05	0.15	80			
Kumar and Murthy (2011)	Dilute alkali	tall fescue	0.29	0.72	25	0.01	0.01	84.8	80	95	70
Eggeman and Elander (2005)	Lime	corn stover	0.5	0.8				91.3	51.8		
Eggeman and Elander (2005)	Ammonia recycle percolation	corn stover	1.4	0				90.1	41.1		
Kumar and Murthy (2011)	Hot water	tall fescue	0.43	70	5	2.5	2.5	78.5	80	95	70
Littlewood et al. (2013)	Liquid hot water	wheat straw	0	91	19			76.3	20.5		
Littlewood et al. (2013)	Wet oxidation	wheat straw	1.2	7.1				56	65		

Table 2-9: Overview of techno-economic studies.

Reference	Pretreatment technologies						Remarks	Study characteristics			
	DA	AFEX	SE	Alkali	LHW	Other		Model provided	Flowsheet	Process conditions	Utilities
Humbird et al. (2011)	✓						ASPEN Plus	✓	✓	✓	✓
Cardona and Sánchez (2006)	✓						ASPEN Plus (based on NREL)		✓	✓	(✓)
Eggeman and Elander (2005)	✓	✓		✓[a]	✓	ARP[b]	ASPEN Plus			✓	(✓)
Hamelinck et al. (2005)	✓[c]				✓		Excel spreadsheet; ASPEN Plus for thermal conversion			✓	(✓)
Kazi et al. (2010)	✓	✓			✓	TSDA[d]	Flowsheets and process conditions of various pretreatment technologies in ASPEN Plus (based on NREL)		✓	✓	
Klein-Marcuschamer et al. (2010)	✓						SuperPro Designer	✓	✓	✓	✓
Kumar and Murthy (2011)	✓		✓	✓	✓		SuperPro Designer	✓	✓	✓	✓
Laser et al. (2009)	✓	✓					ASPEN Plus (based on NREL); beside different pretreatment processes, also other parameters are changed		✓	✓	✓
Littlewood et al. (2013)	✓		✓		✓	WO[e] SECA[f]	ASPEN Plus; article including process design pretreatment		✓	✓	
Quintero and Cardona (2011)	✓				✓		ASPEN Plus		✓	✓	
Sassner et al. (2008)			✓				Different feedstocks; less information on inputs			✓	(✓)
Wang et al. (2012b)	✓			✓[g]			ASPEN Plus (based on NREL)		✓	✓	(✓)

[a] using lime
[b] ammonia recycle percolation
[c] including milling
[d] two-stage dilute acid
[e] wet oxidation
[f] steam explosion with H_2SO_4 catalyst
[g] oxidative lime pretreatment

3. Methodology

3.1   Introduction

The sustainability of second generation ethanol production process is determined by the complete production chain (Figure 3-1). This production chain includes the agricultural production of the feedstock, the preprocessing step and the production process. The production process is the focus of this study because it includes the pretreatment technologies. Since measured data from pilot, demonstration or commercial plants is not publicly available to our knowledge, the production process of bioethanol is modeled using the NREL model (Humbird et al. 2011). The NREL model is described in section 3.2 and followed by a description of the life cycle assessment methodology in section 3.3.
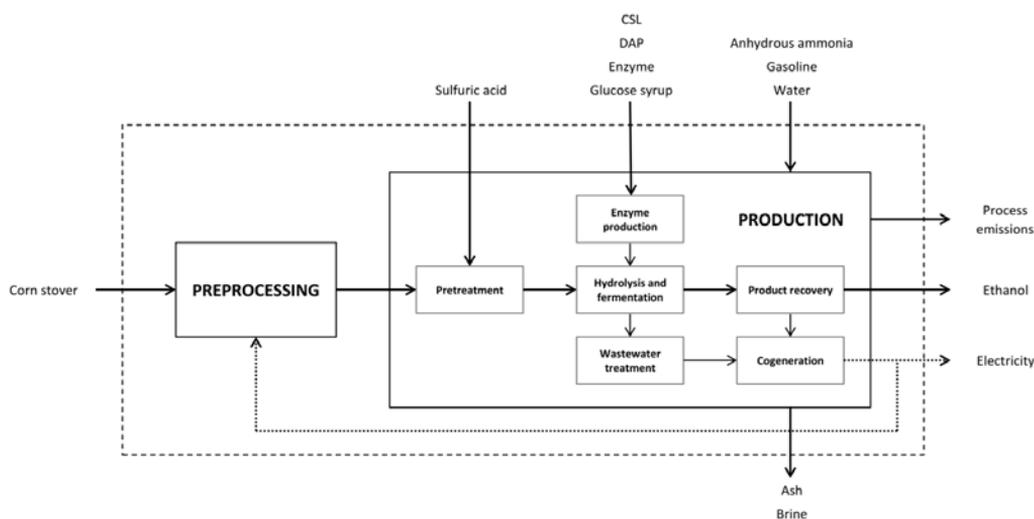
Figure 3-1: Flowsheet of the bioethanol production chain.

3.2   Process model description

For the life cycle assessment of the production of bioethanol from lignocellulosic biomass, the process model from the NREL is used. This section contains a description of the model (section 3.2.1 and 3.2.2), an overview of the sensitivity analysis (section 3.2.3) and a description of the adaptations made to the model in order to model other pretreatment techniques (section 3.2.4).

3.2.1   Description

NREL developed an Aspen Plus (Aspen Tech 2010) model for the biochemical conversion of lignocellulosic biomass to ethanol, more specifically, dilute-acid pretreatment, enzymatic hydrolysis and fermentation of corn stover. In their report, Humbird et al. (2011) extensively describe the process design and economics of the ethanol production plant. We do not intend to reproduce here the whole process design description, but instead to provide a good

understanding of the properties of the process model. Parts that are relevant for this study, including the pretreatment block, are described more elaborately.

The plant described has a capacity of 2000 dry metric tonnes per day and the operation time is 8410 hours per year (96%). The feed for the plant is milled corn stover, delivered from a storage and processing facility described by Hess et al. (2009) from Idaho National Laboratory (INL). In this facility corn stover is collected and preprocessed to obtain feedstock with standardized properties like size and moisture content. Figure 3-2 shows a general overview of the process. In *Appendix II: Process scheme of NREL model* on page 69 an extensive process scheme is given.
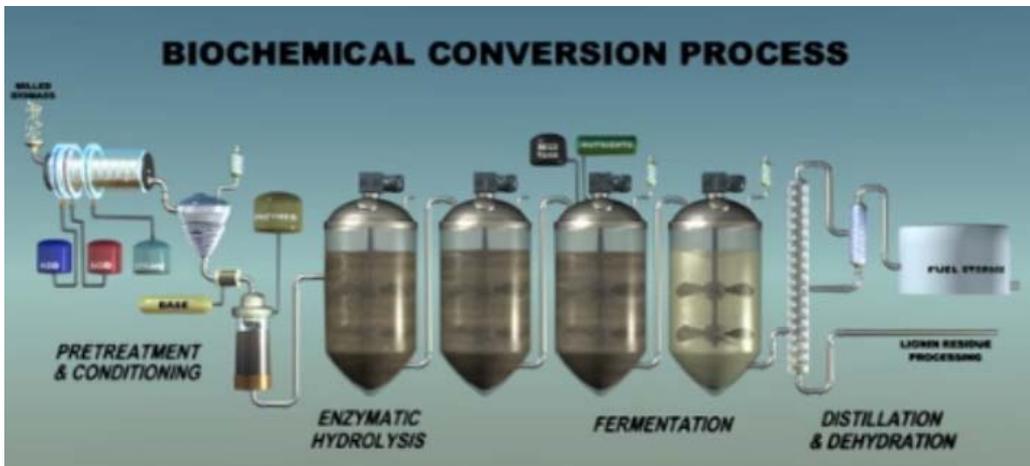
Figure 3-2: Overview of the biochemical conversion process (NREL 2012).

Area 100: Feedstock Storage and Handling

This area is designed to receive the preprocessed corn stover from trucks. The corn stover feed is stored in domes for a maximum of 72 hours. It is assumed that the corn stover is milled to a mean size of 4-6 mm and has a bulk density of 144-176 kg/m^3. The feedstock is transported to the pretreatment area using conveyors (stream 105).

Area 200: Pretreatment and Conditioning

In area 200, pretreatment and subsequent conditioning are performed (Figure 3-3). The feedstock is first mixed with hot water in order to obtain a solid loading of 30%. After that the mixture is heated with steam in the vertical presteamer up to 100 °C. Then, 22.1 mg acid per g dry biomass is added for pretreatment at 158 °C and 5.68 atm for 5 minutes in the horizontal screw-feed pretreatment reactors. The conversion achieved during pretreatment is given in Table 3-1. The pretreatment reactor content is discharged to a blowdown tank and followed by a secondary oligomer conversion reaction at 130 °C. In the default model the full pretreatment is performed in the horizontal pretreatment reactors. The secondary oligomer conversion rates are set to zero in pretreatment and are assumed to exclusively take place in the oligomer conversion reactor. The content of the latter is discharged into a flash tank (not shown in figure), resulting in a temperature of 100 °C and a pressure of 1 atm.

In order to avoid low pH, the acid needs to be neutralized using ammonia gas mixed in the dilution water. The mixture is diluted to approximately 20% total solids loading. Dilution with water and ammonia cools the slurry to 75 °C. After conditioning the hydrolysate is transferred to the enzymatic hydrolysis and fermentation area.
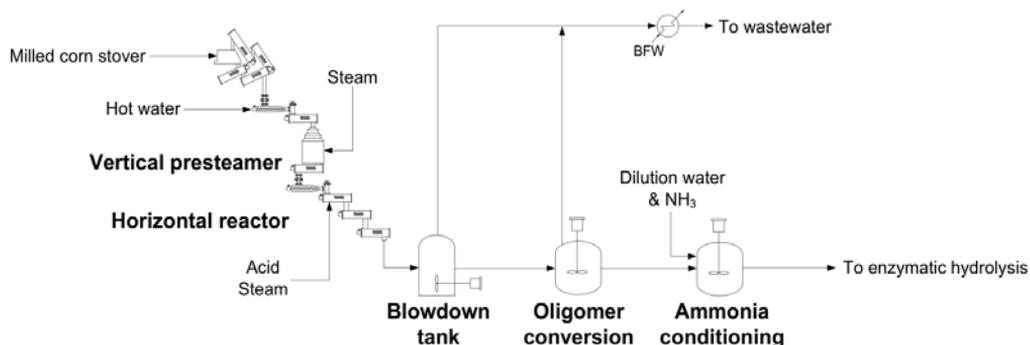
Figure 3-3: Simplified flowsheet of the pretreatment and conditioning process (Humbird et al. 2011).

Table 3-1: Pretreatment reactions and their conversion factors (Humbird et al. 2011).

Reaction	Conversion
Pretreatment	
$(Glucan)_n + n\ H_2O \rightarrow n\ Glucose$	0.099
$(Glucan)_n + n\ H_2O \rightarrow n\ Glucose\ Oligomer$	0.003
$(Glucan)_n \rightarrow n\ HMF + 2n\ H_2O$	0.003
$Sucrose \rightarrow HMF + Glucose + 2\ H2O$	1
$(Xylan)_n + n\ H_2O \rightarrow n\ Xylose$	0.9
$(Xylan)_n + m\ H_2O \rightarrow m\ Xylose\ Oligomer$	0.024
$(Xylan)_n \rightarrow n\ Furfural + 2n\ H_2O$	0.05
$Acetate \rightarrow Acetic\ Acid$	1
$(Lignin)_n \rightarrow n\ Soluble\ Lignin$	0.05

Area 300: Enzymatic Hydrolysis and Fermentation

In the enzymatic hydrolysis and fermentation area further hydrolysis of cellulose occurs, followed by fermentation to ethanol (Figure 3-4). The process is known as separate hydrolysis and fermentation (SHF), which means that enzymatic hydrolysis and fermentation are two separate processes. This is done to optimize each of the two steps.

The process starts with a continuous hydrolysis of the slurry using cellulase enzymes at 48 °C (high-solids hydrolysis). This first stage has a residence time of 24 h after which the slurry is transported to the batch reactors where the enzymatic hydrolysis proceeds for 60 h. The amount of enzyme needed is determined based on the amount of cellulose in the hydrolysate,

the loading used is 20 mg enzyme protein per g cellulose[4]. After hydrolysis the slurry is cooled down to 32 °C and fermentation is started. A recombinant *Zymomonas mobilis* bacterium is used to ferment the ethanol. It can simultaneously ferment glucose and xylose. After 5 days of sequential enzymatic hydrolysis and fermentation the resulting beer is sent to the product recovery (area 500). The enzymatic hydrolysis and fermentation reactions are given in Table 3-2.
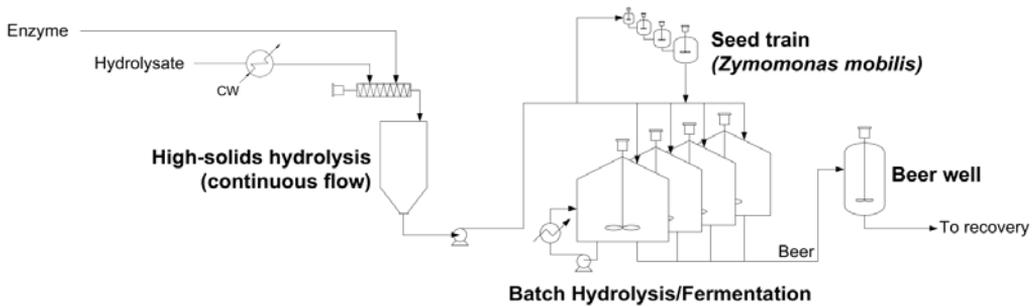
Figure 3-4: Simplified flowsheet of the enzymatic hydrolysis and fermentation process (Humbird et al. 2011).

Table 3-2: Enzymatic hydrolysis and co-fermentation reactions and their conversion factors (Humbird et al. 2011).

Reaction	Conversion
Enzymatic hydrolysis	
$(Glucan)_n \rightarrow n$ Glucose Oligomer	0.04
$(Glucan)_n + \frac{1}{2}n\ H_2O \rightarrow \frac{1}{2}n$ Cellobiose	0.012
$(Glucan)_n + n\ H_2O \rightarrow n$ Glucose	0.90
Cellobiose $+ H_2O \rightarrow 2$ Glucose	1
Co-fermentation	
Glucose $\rightarrow 2$ Ethanol $+ 2\ CO_2$	0.95
Glucose $+ 0.047$ CSL $+ 0.018$ DAP$\rightarrow 6$ *Z. mobilis* $+ 2.4\ H_2O$	0.02
Glucose $+ 2\ H_2O \rightarrow 2$ Glycerol $+ O_2$	0.004
Glucose $+ 2\ CO_2 \rightarrow 2$ Succinic Acid $+ O_2$	0.006
3 Xylose $\rightarrow 5$ Ethanol $+ 5\ CO_2$	0.85
Xylose $+ 0.039$ CSL $+ 0.015$ DAP$\rightarrow 5$ *Z. mobilis* $+ 2\ H_2O$	0.019
3 Xylose $+ 5\ H_2O \rightarrow 5$ Glycerol $+ 2.5\ O_2$	0.003
Xylose $+ H_2O \rightarrow$ Xylitol $+ 0.5\ O_2$	0.046
3 Xylose $+ 5\ CO_2 \rightarrow 5$ Succinic Acid $+ 2.5\ O_2$	0.009
Glucose $\rightarrow 2$ Lactic Acid	0.03
3 Xylose $\rightarrow 5$ Lactic Acid	0.03
3 Arabinose $\rightarrow 5$ Lactic Acid	0.03
Galactose $\rightarrow 2$ Lactic Acid	0.03
Mannose $\rightarrow 2$ Lactic Acid	0.03

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[4] Enzyme protein refers to the total concentration of protein in the enzyme broth; part of this protein is not enzymatically active (Humbird et al. 2011).

Area 400: Cellulase Enzyme Production

The model includes a section for on-site cellulose enzyme production. This option can be easily switched off, in case the enzymes are purchased.

Area 500: Products, Solids, and Water Recovery

The beer from the enzymatic hydrolysis and fermentation section is separated in ethanol, water and residual solids using distillation[5]. Ethanol is further dehydrated using vapor-phase molecular sieve adsorption. The resulting ethanol has a purity of 99.5%. Solids are sent to the combustor in area 800 and the liquid is sent to the waste water treatment in area 600.

Area 600: Wastewater Treatment

In the wastewater treatment area, the process water is treated using anaerobic and aerobic digesting. The resulting biogas and sludge is burned in the combustor. The treated water can be used again in the process.

Area 700: Product and Feed Chemical Storage

The storage area is used for the storage of chemicals used and produced in the process. In this area no conversion processes takes place.

Area 800: Combustor, Boiler, and Turbogenerator

Residuals from distillation and wastewater treatment, including biogas, are combusted for the production of high pressure steam for electricity production and process heat. Excess electricity is sold to the grid.

Area 900: Utilities

In the utilities area the cooling water, chilled water, process water and power is managed. Excess power is delivered to the grid.

3.2.2 Data

The process streams that describe the inputs and outputs of the bioethanol production process and the corresponding values in the default model are given in Table 3-3.

3.2.3 Sensitivity

A single-point sensitivity analysis (*ceteris paribus* analysis) is performed in order to investigate the effect on the plant performance and on the environmental impact. The sensitivity to on-site enzyme production, solids loadings, acid loading, temperature, enzyme loading and reaction conversion parameters are studied. In this way one can identify which parameters should be modified for further environmental improvement. The sensitivity results (section 4.1.2) also provide guidance for the assessment of other pretreatment techniques. Exact descriptions are given in Table 3-4.

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[5] Distillation is performed in the beer column and the rectification column. In the beer column, the dissolved CO_2, most of the water and unconverted insoluble and dissolved solids are removed. In the rectification column the ethanol is further concentrated up to 92.5%.

Table 3-3: Process streams describing the process inputs and outputs in the default process model (Humbird et al. 2011).

Stream	Utility	Amount	Unit
Stream 101	Corn stover	104167	kg/h
Stream 401	Glucose syrup	2845	kg/h
Stream 701	Gasoline denaturant	465	kg/h
Stream 703	Ethanol	22273	kg/h
Stream 710	Sulfuric acid	1981	kg/h
Stream 717	Anhydrous ammonia	1166	kg/h
Stream 735	Corn steep liquor	1324	kg/h
Stream 750	Purchased enzyme	0[a]	kg/h
Stream 755	Diammonium phosphate	142	kg/h
Stream 903	Water	147522	kg/h
Stream 423, 435, 550, 622, 810	Process CO_2 emissions	100508	kg CO_2 eq./h
Stream 809	Ash	5724	kg/h
Stream 627	Brine	9928	kg/h
Stream WKNET	Electricity	-12801[b]	kW

[a] Purchased enzyme stream is zero as result of on-site enzyme production.
[b] Negative power value indicates excess electricity production.

Table 3-4: Description of sensitivity analysis.

Properties	Location	Values
General		
On site enzyme production	Global calculator A400-ENZ	TRUE/FALSE
Pretreatment		
Solids loading	Global design spec PTSOLID	25 - 40%
Acid loading	Calculator A200.ACIDFLO	10 - 35 mg/g
Temperature	Block M207, temperature	150 - 170 °C
Xylan -> xylose conversion	Block M207, reaction 6	0.8 - 0.92
Xylan -> furfural conversion	Block M207, reaction 7	0.03 - 0.08
Glucan -> glucose conversion	Block M207, reaction 3	0.06 - 0.12
Enzymatic hydrolysis		
Solids loading	Global design spec SACSOLID	17.5 - 25%
Enzyme loading	Global calculator A400-ENZ, ENZYL=x	10 - 30 mg/g
Glucan -> glucose conversion	Block F300SAC, reaction 3	0.75 - 0.95

3.2.4 Adapted cases

The pretreatment, hydrolysis and fermentation efficiency data used in the NREL model are defined as '2012 Targets'. These targets are based on the state of technology of previous years and reflect the expected performance of near-future processes. While the data used in the NREL model is based on state of technology and experimental data, it does not directly refer to an experimental study. In order to investigate also production with data based on actual experimental studies, some adapted cases were designed by implementing experimental data in

the NREL model. All experimental data used is obtained from Wyman et al. and is related to pretreatment of corn stover (CS) (Wyman et al. 2005) and switchgrass (SW) (Wyman et al. 2011). Data on dilute acid pretreatment (CS-DA) and liquid hot water pretreatment (CS-LHW)[6] are obtained from the experimental study with corn stover and data on dilute acid pretreatment (SW-DA) and liquid hot water pretreatment (SW-LHW) are obtained from the experimental study with switchgrass. In the NREL model adaptations were made with respect to the feedstock composition (Table 3-5), the pretreatment temperature, the pretreatment loading and the added chemicals (Table 3-6). In addition, the conversion parameters of the pretreatment and subsequent hydrolysis are adapted to correspond the results reported by Wyman et al.[7] (Table 3-6). When the solid loading in pretreatment is < 20% the solids loading in the subsequent hydrolysis step is automatically adapted to the lower concentration of the input stream. Due to the process parameters defined additional processing may be required in the recovery step as result of lower product concentrations. Only when the model does not converge and associated errors occur, the process parameters in the recovery step are adapted. For example, lower product concentrations as result of lower solids loadings, can require distillation characteristics that are outside the initial boundaries defined in the NREL model. All required adaptations to avoid errors are described in the results.

Table 3-5: Feedstock compositions of corn stover (dry wt%) in the default NREL model and of corn stover and switchgrass in the adapted models (Humbird et al. 2011; Wyman et al. 2005; Wyman et al. 2011).

Component	Default	Corn stover (CS)	Switchgrass (SW)
Cellulose	0.351	0.361	0.356
Xylose	0.195	0.214	0.226
Galactose	0.014	0.025	0.000
Arabinose	0.024	0.035	0.031
Mannose	0.006	0.018	0.000
Sucrose	0.008	0.000	0.000
Lignin	0.158	0.172	0.211
Extractives	0.147	0.032[a]	0.140[b]
Acetate	0.018	0.032	0.036
Ash	0.049	0.071	0.000
Protein	0.031	0.040	0.000
Moisture content	0.2	0.2	0.2

[a] Corn stover extractives include uronic acid, non-structural sugars and some correction to obtain a sum of 1.
[b] Switchgrass extractives include also proteins and ash, since this is not reported separately.

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[6] Described as partial flow pretreatment in Wyman et al. (2005).
[7] Total sugar yield consists of sugars as monomers and sugars as oligomers: *total sugar = monomers + oligomers*. In Wyman et al. (2005) yields are reported for the total sugars produced and the monomers produced as percentage of the theoretical maximum potential sugar yield. However, in Wyman et al. (2011) yields are reported for the total sugars produced and the oligomers produced. Both the monomer and oligomer yields are needed to calculate the conversion parameters. For Wyman et al. (2005) the oligomers produced are calculated by: *oligomers = total sugar - monomers* and for Wyman et al. (2011) the monomers produced are calculated by: *monomers = total sugar - oligomers.* Conversion to other compounds, like HMF, furfural or cellobiose is excluded because no data is available in the experimental studies.

Table 3-6: Process parameters of the default NREL model and the adapted models (Humbird et al. 2011; Wyman et al. 2005; Wyman et al. 2011).

ID	Default	CS-DA	SW-DA	CS-LHW	SW-LHW
Process					
Feedstock[a]	CS	CS	SW	CS	SW
Technology[b]	DA	DA	DA	LHW	LHW
Temperature (°C)	158	160	140	200	200
Loading (wt%)	30%	25%	25%	15%	15%
Additives	22.1 mg H_2SO_4/g	14.7 mg H_2SO_4/g	99.1 mg H_2SO_4/g	–	–
Other	–	–	c,d,e	d,e	–
Pretreatment conversion factors					
Glucan → Glucose Oligomer	0.003	0	0.0083	0.0016	0.0627
Glucan → Glucose	0.099	0.0626	0.0627	0.0674	0.0050
Glucan → HMF	0.003	0	0	0	0
Xylan → Xylose Oligomer	0.024	0.0239	0.0431	0.7613	0.4365
Xylan → Xylose	0.9	0.8276	0.7005	0.0743	0.2208
Xylan → Furfural	0.05	0	0	0	0
Others[f]	*various*	0	0	0	0
Hydrolysis conversion factors					
Glucan → Glucose Oligomer	0.04	0	0	0	0
Glucan → Glucose	0.9	0.8555	0.6931	0.8218	0.7805
Xylan → Xylose Oligomer	0	0	0	0.0053	0.0279
Xylan → Xylose	0	0.0875	0.0863	0.0637	0.1066
Xylose Oligomer → Xylose	0	0	0	0	0
Others[g]	*various*	0	0	0	0

[a] CS = corn stover, SW = switchgrass
[b] DA = dilute acid pretreatment, LHW = liquid hot water pretreatment,
[c] As result of the lower biomass loading, modeling result into error in the recovery stage, therefore, the target mass purity in block D501 is increased from 0.0005 to 0.002.
[d] As result of the lower biomass loading, modeling result into error in the recovery stage, therefore, the maximum reflux ratio and maximum bottoms to feed ratio in block D502 is increased from 5 to 7.
[e] As result of the lower biomass loading, modeling result into error in the recovery stage, therefore, the maximum bottoms to feed ratio in block D502 is increased 0.7 to 0.8.
[f] Including mannose, galactose and arabinose conversion.
[g] Include cellulose -> cellobiose and cellobiose -> glucose conversion.

3.3 Life cycle assessment

Life cycle assessment (LCA) is a methodological tool for the environmental evaluation of products, technologies and services. It addresses the environmental aspects throughout a product's life cycle, e.g. from raw material extraction (or agriculture/forestry) to recycling and final disposal. The framework for LCA is provided by the International Standardization Organisation in 1997 and was last updated in 2006 (ISO 14040:2006; ISO 14044:2006). ISO 14040 deals with the general framework for LCA and ISO 14044 describe the requirements and guidelines.

The LCA procedure consists of four steps: goal and scope definition, inventory analysis, impact assessment and interpretation. The goal and scope definition defines the purpose and the methodology of the LCA. This step includes the definition of the system boundaries, the choice of functional units and the selection of environmental impact parameters. The inventory analysis, also called the life cycle inventory (LCI) analysis phase, starts with the construction of a flow diagram, to identify which process steps are involved and what are the inputs and outputs of each step. In case of a process leading to multiple outputs, choices have to be made with regard to the allocation. Allocation can be done with respect to the mass, the energy content or the economic value of the products. The allocation procedure can influence the outcomes substantially, so when possible allocation needs be avoided, e.g. by using system expansion; this is a preferred approach according to ISO 14044. After the inventory analysis, the environmental impacts of the inputs and outputs are assessed in the life cycle impact assessment (LCIA) phase. Finally, the result of the inventory analysis and the impact assessment are discussed and conclusions are drawn in the interpretation part.

3.3.1   Goal and scope definition

The goal of our LCA study is to investigate the system-wide non renewable energy use (NREU), renewable energy use (REU) and greenhouse gas emissions (GHG) for the production of ethanol from lignocellulosic biomass using the biochemical pathway. In addition, the effect of various process parameters on the environmental impact is studied. As the production of ethanol is the key process, the functional unit is 1 kg of ethanol, either for fuel or chemical use. Since bioethanol is mainly used as fuel, lower heating values were used for energy calculations.

A simplified overview of the bioethanol production chain was already given in Figure 3-1. Since the focus of this study is the conversion process, the production process is explicitly modelled. Data on agricultural production and the production of input chemicals and energy are obtained from literature. Energy requirements for preprocessing are calculated based on literature. Ethanol distribution is not included.

3.3.2   Inventory analysis

The feedstock input is defined in the NREL model. Impact data on agricultural production of corn stover is obtained from the GREET (Greenhouse gases, Regulated Emissions and Energy use in Transportation) model developed by the Argonne National Laboratory (GREET 2012). The characteristics of this data are described in the report 'Well-to-Wheel Analysis of Fast Pyrolysis Pathways with GREET' by Han et al. (2011). As corn stover is seen as a residual stream, farming of corn is not taking into account. However, the impacts from corn stover collection and likewise the impact of extra fertilizer needed to compensate for the corn stover that was formerly left on the fields to replenish the soil, next to processing needed before transport and the transport

itself, is included. Additional assumptions are made related to the moisture content[8] and the avoided greenhouse gasses[9].

Preprocessing is performed using the feedstock supply system developed by Idaho National Laboratory (INL). The energy requirements of the preprocessing steps are obtained from the report 'Commodity-scale production of an infrastructure-compatible bulk solid from herbaceous lignocellulosic biomass' (Hess et al. 2009). The preprocessing chain consists of receiving the raw feedstock, grinding of the biomass and additional dust collection. Transportation to the plant is also included. It is assumed that no matter loss occurs in this step. A total energy requirement for the preprocessing of corn stover with 20% moisture content is 0.35 MJ/kg (Table 3-7). The energy demand is assumed to be fully covered with electricity. It is assumed that the excess electricity of the bioethanol production stage is used for preprocessing.

Table 3-7: Energy use of preprocessing steps as reported by Hess et al. (2009) in MBtu per dry matter (DM) tonne of feedstock and converted to MJ per tonne as delivered.

Process	Energy use (MBtu/DM short ton)[a]	Energy use (MJ/metric tonne)
Preprocessing		
Grinder loader	15.9	14.8
Grinder infeed system	4.1	3.8
Grinder	129.8	120.8
Dust collection	not available	not available
Surge metering bin	79.6	74.1
Bale and twine disposal	2	1.9
Transport		
Conveying	85.7	79.7
Transport	54.4	50.6
Total	371.5	345.6

[a] 1 MBtu = 1.055056 MJ; 1 short ton = 0.9072 metric tonne; dry matter (DM) content = 80%

The input and output data of the bioethanol production process is modelled using the NREL model. A description of the model is given in section 3.2. Table 3-3 on page 29 contains the default values of the inputs and outputs that are used in this LCA.

As in this process both ethanol and electricity is produced, one has to deal with allocation. In this study we deal with allocation in two different ways, i.e. by system expansion and by allocation based on energy content. In the system expansion approach it is assumed that the electricity produced, replaces average electricity production in the European Union. In the LCA

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[8] The properties of the corn stover reported in the GREET and in the NREL model do not completely match. The moisture content in the GREET model is 12%, while in the NREL model biomass with 20% moisture content is used. It is however assumed that this has no influence on further processing.

[9] In the GREET model the avoided greenhouse gas emissions as result carbon sequestration in the biomass are not taken into account. We therefore calculated carbon sequestration from the carbon content of the feedstock by multiplying the molar carbon content with the molecular mass of CO_2, which is 44.01 g/mol. The carbon content is obtained from the NREL model. In addition, also the renewable energy input in corn stover need to be calculated. According to Humbird et al. (2011), the total corn stover flow of 104 tonne corn stover is equivalent to 316 MMkcal energy flow, resulting in a renewable energy input of 12.7 MJ/kg corn stover. Using these assumptions, the carbon balance of the production process can be closed (see *Appendix III: Carbon balance*).

the electricity gets negative energy and greenhouse gas emission impacts. In the energy allocation approach, the total energy and greenhouse gas emission impacts are divided among ethanol and electricity, based on their energy content.[10] Allocation of the final emission to ethanol and electricity result in negative greenhouse gas emissions for electricity. The greenhouse gas emissions are therefore split in two categories, the physical streams and the impacts of the utilities. The physical streams are completely allocated to ethanol, while the impacts of the utilities are allocated to ethanol and electricity based on their energy content.

3.3.3   Impact assessment

Data on the impact of the process inputs are obtained from the EcoInvent database (ecoinvent Centre 2007) and the GREET model (GREET 2012). An overview of the impact data is given in Table 3-8. Impact data on the production of corn stover, corn steep liquor, enzymes and glucose syrup is obtained from the GREET database, where the impact data of ethanol, electricity, anhydrous ammonia, diammonium phosphate (DAP)[11], gasoline, sulfuric acid and water are obtained from the EcoInvent database. The impact of ethanol and electricity is given to function as reference and in the system expansion approach. Ash is assumed to be comparable with the average incineration residue. The resulting brine with approximately 50% sodium nitrate concentration is not further used in this process. It can further crystallized for solid disposal. According to Humbird et al. (2011) some biomass burners can handle the salt. The salt can potentially also be used for other applications like use as fertilizer or for the production of nitric acid. In this study no credit or impact given to the brine stream.

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[10] Calculated using $I_{ethanol} = I_{total} \cdot [E_{ethanol} / E_{total}]$ and $I_{electricity} = I_{total} \cdot [E_{electricity} / E_{total}]$, where I is the impact and E is the energy content.
[11] Since DAP is mainly used as fertilizer, the impact of DAP is reported as the impact per kg N or kg P_2O_5, so these are combined and scaled to obtain the impact of DAP per kg.

Table 3-8: Description, data source and impact data (non-renewable energy use, renewable energy use and greenhouse gas emissions) used for utilities.

Utility	Description	Reference	Unit	Impact NREU (MJ)	Impact REU (MJ)	Impact GHG (kg CO₂ eq.)
Reference						
Electricity	electricity, production mix RER/kWh/RER	Frischknecht et al. (2007)	MJ	2.740	0.248	0.135
Ethanol	ethanol from ethylene, at plant/kg/RER	Sutter (2007)	kg	47.499	0.293	1.233
Gasoline	petrol, unleaded, at refinery/kg/RER	Jungbluth (2007)	kg	56.702	0.137	0.676
Agriculture						
Corn stover	corn stover, transport included/kg	GREET (2012)	kg	0.827	0.014	0.058
Production						
Anhydrous ammonia	ammonia, liquid, at regional storehouse/kg/RER	Althaus et al. (2007)	kg	41.672	0.281	2.089
Corn steep liquor	corn steep liquor/kg	GREET (2012)	kg	10.925	0.147	0.058
Diammonium phosphate	calculated using 0.46 * diammonium phosphate, as P_2O_5 + 0.18 * diammonium phosphate as N, both at regional storehouse/kg/RER	Nemecek and Kägi (2007)	kg	21.396	0.887	1.911
Enzyme	cellulose/kg	GREET (2012)	kg	39.965	1.716	2.601
Gasoline	petrol, unleaded, at regional storage/kg/RER	Jungbluth (2007)	kg	57.152	0.158	0.702
Glucose syrup	glucose/kg	GREET (2012)	kg	2.532	0.049	0.155
Sulfuric acid	sulfuric acid, liquid, at plant/kg/RER	Althaus et al. (2007)	kg	2.020	0.101	0.124
Water	process water, ion exchange, production mix, at plant, from groundwater RER S	ELCD database 2.0 (2008)	kg	0.084	0.003	0.006
Ash	disposal, average incineration residue, 0% water, to residual material landfill	Doka (2007)	kg	2.079	0.084	0.329
Brine	can be potentially further processed, no impact or credit given	–	kg	0.000	0.000	0.000
Adapted cases						
Switchgrass	switchgrass, transport included/kg	GREET (2012)	kg	0.617	0.008	0.043

4. Results

4.1   Life cycle assessment of NREL model

In this section the results of the LCA of the NREL model are given. The LCA based on the default case is extensively described (section 4.1.1) and functions as basis for the sensitivity analysis (section 4.1.2) and adapted cases (section 4.1.3).

4.1.1   Default case

Figure 4-1 summarizes the inventory assessment of the LCA. For the production of 1 kg ethanol, 4.68 kg raw corn stover is needed. Co-production of electricity results in an excess of 0.13 kWh/kg ethanol. Using the inventory assessment the life cycle impact is determined. The corresponding life cycle results are given in respectively Table 4-1 and Table 4-2.
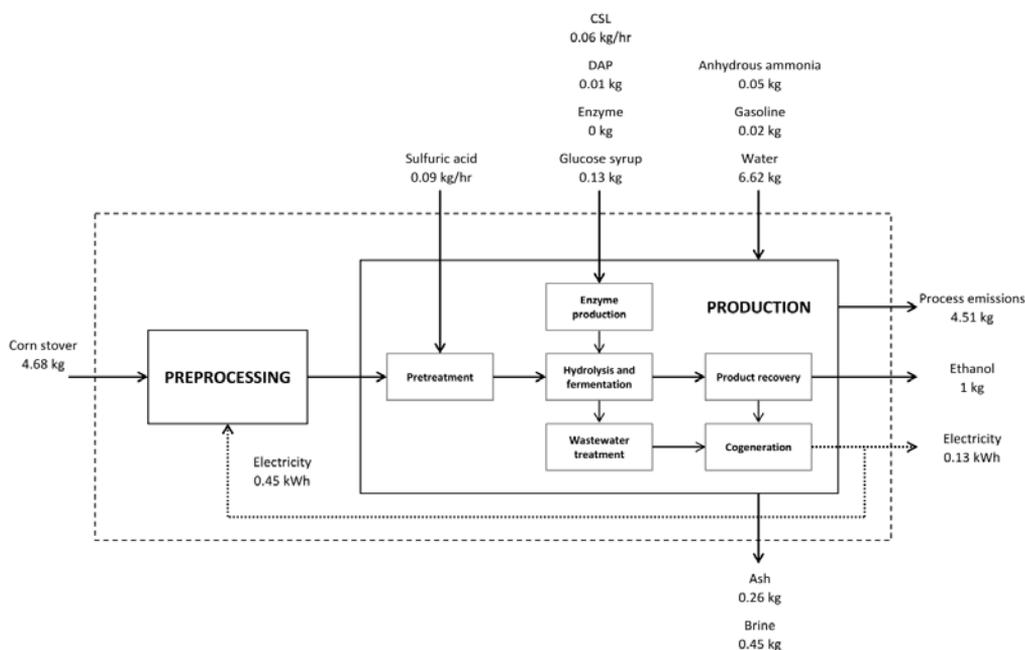
Figure 4-1: Flowsheet with inventory needed to produce 1 kg of ethanol in the default case.

Table 4-1: LCA results of the default case with the system expansion approach.

	NREU		REU		GHG	
Agriculture						
Corn stover growth[a]	–		59.400	MJ	-6.159	kg CO$_2$ eq.
Corn stover production[b]	3.867	MJ	0.067	MJ	0.272	kg CO$_2$ eq.
Production						
Anhydrous ammonia	2.181	MJ	0.015	MJ	0.109	kg CO$_2$ eq.
Corn steep liquor	0.649	MJ	0.009	MJ	0.048	kg CO$_2$ eq.
Diammonium phosphate	0.137	MJ	0.006	MJ	0.012	kg CO$_2$ eq.
Enzyme[c]	–	MJ	–	MJ	–	kg CO$_2$ eq.
Gasoline	1.193	MJ	0.003	MJ	0.015	kg CO$_2$ eq.
Glucose syrup	0.323	MJ	0.006	MJ	0.020	kg CO$_2$ eq.
Sulfuric acid	0.180	MJ	0.009	MJ	0.011	kg CO$_2$ eq.
Water	0.557	MJ	0.023	MJ	0.043	kg CO$_2$ eq.
Ash	0.534	MJ	0.021	MJ	0.084	kg CO$_2$ eq.
Brine	0.000	MJ	0.000	MJ	0.000	kg CO$_2$ eq.
Process emissions[d]	–		–		4.512	kg CO$_2$ eq.
Electricity credit	-1.240	MJ	-0.112	MJ	-0.061	kg CO$_2$ eq.
Total (per kg ethanol)	**8.381**	**MJ**	**59.447**	**MJ**	**-1.093**	**kg CO$_2$ eq.**

[a] Renewable energy incorporated and CO$_2$ sequested into corn stover during growth.
[b] Including fertilizer use, diesel use and transport to preprocessing facility.
[c] In case of on-site enzyme production, energy use and emissions of the enzyme production part are integrated in the process and the impact of purchased enzyme will be zero.
[d] Emissions from fermentation (C$_6$H$_{12}$O$_6$ → 2 C$_2$H$_5$OH + 2 CO$_2$) and combustion (C$_6$H$_{12}$O$_6$ + 6 O$_2$ → 6 H$_2$O + 6 CO$_2$).

Table 4-2: LCA results of the default case with the energy content based allocation approach.

	NREU		REU		GHG	
Agriculture						
Corn stover growth[a]	–		59.400	MJ	-6.159[e]	kg CO_2 eq.
Corn stover production[b]	3.867	MJ	0.067	MJ	0.272[f]	kg CO_2 eq.
Production						
Anhydrous ammonia	2.181	MJ	0.015	MJ	0.109[f]	kg CO_2 eq.
Corn steep liquor	0.649	MJ	0.009	MJ	0.048[f]	kg CO_2 eq.
Diammonium phosphate	0.137	MJ	0.006	MJ	0.012[f]	kg CO_2 eq.
Enzyme[c]	–	MJ	–	MJ	–	kg CO_2 eq.
Gasoline	1.193	MJ	0.003	MJ	0.015[f]	kg CO_2 eq.
Glucose syrup	0.323	MJ	0.006	MJ	0.020[f]	kg CO_2 eq.
Sulfuric acid	0.180	MJ	0.009	MJ	0.011[f]	kg CO_2 eq.
Water	0.557	MJ	0.023	MJ	0.043[f]	kg CO_2 eq.
Ash	0.534	MJ	0.021	MJ	0.084[f]	kg CO_2 eq.
Brine	0.000	MJ	0.000	MJ	0.000[f]	kg CO_2 eq.
Process emissions[d]	–		–		4.512[e]	kg CO_2 eq.
Electricity credit	–	MJ	–	MJ	–	kg CO_2 eq.
Total	**9.621**	**MJ**	**59.559**	**MJ**	**-1.032**	**kg CO_2 eq.**
per kg ethanol	9.461	MJ	58.570	MJ	-1.042[g]	kg CO_2 eq.
per kWh electricity	1.271	MJ	7.868	MJ	0.081[g]	kg CO_2 eq.

[a] Renewable energy incorporated and CO_2 sequestrated into corn stover during growth.
[b] Including fertilizer use, diesel use and transport to preprocessing facility.
[c] In case of on-site enzyme production, energy use and emissions of the enzyme production part are integrated in the process and the impact of purchased enzyme will be zero.
[d] Emissions from fermentation ($C_6H_{12}O_6 \rightarrow 2\ C_2H_5OH + 2\ CO_2$) and combustion ($C_6H_{12}O_6 + 6\ O_2 \rightarrow 6\ H_2O + 6\ CO_2$).
[e] Included in 'utilities impacts'.
[f] Included in 'process streams'.
[g] Since it is physical incorrect to allocate greenhouse gas credits to electricity as result of the carbon sequestration, the impact of electricity is only calculated based on the impacts of the utilities. The impact of the ethanol is calculated based on the impact of the utilities and the process emissions. The following calculations were used: $I_{ethanol} = I_{utilities\ impacts} \cdot [E_{ethanol} / E_{total}] + I_{process\ streams}$ and $I_{electricity} = I_{utilities\ impact} \cdot [E_{electricity} / E_{total}]$, where I is the greenhouse gas emissions impact and E is the energy content.
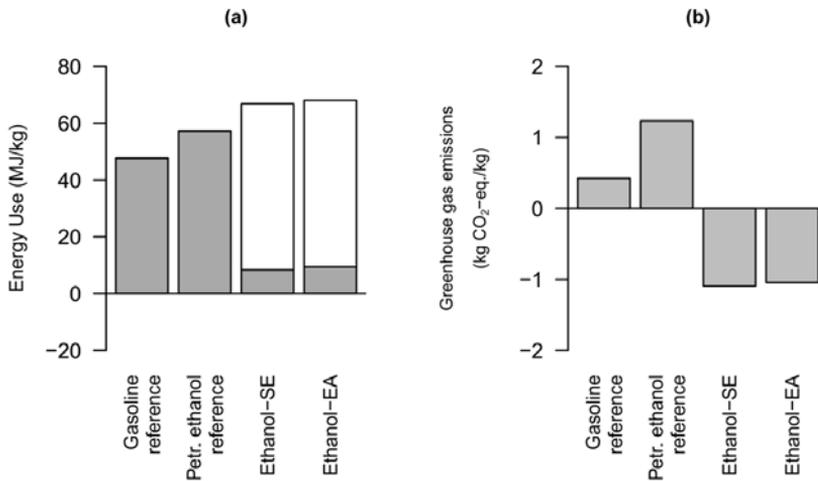
Figure 4-2: Comparison of gasoline reference, petrochemical ethanol reference and bioethanol in system expansion (SE) and energy content based allocation (EA) approach, for (a) the non-renewable energy use (grey), the renewable energy use (white) and (b) the greenhouse gas emissions per kg ethanol eq.
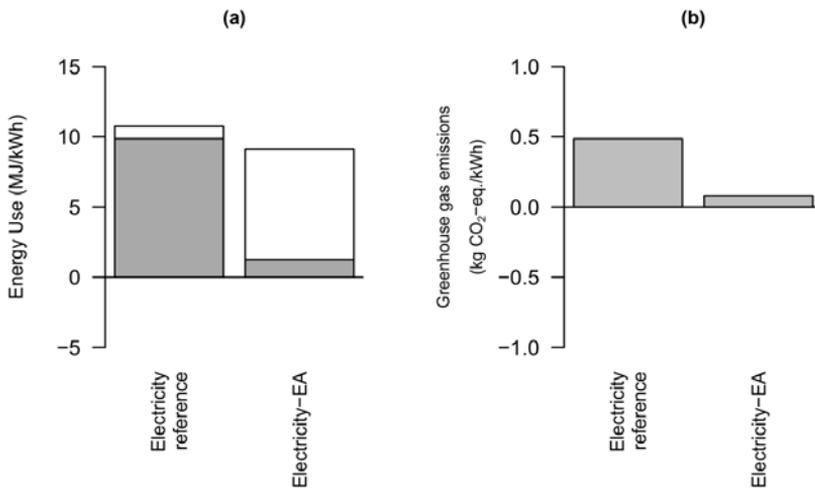
Figure 4-3: Comparison of reference electricity and electricity in energy allocation (EA) approach, for (a) the non-renewable energy use (grey), the renewable energy use (white) and (b) the greenhouse gas emissions per kWh.

4.1.2 Sensitivity

In Figure 4-4 the effect of on-site enzyme production on the results of the system expansion approach is given. It can be seen the difference is very small. On-site enzyme production leads to a somewhat lower energy use and higher greenhouse gas reduction, caused by the lower impact of on-site enzyme production (e.g. due to heat integration) compared to the impact given to purchased enzyme.
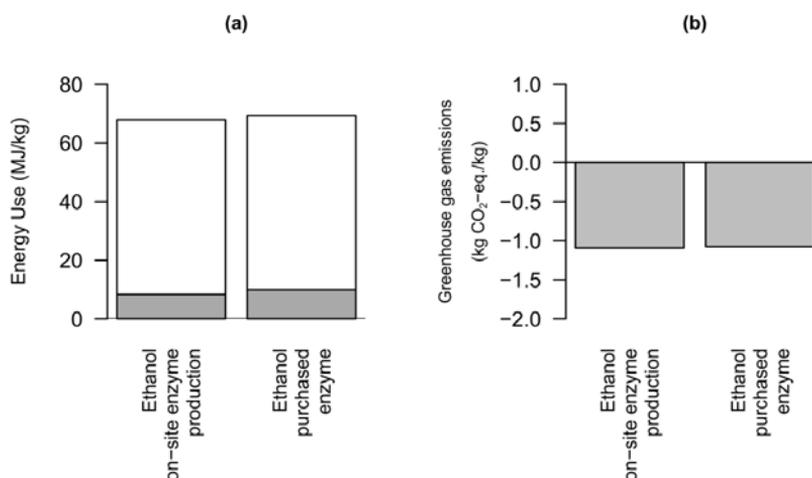
Figure 4-4: Comparison of production with and without on-site enzyme production in system expansion (SE) approach for (a) the non-renewable energy use (grey), the renewable energy use (white) and (b) the greenhouse gas emissions per kg ethanol.

A single-point sensitivity analysis (*ceteris paribus* analysis) is performed with respect to the solids loading, acid loading, temperature, xylan to xylose conversion, xylan to furfural conversion and glucan to glucose conversion in the pretreatment part. In the enzymatic hydrolysis part a single-point sensitivity analysis is performed with respect to the solids loading, enzyme loading and glucan to glucose conversion efficiency. The exact change of parameters is described in Table 3-4 on page 30.

The corresponding results are visualized in tornado charts for all parameters (Figure 4-5 and Figure 4-6) and in spider charts for pretreatment parameters (Figure 4-7 and Figure 4-8). These show that the non-renewable energy use and the greenhouse gas emissions are especially sensitive to the pretreatment temperature, acid loading and solid loading and the hydrolysis enzyme loading, glucan to glucose conversion and solids loading for the system expansion approach (Figure 4-5a). In case of the energy content based allocation approach, the results are especially sensitive to the pretreatment acid loading and the hydrolysis enzyme loading and glucan to glucose conversion (Figure 4-6b). It can be seen that the sensitivity of the non-renewable energy use is substantially smaller in case of the energy content based allocation approach. The sensitivity of the greenhouse gas emissions is comparable in both approaches.

From the spider charts it can be seen that non-renewable energy use and greenhouse gas emissions follow similar trends. It can be seen that the environmental impact is especially sensitive to the pretreatment temperature and the xylan to xylose conversion. However, counter intuitively the increase in conversion efficiencies results in an increase in the non-renewable energy use and greenhouse gas emissions (Figure 4-7), which is caused by a reduction in electricity production which gives a large credit. From this view one may better optimize electricity production instead of ethanol production. Therefore, it is also recommended to investigate the sensitivity in case of energy content based allocation (Figure 4-8). As the impact of the coproduced electricity is smaller in case of energy content based allocation, efficiency improvement now result in a lower non-renewable energy use and greenhouse gas

emissions, especially for xylan to xylose conversion. It can be seen that the impact is quite sensitive to the acid concentration, higher acid requirements result in a higher non-renewable energy use and greenhouse gas emissions.
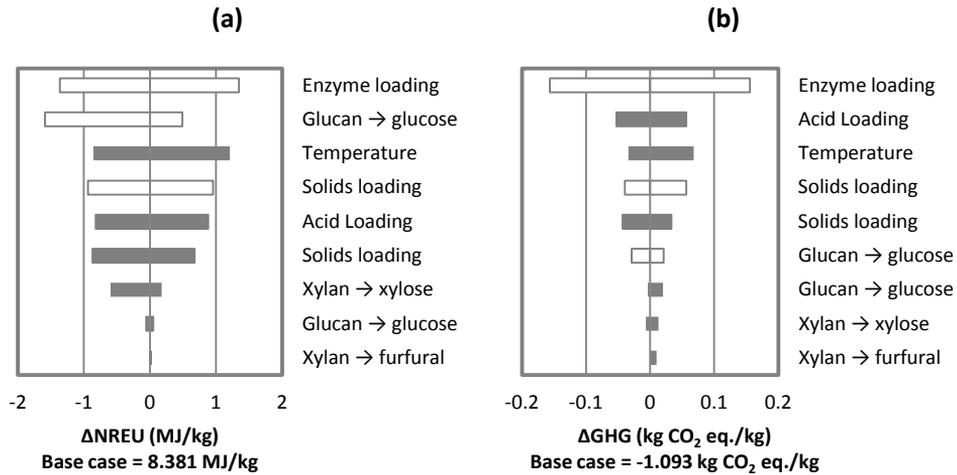
Figure 4-5: Single-point sensitivity tornado charts for (a) non-renewable energy use and (b) greenhouse gas emissions based on system expansion approach. Grey bars represent pretreatment parameters and white bars represent hydrolysis parameters.
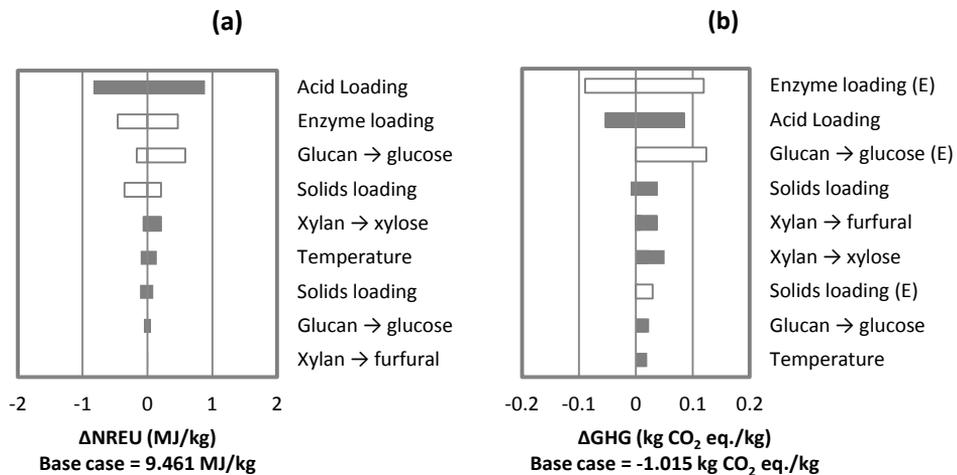
Figure 4-6: Single-point sensitivity tornado charts for (a) non-renewable energy use and (b) greenhouse gas emissions based on the energy content based allocation approach. Grey bars represent pretreatment parameters and white bars represent hydrolysis parameters.
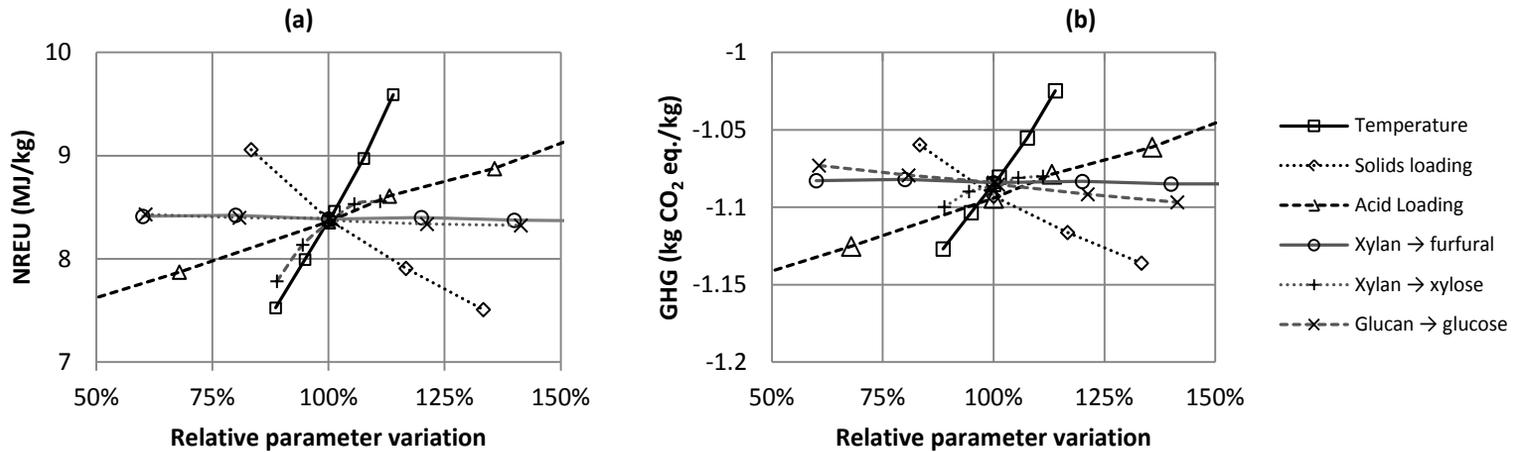
Figure 4-7: Single-point sensitivity spider charts for (a) non-renewable energy use and (b) greenhouse gas emissions based on system expansion approach.
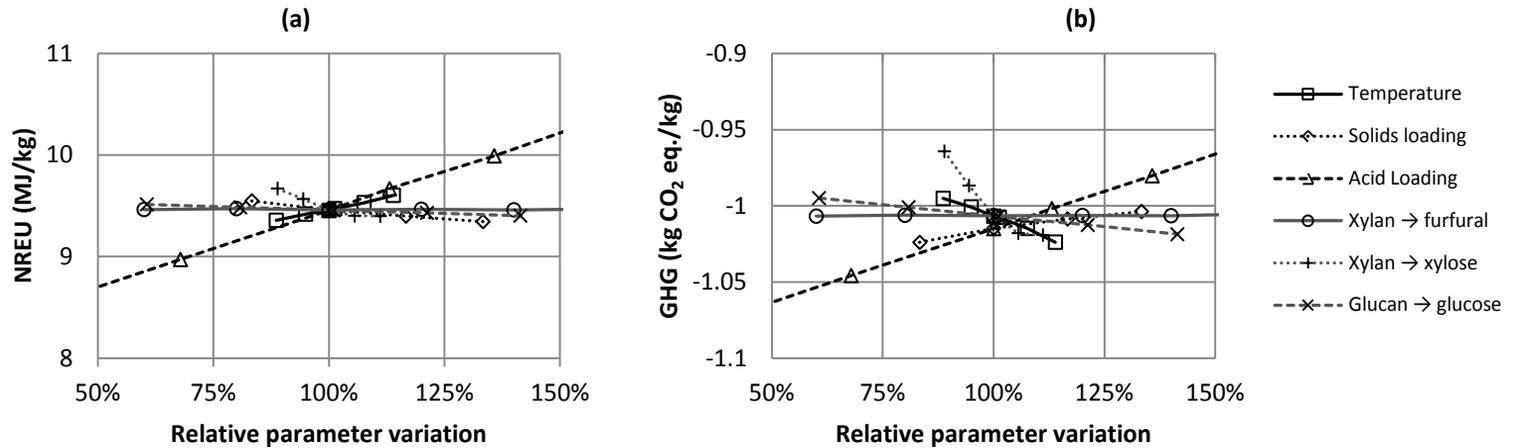
Figure 4-8: Single-point sensitivity spider charts for (a) non-renewable energy use and (b) greenhouse gas emissions based on energy allocation approach.

4.1.3 Adapted cases

Similarly, an environmental assessment is performed for the adapted cases described in section 3.2.4. The results of those inventory analyses and impact assessments are given in Table 4-3 and Table 4-4. The complete inventory analyses are given in *Appendix IV: Results of adapted cases* on page 69.

According to Table 4-3 the ethanol and electricity output of the bioethanol production process[12] vary largely, ranging from 13.9-22.3 tonne ethanol and 4.9-13.7 MWh per hour. Also the final energy output varies from 393.3-643.0 GJ per hour. The default case (NREL model with dilute acid pretreatment) and the CS-DA show the highest ethanol and final energy production. Since the CS-DA case is very similar to the default case, results are also similar.

The range in outcomes mainly depends on the composition of the feedstock, the component conversions and the process parameters like solids loading. Less cellulose and xylose in the feedstock result in reduced ethanol production; similarly, since all other component are used to co-produce electricity, higher fractions of arabinose, galactose, mannose and lignin result in higher electricity production. Lower conversion factors result also in more biomass in the waste stream to co-generation unit and more electricity production. Lower solids loadings lead to higher electricity requirements in the production process.

Since the NREL model is optimized for the reaction parameters defined in the design report, modelling of the adapted cases came with some warnings or errors, described in Table 4-3. Since the errors are mainly related to the calculation of the dilution of the feed stream[13], these warnings and errors are ignored.

Table 4-3: Inventory results of the bioethanol production process of the adapted cases.

ID	Ethanol (kg/h)	Electricity (kWh/h)	Final energy (GJ/h)[a]	Notes
default	22,273	12,801	643.0	–
CS-DA	21,198	13,699	617.4	–
SW-DA	16,487	10,284	478.9	Warnings[b]
CS-LHW	14,009	4,949	393.3	Warnings[c]
SW-LHW	13,864	11,852	414.2	Warnings[d]

[a] Final energy = (ethanol · 26.8 GJ/kg + electricity · 3.6 MJ/kWh) · 10^{-3} GJ/MJ
[b] Warnings in block A200, unit DILUT and H244
[c] Warnings in block A200, unit DILUT and P201, and the design specification SACSOLID
[d] Warnings in block A200, unit DILUT and P201, and the design specification SACSOLID

From Table 4-3 and Table 4-4 it can be seen that with the range in ethanol and electricity the LCA results also varies. In case of the system expansion approach the default model and CS-DA performs best. In general, higher electricity output comes with lower non-renewable energy use requirements as result of the co-production credit, but higher renewable energy use requirements as result of the lower ethanol production efficiency (e.g. SW-LHW). However, the

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[12] In the bioethanol production process the preprocessing step is excluded. The electricity output is therefore higher than the net energy production of the whole system.
[13] In the NREL model the biomass stream is mixed with water to obtain a solids loading of 30%. After pretreatment the mixture is further diluted to 20% solids loading. If the solids loading of the adapted cases is already 20% or below, this results in errors or warnings.

reaction parameters also influence the impact: higher acid requirements in SW-DA and the absence of chemicals in CS-LHW and SW-LHW result in either higher or lower non-renewable energy use, renewable energy use and greenhouse gas emissions.

The results in the energy allocation approach show less correlation with the total amount of electricity produced. It is clear that also in case of the energy allocation approach the default model and CS-DA performs best. All other cases show higher non-renewable energy use and greenhouse gas emissions as result of the increased chemical used, reduced conversion efficiencies and increase in required biomass. The impact of the increase in biomass needed is also visible in an increase in renewable energy use.

Table 4-4: LCA results of the adapted cases. Impacts are given for the production of ethanol.

ID	System expansion approach			Energy allocation approach		
	NREU (MJ/kg)	REU (MJ/kg)	GHG (kg CO_2 eq./kg)	NREU (MJ/kg)	REU (MJ/kg)	GHG (kg CO_2 eq./kg)
default	8.381	59.447	-1.093	9.461	58.57	-1.042
CS-DA	8.650	62.256	-1.061	10.134	60.983	-0.992
SW-DA	19.705[a]	85.779	-0.335	19.828	85.598	-0.330
CS-LHW	17.538[b]	94.751	-0.381	—[c]	—[c]	—[c]
SW-LHW	10.651	101.747[d]	-0.838	11.758	100.071	-0.786

[a] Higher non-renewable energy use for SW-DA is result of an increase in ammonia requirements due to higher acid requirements.
[b] The electricity produced in the bioethanol production step of CS-LHW is not enough to cover the preprocessing electricity. This electricity is now purchased and results in a higher non-renewable energy use.
[c] Since no excess electricity is produced, the energy allocation approach is not used for CS-LHW.
[d] High renewable energy use is result of low conversion to ethanol.

From this analysis it is clear that the default NREL model is indeed an optimized situation. However, the experimental study from Wyman et al. dates back to 2005 and improvement has been achieved in recent years, as described in the NREL report (Humbird et al. 2011). Based on the energy allocation approach the experimental studies result mainly in higher renewable energy use and moderate increase in non-renewable energy use or greenhouse gas emissions compared to the default case. Unless the default NREL model is an optimized situation, the environmental performance is quite near the environmental performance of the CS-DA case, which is very similar.

4.2 Literature review of the environmental performance of bioethanol

4.2.1 Environmental performance of first and second generation bioethanol

While the aim of this research is to compare different types of pretreatment technologies for second generation bioethanol production, the current production of first generation bioethanol exceeds second generation bioethanol production by far (compare Figure 1-1 and Figure 1-2). A short overview of the environmental performance of first and second generation bioethanol is given to provide the background for the environmental assessment of second generation bioethanol.

In the International Energy Agency's report 'From 1st- to 2nd-generation biofuel technologies' (2008) the results of a review of 44 published LCA studies of first- and second generation bioethanol production are given (IEA 2008). Although the results of IEA study are given as greenhouse savings of bioethanol use compared to gasoline and therefore differs from the results in section 4.1, the ranking of the performance is not influenced. With respect to the change in greenhouse gas emissions, lignocellulosic ethanol production performs generally better compared to ethanol based on wheat, corn and beet (Figure 4-9).
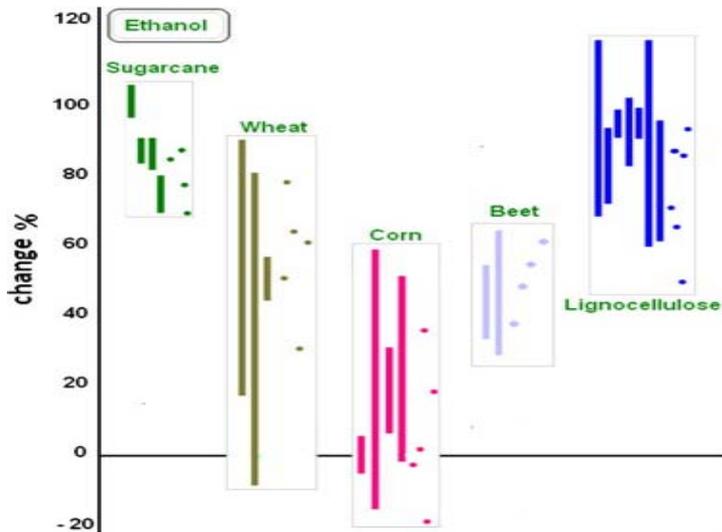
Figure 4-9: Well to wheel change in greenhouse gas emissions from bioethanol based on 44 LCA studies. Ranges are shown by bars, specific data by dots. Adapted from: IEA (2008).

Cherubini et al. (2009) compared the energy use and greenhouse gas emission of various biofuels and fossil fuels. The energy performance parameters and greenhouse gas emissions of first generation bioethanol, second generation bioethanol and gasoline are given in Table 4-5 (upper part). As shown the fossil energy use (FEU) and the greenhouse gas emissions (GHG) for second generation bioethanol can be substantially lower compared to bioethanol from first generation biomass and gasoline.

The Argonne National Laboratory developed a full life cycle model for transportation fuels, called GREET (Greenhouse gases, Regulated Emissions and Energy use in Transportation) (GREET 2012). This model was first published in 1996 and has been continuously updated. The most recent version is from December 2012. The GREET model also includes bioethanol as fuel, both from first and second generation feedstocks. Some data from this model is given in Table 4-5 (lower part).

From all studies it is clear that the fossil energy input and the greenhouse gas emissions for first and especially for second generation bioethanol is substantially lower compared to gasoline. Our own study leads to comparable findings. The calculated cumulative energy use, fossil energy

use and greenhouse gas emissions are generally somewhat higher than the other data from lignocellulosic sources.

Table 4-5: Ratio of non-renewable energy input to energy output ($E_{NREU-in}/E_{out}$), cumulative energy demand (CED), fossil energy use (FEU) and greenhouse gas emissions (GHG) of various types of bioethanol, given per km or per MJ. Adapted from: Cherubini et al. (2009) and GREET (2012).

Feedstock	$E_{NREU-in}/E_{out}$	CED	FEU	GHG
Cherubini et al. (2009)		MJ/km	MJ/km	g CO_2 eq./km
Sugar cane	0.15-0.25	12-13	0.2-0.3	50-75
Other crops (corn, sugar beet, wheat)	0.50-0.85	3.5-5.5	0.7-1.5	100-195
Lignocelluloses	0.15-0.45	6.1-9.3	0.1-0.8	25-50
Gasoline *(reference)*	1.20	1.7-2.4	1.7-2.4	210-220
GREET (2012)		MJ/MJ	MJ/MJ	g CO_2 eq./MJ[a]
Corn	–	2.33	0.55	62
Switchgrass	–	2.22	0.093	16
Corn stover	–	2.16	0.121	13
Forest residues	–	1.85	0.150	15
Sugar cane	–	2.04	-0.061[b]	9
Miscanthus	–	2.28	0.074	-9[b]
Gasoline (reference)[c]	–	1.24	1.19	92
This study		MJ/MJ	MJ/MJ	g CO_2 eq./MJ
System expansion approach	0.313	2.531[d]	0.313[e]	30.5[f]
Energy allocation approach	0.353	2.538[d]	0.353[e]	33.4[f]

[a] Well-to-wheel emissions
[b] Negative values caused by co-product credit
[c] U.S. average
[d] Calculated using CED = [NREU + REU]/26.8
[e] It is assumed that FEU = NREU/26.8
[f] To compare the well-to-gate LCA results with the well-to-wheel results the stochiometric emissions from ethanol are added to the total greenhouse gas emissions, so GHG = [GHG_{LCA} + 1.911]/26.8

4.2.2   Life cycle assessment studies on second generation bioethanol

A large number of LCA studies of lignocellulosic conversion to ethanol were recently reviewed by Bonin and Lal (2012), Wiloso et al. (2012) and Borrion et al. (2012b).

Bonin and Lal (2012) describe first, second and third[14] generation bioethanol with a focus on the agricultural phase of the bioethanol production chain. In the articles reviewed, they find a range of 0.64 to 13.10 for the net energy balance[15] and values from -117 to 93% greenhouse gas displacement for ethanol production compared to gasoline. For biodiesel, including algae, they identify a range of 0.26 to 3.55 for the net energy balance and -537% to 14% greenhouse gas displacement.

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[14] Third generation bioethanol is produces from algae.
[15] The net energy balance (NEB) is the ratio between energy produced and energy required. A NEB of 10 means that for each MJ of input energy 10 MJ of ethanol is produced, a NEB of 0.5 meas that for each MJ of input energy, only 0.5 MJ of ethanol is produced. An ideal feedstock should have at least an NEB of 1 or higher. Note that the energy required does not include the renewable energy that is incorperated during feedstock growth.

Wiloso et al. (2012) provide an extensive review of 22 papers published between 2005 and 2011 describing the system components of the agricultural chain, the production chain and the use chain. The production chain includes pretreatment technologies and hydrolysis and fermentation technologies. They also describe the aspects of the LCA methodology. They identify that 14 studies show a positive net energy output and only 2 studies show a negative net energy output. With respect to the greenhouse gas emission, 28 studies show fewer emissions than the reference fossil system and 3 studies show more emissions. Total numbers exceed the number of 22 papers, as in some papers various feedstocks are assessed.

Finally, Borrion et al. (2012b) provide a review of 53 papers on the LCA of lignocellulosic ethanol, focussing on the impact indicators, system boundaries and allocation method. Greenhouse gas emissions for pure ethanol range from -1.25 to 0.84 kg CO_2 eq./km, compared to 0.26 kg CO_2 eq./km for conventional gasoline. Two studies report higher emissions compared to gasoline, but it is shown that this depends on the way of allocation.[16]

In order to map the state-of-the-art performance of lignocellulosic bioethanol, 30 LCA studies between 2005 and 2012 are selected and reviewed with respect to system boundaries, the feedstock choice, the way pretreatment is included, the process configurations and the respective energy use and greenhouse gas emissions. Articles were selected based on the availability of NREU and GHG as environmental indicator and the availability of information, allowing present the results for one kg ethanol as functional unit.

Scope

The goal and scope of the LCA studies reviewed differs with respect to the system boundary and the functional unit. Generally, in accordance with the use of bioethanol as fuel, two different system boundaries can be identified: well-to-gate or well-to-wheel, depending on whether the use phase is included. Including the use phase increases the absolute greenhouse gas emissions. Some studies use besides the well-to-gate or well-to-wheel also other system boundaries: cradle-to-gate and well-to-tank are included in the well-to-gate boundary; cradle-to-grave is included in the well-to-wheel boundary. Half of the studies analyzed the performance using well-to-gate boundaries and half of the studies analysed the performance using well-to-wheel boundaries.

Based on the system boundary the functional unit of the studies differ. Generally the functional unit is either per km driven (well-to-wheel) or per MJ, kg of L ethanol produced or delivered (well-to-gate); besides, some other studies based their functional unit on the biomass input.

In Figure 4-10a the LCA studies are characterized with respect to the type of feedstock used. Grasses and hardwood make up the larger part. Others include for example solid municipal waste or waste paper. The total number exceeds the 30 studies reviewed, as in some studies multiple different feedstocks are studied.

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[16] Higher emissions are reported when economic value allocation is used. When mass allocation or system expansion is applied, the resulting emissions are lower (Borrion, McManus, and Hammond 2012b).

Process

In Figure 4-10b the pretreatment technologies analyzed in the LCA studies are given. Dilute acid pretreatment is by far the most studied pretreatment technique. AFEX and steam explosion are also studied in some studies. Kumar and Murthy (Kumar and Murthy 2012) are the only authors who perform a comparative LCA for four different pretreatment techniques, i.e. dilute acid, steam explosion, hot water and alkali pretreatment. The total number exceeds the 30 studies reviewed, as in some studies multiple different technologies are used. The extent to which pretreatment is described varies. Pretreatment can be described extensively with relevant process parameters and the way of calculation, which is denoted as explicit handling of pretreatment. However, many other studies only mention that the pretreatment data is obtained from a certain study (e.g. the NREL model) which is denoted as implicit handling of pretreatment.

In Figure 4-10c the fermentation technologies of the reviewed studies are given. SSCF and co-fermentation are the process configurations that are mostly used. The total number exceeds the 30 studies reviewed, as in some studies multiple process configurations are used.
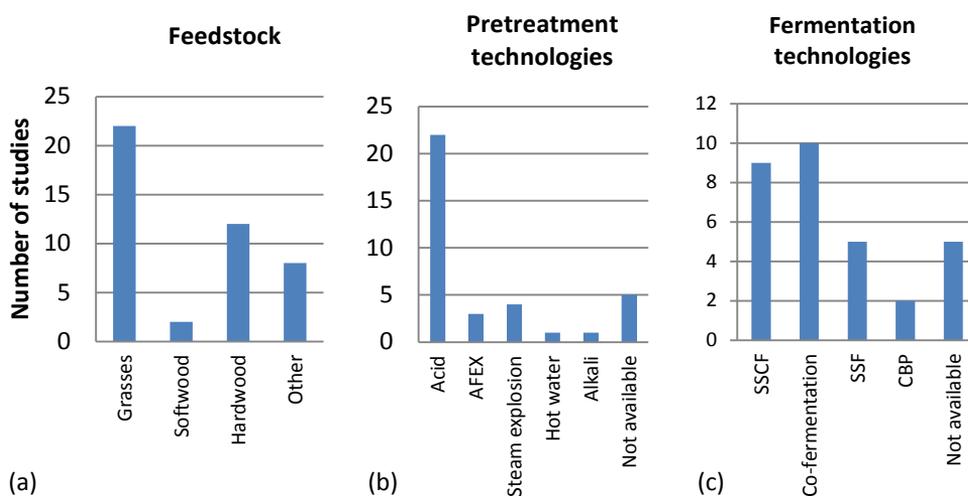
Figure 4-10: (a) Feedstock use, (b) pretreatment technologies and (c) fermentation technologies used in the reviewed studies on lignocellulosic ethanol production.

Results

Energy use is mainly reported in two different ways, either the non-renewable energy use is given or the total energy consumption is given. The non-renewable energy use is an environmental impact indicator and is also described as fossil energy use, fossil fuel depletion or more exclusively, petroleum use[17], with units as g oil eq., kg coal eq. or MJ per kg, per L, per MJ ethanol or per km driven. The total energy consumption is more an overall process performance

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[17] Fossil energy use, fossil fuel depletion and petroleum use deviate from the non-renewable energy use by what is either or not included. Strictly spoken fossil energy use does not include nuclear energy, where the non-renewable energy use does. In case of reporting petroleum use, the objective is most likely strategic due to import dependencies.

parameter, for example described by the net energy yield, net energy value, with units as MJ per kg, L or MJ ethanol. In Figure 4-11 the non-renewable energy use of bioethanol production reported in the reviewed studies is given. For consistency reasons, the total energy consumption and net energy values reported are not included. The results from our own LCA study are represented by the filled circles. The horizontal line indicates the non-renewable energy use of gasoline, scaled to the energy content of ethanol, which is 34.5 MJ/kg ethanol eq.[18] The non-renewable energy use for most studies range up to 20 MJ/kg[19], clearly lower compared to gasoline.
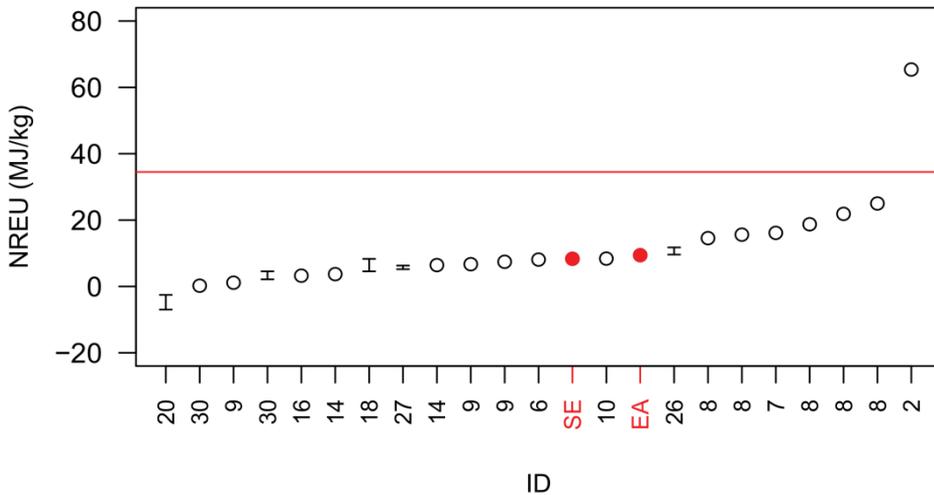
Figure 4-11: Overview of non-renewable energy use reported in the reviewed studies on lignocellulosic ethanol production. Circles and bars represent single values and ranges respectively. The filled circles indicate our own LCA study for the system expansion approach (SE) and the energy allocation approach (EA).

Greenhouse gas emissions are reported mainly as kg CO_2 eq./km or per amount of ethanol. Well-to-wheel emissions are converted to well-to-gate emissions by subtracting the stoichiometric CO_2 emissions from ethanol combustion, which is 1.911 kg CO_2/kg ethanol. The results are given in Figure 4-12. Results from our own LCA study are given with the filled circles. The horizontal line indicates the greenhouse gas emissions of gasoline, scaled to the energy content of ethanol which is 0.439 kg CO_2 eq./kg ethanol eq.[20] The greenhouse gas emissions for most studies range from -3 up to 1.5 kg CO_2 eq./kg ethanol eq.[21] Largest part of the studies report greenhouse gas emissions lower than gasoline, but for some studies the values are slightly higher. A complete overview of the reviewed studies can be found in *Appendix V: Overview of reviewed LCA studies* on page 77.

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[18] $NREU_{gasoline, scaled} = NREU_{gasoline} \cdot [LHV_{ethanol} / LHV_{gasoline}] = 56.7 \cdot [26.8/44.0] = 34.5$ MJ/kg ethanol eq.
[19] The NREU the LCA study with ID = 2 is unexpectedly high. It is not completely clear what caused this outlaying value. The reported value is 146.88 g oil eq for driving 1 km with E85. This is converted to MJ/kg by NREU = 146.88 g oil eq/km / [0.1206 L/km · 0.79 kg/L] · 0.041868 MJ/g oil eq. = 64.54 MJ/kg. However, in the paper the impact is described as 39% better compared to gasoline (Borrion, McManus, and Hammond 2012a).
[20] $GHG_{gasoline, scaled} = GHG_{gasoline} \cdot [LHV_{ethanol} / LHV_{gasoline}] = 0.676 \cdot [26.8/44.0] = 0.439$ kg CO_2 eq./kg ethanol eq.
[21] The GHG the LCA study with ID = 5 is unexpectedly low. It is not completely clear what caused this outlaying value.

Figure 4-12: Overview of greenhouse gas emissions reported in the reviewed studies on lignocellulosic ethanol production. Circles and bars represent single values and ranges respectively. The filled circle indicates our own LCA study for the system expansion approach (SE) and the energy allocation approach (EA).

From Figure 4-11 and Figure 4-12 it can be seen that bioethanol production from second generation biomass performed better on non-renewable energy use and greenhouse gas emissions for almost all cases with respect to gasoline. For the greenhouse gas emissions some studies lie above the reference emissions and some ranges cross the reference emissions. Differences in non-renewable energy use and the greenhouse gas emissions are related to the type of biomass that is used, the performance of the production process and the way of allocation. Since the greenhouse gas emission reduction can be very little or even absent, second generation bioethanol is not always a suitable option for greenhouse gas emission reduction. Further development of technologies should therefore also focus on the greenhouse gas emission reduction that can be achieved, including the impact of land use change related emissions in the agricultural phase, which is generally not included in the studies yet.

For both the non-renewable energy use and the greenhouse gas emissions, the results of our own LCA perform well compared to the reviewed studies. The ethanol production processes analysed in our LCA show clearly lower non-renewable energy use and the greenhouse gas emissions compared to the reference impact of gasoline. Performance is best in case of the system expansion approach were electricity gets a credit based on average electricity production in the European Union. Since the energy content of co-produced electricity is small compared to energy content of the ethanol, the allocation approach does not have a large impact on the position of our results within the benchmark. However, with increasing electricity production, the difference between the different allocation approaches will be larger. It is therefore very important that consistent choices are made and reported with respect to the allocation method.

5. Discussion

The concept of the bio-based economy provides possibilities to produce clean, low carbon and secure chemicals and fuels. Second generation bioethanol production and especially the processing steps needed for obtaining processable sugars from agricultural residues and wood are key developments for the feasibility of the bio-based economy. Research on second generation bioethanol production is an emerging scientific area and in the last decade the amount of papers published with respect to lignocellulosic ethanol increased 20-fold.[22] The results presented in this thesis are based on the most recent literature. In this chapter the literature used, the methodological choices and the obtained results are discussed. Section 5.1 deals with the literature on pretreatment technologies, section 5.2 with the life cycle assessment methodology and section 5.3 with the results.

5.1   Pretreatment technologies

There are numerous routes leading to lignocellulosic bioethanol. One has to make choices regarding either the thermochemical pathway or the biochemical pathway. After that, the possibilities are still abundant. Focussed on the biochemical pathway, choices need to be made regarding the feedstock, suitable pretreatment and subsequent hydrolysis and fermentation configuration. The pretreatment options described in chapter 2 all have their advantages and disadvantages and are more or less suitable for certain types of biomass. Most of the options are mainly studies using lab-scale experiments and since most of the research is performed by different research groups, the lab-scale literature is often hard to compare as result of the use of different feedstocks, process conditions and analytic protocols. However, there are also some studies where different types of pretreatment are compared using a consistent procedure, providing insights in techniques that may be promising for certain types of feedstock.

Since commercial second generation ethanol production is in an early stage, process data is hardly available or confidential. Nevertheless, the amount of pilot projects will be increasing in the coming years, thereby facilitating further analysis of the life cycle performance of second generation bioethanol production based on actual results from production plants. Currently, the techno-economic models bridge the gap between experimental data and the environmental assessment in providing data on the inputs and outputs of the whole production process. Although techno-economic models provide valuable information, they also come with numerous assumptions and are likely to be optimistic, i.e. the performance still needs to be proven in an industrial setting. Nevertheless, these models provide insight into the expected performance of second generation bioethanol production plants.

To gain deeper understanding about the performance of pretreatment technologies, the scientific community has to perform comparative studies for multiple pretreatment technologies and for multiple types of biomass using a consistent procedure, facilitating reproducibility and comparative assessment. For performing environmental assessment, data

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[22] Based on document count with query "lignocellulos* AND ethanol" in Scopus on March 19, 2013; 2002: 28, 2007: 154, 2012: 470, total: 2865

availability from pilot, demonstration and commercial production facilities is of great importance.

5.2 Life cycle assessment methodology

LCA is a powerful tool in determining the environmental performance of processes and products, but requires data and assumptions about the process. In addition choices have to be made regarding the impact of utilities and the allocation of the impacts in case of multi-output processes. Since industrial process data on second generation bioethanol production was not available at the time of writing this thesis, the NREL model was used to generate data on the production process.

Data on the agricultural stage were obtained from literature and requires some explanation. First of all it is assumed that the corn stover is a waste product and, beside some extra impacts as result of the stover gathering, no impacts of the farming process were allocated to it. On the first sight this is a correct procedure as corn stover is currently mainly a low-value waste stream. However, when corn stover will be suitable for fuel production it is not correct consider it as waste, since corn production will partly be driven by the revenues created from corn stover. As result of dealing with corn stover as waste, agricultural data on the production of corn stover itself is scarce. Obtaining data specific for corn stover data from corn production data requires choices regarding the impact allocation and correction for corn stover that is not available anymore for replenishing the soil. The agricultural data used in this study is specific for the US while impacts of the utilities are mainly specific for the EU. Further research is needed to deal with the allocation of the agricultural impact to waste streams and the EU specificity of the agricultural activities.

Prior to the bioethanol production process, preprocessing is performed to obtain uniform corn stover with reduced size. However, the physical properties of corn stover described in the GREET database do not completely match the physical properties of corn stover in the NREL report. The LCA can therefore be further optimized when these properties match.

The NREL model is developed as n^{th} plant, which means that it is assumed that it is an industrial facility that has already overcome cost and performance penalties of the pioneer facility (Spatari, Bagley, and MacLean 2010), thereby assuming future performance. On the other hand, assuming future performance results in some discrepancy between the modeled process and the status quo. When examining the efficiencies of the plant they are somewhat higher compared to the achievements in lab-scale experiments. The NREL model is very suitable to calculate required utilities and the expected production of ethanol and electricity; however, efficiencies remained unchanged if one changes parameters like temperature and loading. Since the chemical conversion is influenced by these parameters, this does not represent reality. However, the model can be used to examine what the effect is of single parameter with constant efficiency, providing insight for initial selection of pretreatment technologies (*ceteris paribus* analysis). When one aims to model the effect of temperature on the whole process, including the reaction efficiency, one has to import a complete dataset contain both temperature data and data on efficiencies.

The output of the NREL process are the products ethanol and electricity and the waste streams like ash, brine and the process emissions. Since it is not clear whether and if so, how ash and brine will be further used, ash is processed as disposal and brine is completely excluded. Different use of ash and brine could influence the overall life cycle performance. In a bio-economy, production of both bio-based fuels and bio-based chemicals can come together in a single production facility. While in calculations dealing with fuels mainly the lower heating value of a product is used, for chemicals the higher heating value is more common, influencing the calculations on energy use. Future usage of the products determines which comparison is most suitable. In this LCA study calculations based on the lower heating value are used.

5.3   Results

Various factors influence the actual LCA results, like agricultural activities, type of feedstock, process type and reaction conditions. From the sensitivity analysis it is clear that various process parameters influence the environmental performance of second generation bioethanol production, but this is also dependent on the way of allocation.

From the comparison with the literature the LCA results are shown to be robust and in line with the published literature (see section 4.2.2). Since the energy content of the co-produced electricity is small (up to ~2%) compared to the energy content of the ethanol, differences between the system expansion and energy content based allocation approach are minor. However, when the energy content of the co-produced electricity is higher (up to ~25%) allocation based on energy content will be favourable. Moreover, since the impact of average electricity production is likely to decrease in the coming year, allocation without co-production credit results in more stable and robust results.

Adaption of the NREL model with parameters from lab-scale experiments by Wyman et al. show results that are in the same order of the results in the default case. However, in all cases the environmental performance is slightly too significantly worse. This is caused mainly by lower solids loadings, higher chemicals or temperature requirements and lower conversion efficiencies. However, it should also be noted that the NREL model is optimized for the parameters defined in the NREL report. Lower solids loading, higher acid loading and higher temperatures can therefore require other adaption in the process, which is not included in the model yet. Some indications for these requirements come from the occurrence of warnings or errors in the model and the need of small adaptations in the recovery process to avoid failure of ethanol recovery in desirable concentrations. However, from the results of the adapted cases it becomes clear that the environmental performance according to the default model is somewhat optimistic, but probably feasible in the coming years. In this report, adapted cases are analysed for the simple pretreatment techniques that do not require further process adaptations, like pretreatment with alkaline agents, like AFEX, or with organic solvents. Further adaptations of the model could be based on Kabir Kazi et al. (2010), who describe adaptations of the NREL model for various pretreatment technologies and hydrolysis and fermentation configurations.

6. Conclusion

Driven by the concerns about first generation bioethanol production, research on second generation bioethanol, based on lignocellulosic biomass, has increased drastically. While first generation biomass is quite easily processable, lignocellulosic biomass requires pretreatment to overcome its recalcitrant properties and enable subsequent hydrolysis and fermentation.

In the last decade various pretreatment techniques on physical, chemical, physicochemical and/or biological basis, were developed and optimized. The various types of biomass and the desired products call for a variety of pretreatment technologies, including dilute acid pretreatment, steam explosion, ammonia fibre explosion, organosolv pretreatment. Dilute acid pretreatment is the major pretreatment technology studied, but other techniques have potential for specific feedstocks and upstream requirement. The literature on pretreatment technologies consists mainly of lab-scale experiments and techno-economic models. The literature on lab-scale experiments is scattered and often hard to compare, however Wyman et al. made some efforts in comparing different technologies using consistent procedures. Since actual process data is hardly available, techno-economic models are used to predict the present and future performance. Currently, the model developed by NREL is the most widely used techno-economic model.

In this study a life cycle assessment is performed to determine the environmental performance of lignocellulosic ethanol production. The lignocellulosic ethanol production chain studied consists of the agricultural production of corn stover, required preprocessing and the production of ethanol using dilute acid pretreatment, enzymatic hydrolysis and fermentation. The production step is modelled in Aspen Plus using the NREL model. To identify influential parameters for lignocellulosic ethanol production, a *ceteris paribus* sensitivity analysis is performed on various reaction parameters in the production step. The life cycle impact is determined using a system expansion approach where co-produced electricity replaced average electricity production in the EU and an energy allocation approach where the impact is divided on the respective energy content of the produced ethanol and electricity. Finally, the NREL model is adapted using lab-scale data to obtain results that resemble the status quo in pretreatment technologies.

The non-renewable energy use needed to produce 1 kg of ethanol is 8.4 MJ in case of the system expansion approach and 9.5 MJ in case of the energy allocation approach. The corresponding greenhouse gas emissions are -1.1 kg CO_2 eq. and -1.0 kg CO_2 eq. The life cycle assessment results are especially sensitive to the pretreatment and hydrolysis conversion efficiencies in the system expansion approach and to the hydrolysis efficiency, furfural formation and acid loading in the energy allocation approach. The environmental performance of the adapted cases is in the same order of the performance of the default NREL model; however, in all cases the performance is slightly too significantly worse, as result of lower solids loadings, higher chemical or temperature requirements and lower conversion efficiencies.

Comparison of the life cycle assessment results with published life cycle assessment studies for second generation bioethanol show average environmental performance. Comparison of the results of second generation bioethanol production show better performance compared to usage of gasoline as fuel or petrochemical ethanol as chemical. Also the performance compared to first generation bioethanol production is likely to be better.

Further research is needed on the agricultural production phase, especially to obtain a better understanding to which extend second generation biomass can be produced and how much agricultural and forestry residues can be removed without comprising ecosystems. Based on the environmental assessment in this study, producing bioethanol from corn stover using dilute acid pretreatment is most promising. However, the scope of this study is limited and further research is needed to make strategic decisions about pretreatment preferences. Especially experimental research that compares different types of pretreatment with different types of biomass in a pilot process setting could provide valuable insights in the potential performance of future plants.

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Appendix I: Advantages and disadvantages of pretreatment technologies

Pretreatment	Mode of action	Advantages	Disadvantages	Other remarks
Milling	• Reduces cellulose crystallinity (Tomás-Pejó et al., 2011) • Promotes the reduction of the degree of polymerization (DP) (Quintero, 2011)	• No formation of inhibitors • Reduces technical digestion time (Quintero, 2011)	• High power and energy consumption (Tomás-Pejó et al., 2011; Quintero, 2011; Alvira et al., 2010), usually higher than inherent biomass energy (Kumar et al., 2009)	
Acid pretreatment (dilute acid)	• Removal of hemicelluloses (major) • Alteration of lignin structure (minor) (Harmsen et al., 2010)	• Most commonly used chemical pretreatment technique (Taherzadeh and Karimi, 2008) • Performs well on most biomass materials (Kumar et al., 2009; Zheng et al., 2009)	• Sugar degradation (temperature dependent) resulting in formation of inhibiting compounds (Alvira et al., 2010) • Risk of formation of volatile degradation products (Hendriks and Zeeman, 2009) • Low sugar concentration in exit stream (Tomás-Pejó et al., 2011) • Corrosive conditions (Zheng et al., 2009) • Need of acid neutralization (Zheng et al., 2009)	• Most suitable for biomass with low lignin content, as little lignin is removed (Harmsen et al., 2010)
Acid pretreatment (concentrated acid)	• Hydrolysis of cellulose and hemicelluloses (Harmsen et al., 2010)	• Flexibility in feedstock choice • High monomeric sugar yield • Mild temperature conditions (Harmsen et al., 2010)	• Slow rate of conversion (Zhang and Shahbazi, 2011) • Sugar degradation (temperature dependent) resulting in formation of inhibiting compounds (Alvira et al., 2010) • Corrosive conditions • Need of recycling acids to lower costs (Harmsen et al., 2010) • High operation and maintenance costs (Alvira et al., 2010)	• Strong acid is hazardous, toxic and corrosive (Harmsen et al., 2010)
Ammonia fiber explosion (AFEX)	• Removal of lignin (major) • Removal of hemicellulose (minor) • Decrystallization of cellulose (Harmsen et al., 2010) • Increase in accessible surface area (Tomás-Pejó et al., 2011; Kumar et al., 2009) • Removal of acetyl groups on hemicelluloses (Menon and Rao, 2012)	• High hydrolysis yield for low lignin content biomass • Low formation of inhibitors • Output is only pretreated solid biomass (Alvira et al., 2010) • No need for small particle size for efficacy (Harmsen et al., 2010) • Low enzyme requirement (Zhang and Shahbazi, 2011) • High solids loading (Zhang and Shahbazi, 2011)	• Not effective for high lignin content (Sun and Chen, 2002; Tomás-Pejó et al., 2011; Alvira et al., 2010) • Need of ammonia recycling • Cost of ammonia (Alvira et al., 2010) • Recovery and recycling is feasible, but complex (Eggemann and Elander, 2005) • Formation of oligormeric form of hemicelluloses degradation products (Zhang and Shahbazi, 2011)	

Pretreatment	Mode of action	Advantages	Disadvantages	Other remarks
Alkaline	• Removal of lignin (major) • Removal of hemicelluloses (minor) (Harmsen et al., 2010; Tomás-Pejó et al., 2011) • Solvation and saphonication (Quintero, 2011) • Affection of crystalline state of cellulose (Quintero, 2011) • Increases accessible surface area (Kumar et al., 2009)	• Effective removal of lignin and hemicelluloses (Tomás-Pejó et al., 2011) • Ambient conditions (Kumar et al., 2009) • Low temperature and pressure (Zhang and Shahbazi, 2011)	• Longer pretreatment time (hours to days) • Less effective with softwood with higher lignin contents (Kumar et al., 2009) • Requires removal of alkali (Tomás-Pejó et al., 2011) • Irrecoverable salts formed and incorporated into biomass (Kumar et al., 2009) • Expensive chemicals (Zhang and Shahbazi, 2011)	
Organosolv	• Removal of lignin (major) • Removal of hemicelluloses (minor), depending on solvent (Harmsen et al., 2010) • Hydrolysis of lignin and hemicelluloses (Tomás-Pejó et al., 2011)	• Relatively pure lignin as by product (Zhao et al., 2009 in Alvira et al., 2010)	• Recycling of solvents is necessary • High commercial price of solvents (Alvira et al., 2010) • Complex process (Kumar et al., 2009) • Solvent may be inhibitor for cell growth (Harmsen et al., 2010)	
Steam explosion (SE)	• Removal of hemicelluloses (major) • Alteration of lignin structure (minor) (Harmsen et al., 2010) • Causes lignin transformation and hemicelluloses solubilization (Tomás-Pejó et al., 2011; Alvira et al., 2010)	• Low use of chemicals • Limited energy consumption • Lower environmental impacts (Harmsen et al., 2010) • Lower capital investment • Complete sugar recovery (Alvira et al., 2009; Menon and Rao, 2012) • Cost effective (Tomás-Pejó et al., 2011; Alvira et al., 2010)	• Formation of degradation products (Harmsen et al., 2010; Tomás-Pejó et al., 2011; Alvira et al., 2010; Kumar et al., 2009) • Partial degradation of hemicelluloses (Alvira et al., 2010; Tomás-Pejó et al., 2011) • Acid catalyst necessary for softwood (Alvira et al., 2010) • Incomplete disruption of the lignin-carbohydrate matrices (Kumar et al., 2009)	• Higher yield of glucose and hemicelluloses in two-step method (Alvira et al., 2010) • Part of hemicelluloses hydrolyze and form acids, which could catalyse the further hydrolysis (Menon and Rao, 2012)
Biological (i.e. fungal)	• Degredation of lignin and hemicelluloses (Tomás-Pejó et al., 2011)	• Low energy requirements (Tomás-Pejó et al., 2011) • No or reduced inhibitor formation (Wan and Li, 2012) • Mild environmental conditions (Cordona et al., 2009) • Low capital costs (Alvira et al., 2010)	• Long incubation times • Requires careful control of growth conditions • (Tomás-Pejó et al., 2011) • Substantial cellulose and hemicelluloses loss • (Wan and Li, 2012) • Low rate of hydrolysis (Alvira et al., 2010)	

Pretreatment	Mode of action	Advantages	Disadvantages	Other remarks
Ammonia recycle percolation (ARP)		• High efficiency in delignification (Zhang and Shahbazi, 2011)	• Low solids loading (Zhang and Shahbazi, 2011)	
Ionic liquids (ILs)	• Effective in solvating cellulose (Zhang and Shahbazi, 2011)	• Low toxicity • Broad selection of anion and cation combinations (Zheng et al., 2009) • Minimal environmental impact (Zhang and Shahbazi, 2011)	• High costs • Lack of knowledge about action mode (Zheng et al., 2009) • Induction of cellulose inactivation; effective regeneration; causticity and toxicity of ILs; selection of stable ILs (Zhang and Shahbazi, 2011)	• Still in initial stages (Manon and Rao, 2012)
Liquid hot water (LHW)	• Removal of hemicelluloses (Harmsen et al., 2010)	• No catalyst of chemical requirement • Low corrosion potential • Low concentration of degradation products (Alvira et al., 2009) • Solubilized hemicelluloses and lignin products are present in lower concentrations • No need for biomass size reduction and therefore attractive for large scale (Menon and Rao, 2012)	• High water consumption • Acetic acid formation (Harmsen et al., 2010) • Catalytic degradation is difficult to control and result in undesirable side products (Quintero, 2011)	
(Supercritical) CO_2 explosion	• Removal of hemicelluloses • Decrystallization of cellulose (Harmsen et al., 2010) • Increase in accessible surface area (Tomás-Pejó et al., 2011; Kumar et al., 2009)	• Cost effective (Tomás-Pejó et al., 2011) • Low temperature of operation (Alvira et al., 2010) • Less formation of inhibitory compounds (Sun and Cheng, 2002; Tomás-Pejó et al., 2011) • Does not cause formation of inhibitory compounds (Kumar et al., 2009)	• Lower sugar yields compared to steam and ammonia explosion (Alvira et al., 2010) • Very high pressure requirements (Tomás-Pejó et al., 2011; Alvira et al., 2010) • Does not affect lignin and hemicelluloses (Tomás-Pejó et al., 2011; Kumar et al., 2009)	• More effective than AFEX (Harmsen et al., 2010)

Appendix II: Process scheme of NREL model
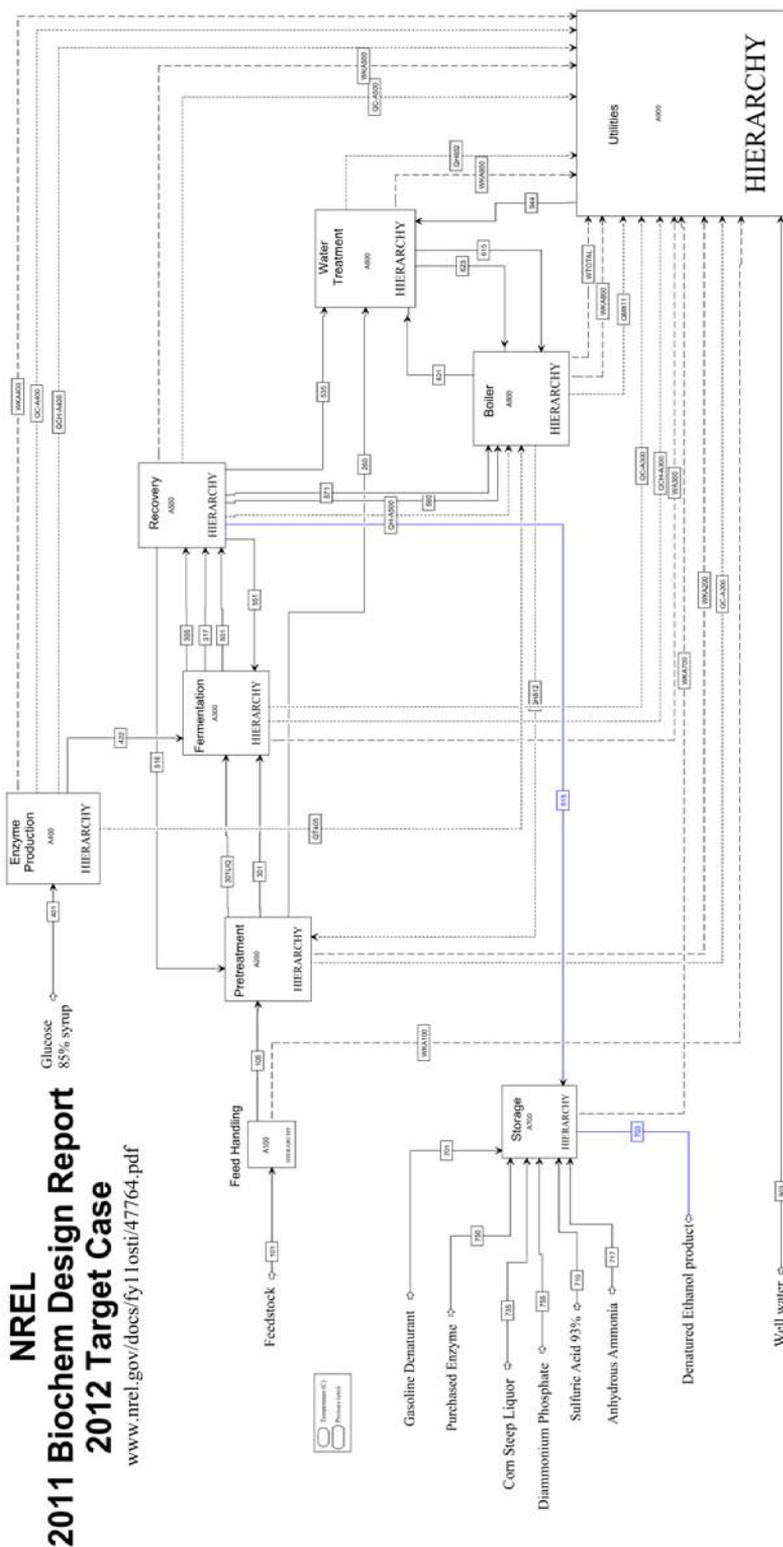
NREL
2011 Biochem Design Report
2012 Target Case
www.nrel.gov/docs/fy11osti/47764.pdf

Appendix III: Carbon balance

Streams	Utility	Total (kg CO_2 eq./h)		Normalized (kg CO_2 eq./kg ethanol)	
		IN	OUT	IN	OUT
Stream 101	Corn stover	3117.08		6.16	
Stream 401	Glucose syrup	80.53		0.16	
Stream 701	Gasoline denaturant	32.48		0.06	
Stream 703	Ethanol		973.95		1.92
Stream 735	Corn steep liquor	25.4		0.05	
Stream 423	Process CO_2 emissions		51.97		0.10
Stream 435	Process CO_2 emissions		2.16		0.00
Stream 550	Process CO_2 emissions		470.52		0.93
Stream 622	Process CO_2 emissions		87.83		0.17
Stream 810	Process CO_2 emissions		1669.86		3.30
Stream 809	Ash		10.2		0.02
Stream 627	Brine		3.86		0.01
Total		**3255.49**	**3270.35**	**6.43**	**6.46**

Appendix IV: Results of adapted cases

Inventory *CS-DA*

Products		Total		Normalized	
Ethanol		21198	kg	1.000	kg
Electricity		-13699	kWh	-0.646	kWh
Agriculture					
Corn stover growth (carbon sequestration)		136797	kg CO_2	6.453	kg CO_2
Corn stover growth (energy content)		1319344	MJ	62.239	MJ
Corn stover production		104167	kg	4.914	kg
Preprocessing					
Electricity		10001	kWh	0.435	kWh
Production					
Anhydrous ammonia		1276	kg	0.060	kg
Corn steep liquor		1296	kg	0.061	kg
Diammonium phosphate		140	kg	0.007	kg
Enzyme		0	kg	0.000	kg
Gasoline		442	kg	0.021	kg
Glucose syrup		3069	kg	0.145	kg
Sulfuric acid		1318	kg	0.062	kg
Water		159396	kg	7.519	kg
Ash		6857	kg	0.323	kg
Brine		10828	kg	0.511	kg
Process emissions		101818	kg CO_2	4.803	kg CO_2

Results *CS-DA | System expansion*

Products				
Ethanol	1.000	kg	26.800	MJ
Electricity	0.174	kWh	0.628	MJ

	NREU		REU		GHG	
Agriculture						
Corn stover growth	-		62.239	MJ	-6.453	kg CO_2 eq.
Corn stover production	4.063	MJ	0.070	MJ	0.286	kg CO_2 eq.
Preprocessing						
Electricity	0.000	MJ	0.000	MJ	0.000	kg CO_2 eq.
Production						
Anhydrous ammonia	2.509	MJ	0.017	MJ	0.126	kg CO_2 eq.
Corn steep liquor	0.668	MJ	0.009	MJ	0.049	kg CO_2 eq.
Diammonium phosphate	0.142	MJ	0.006	MJ	0.013	kg CO_2 eq.
Enzyme	0.000	MJ	0.000	MJ	0.000	kg CO_2 eq.
Gasoline	1.193	MJ	0.003	MJ	0.015	kg CO_2 eq.
Glucose syrup	0.367	MJ	0.007	MJ	0.022	kg CO_2 eq.
Sulfuric acid	0.126	MJ	0.006	MJ	0.008	kg CO_2 eq.
Water	0.632	MJ	0.026	MJ	0.049	kg CO_2 eq.
Ash	0.673	MJ	0.027	MJ	0.106	kg CO_2 eq.
Brine	0.000	MJ	0.000	MJ	0.000	kg CO_2 eq.
Process emissions	-		-		4.803	kg CO_2 eq.
Electricity credit	-1.721	MJ	-0.155	MJ	-0.085	kg CO_2 eq.
Total	**8.650**	**MJ**	**62.256**	**MJ**	**-1.061**	**kg CO_2 eq.**

Results

CS-DA | Energy content based allocation

Products

Ethanol	1.000	kg	26.800	MJ
Electricity	0.174	kWh	0.628	MJ

	NREU		REU		GHG	
Agriculture						
Corn stover growth	-		62.239	MJ	-6.453	kg CO$_2$ eq.
Corn stover production	4.063	MJ	0.070	MJ	0.286	kg CO$_2$ eq.
Production						
Anhydrous ammonia	0.000	MJ	0.000	MJ	0.000	kg CO$_2$ eq.
Corn steep liquor						
Diammonium phosphate	2.509	MJ	0.017	MJ	0.126	kg CO$_2$ eq.
Enzyme	0.668	MJ	0.009	MJ	0.049	kg CO$_2$ eq.
Gasoline	0.142	MJ	0.006	MJ	0.013	kg CO$_2$ eq.
Glucose syrup	0.000	MJ	0.000	MJ	0.000	kg CO$_2$ eq.
Sulfuric acid	1.193	MJ	0.003	MJ	0.015	kg CO$_2$ eq.
Water	0.367	MJ	0.007	MJ	0.022	kg CO$_2$ eq.
Ash	0.126	MJ	0.006	MJ	0.008	kg CO$_2$ eq.
Brine	0.632	MJ	0.026	MJ	0.049	kg CO$_2$ eq.
Process emissions						
Electricity credit	0.673	MJ	0.027	MJ	0.106	kg CO$_2$ eq.
Total	**10.371**	**MJ**	**62.411**	**MJ**	**-0.976**	**kg CO$_2$ eq.**
per kg ethanol	10.134	MJ	60.983	MJ	-0.992	kg CO$_2$ eq.
per kWh electricity	1.361	MJ	8.192	MJ	0.088	kg CO$_2$ eq.

Inventory

SW-DA

Products	Total		Normalized	
Ethanol	16487	kg	1.000	kg
Electricity	-10284	kWh	-0.624	kWh
Agriculture				
Switchgrass growth (carbon sequestration)	146171	kg CO$_2$	8.866	kg CO$_2$
Switchgrass growth (energy content)	1409749	MJ	85.507	MJ
Switchgrass production	104167	kg	6.318	kg
Preprocessing				
Electricity	10001	kWh	0.607	kWh
Production				
Anhydrous ammonia	3820	kg	0.232	kg
Corn steep liquor	2396	kg	0.145	kg
Diammonium phosphate	290	kg	0.018	kg
Enzyme	0	kg	0.000	kg
Gasoline	344	kg	0.021	kg
Glucose syrup	2999	kg	0.182	kg
Sulfuric acid	8881	kg	0.539	kg
Water	207433	kg	12.582	kg
Ash	4409	kg	0.267	kg
Brine	35490	kg	2.153	kg
Process emissions	121254	kg CO$_2$	7.355	kg CO$_2$

Results *SW-DA | System expansion*

Products				
Ethanol	1.000	kg	26.800	MJ
Electricity	0.017	kWh	0.062	MJ

	NREU		REU		GHG	
Agriculture						
Switchgrass growth	-		85.507	MJ	-8.866	kg CO_2 eq.
Switchgrass production	3.898	MJ	0.053	MJ	0.271	kg CO_2 eq.
Preprocessing						
Electricity	0.000	MJ	0.000	MJ	0.000	kg CO_2 eq.
Production						
Anhydrous ammonia	9.656	MJ	0.065	MJ	0.484	kg CO_2 eq.
Corn steep liquor	1.588	MJ	0.021	MJ	0.117	kg CO_2 eq.
Diammonium phosphate	0.377	MJ	0.016	MJ	0.034	kg CO_2 eq.
Enzyme	0.000	MJ	0.000	MJ	0.000	kg CO_2 eq.
Gasoline	1.193	MJ	0.003	MJ	0.015	kg CO_2 eq.
Glucose syrup	0.461	MJ	0.009	MJ	0.028	kg CO_2 eq.
Sulfuric acid	1.088	MJ	0.054	MJ	0.067	kg CO_2 eq.
Water	1.058	MJ	0.044	MJ	0.082	kg CO_2 eq.
Ash	0.556	MJ	0.022	MJ	0.088	kg CO_2 eq.
Brine	0.000	MJ	0.000	MJ	0.000	kg CO_2 eq.
Process emissions	-		-		7.355	kg CO_2 eq.
Electricity credit	-0.169	MJ	-0.015	MJ	-0.008	kg CO_2 eq.
Total	**19.705**	**MJ**	**85.779**	**MJ**	**-0.335**	**kg CO_2 eq.**

Results *SW-DA | Energy content based allocation*

Products				
Ethanol	1.000	kg	26.800	MJ
Electricity	0.017	kWh	0.062	MJ

	NREU		REU		GHG	
Agriculture						
Switchgrass growth	-		85.507	MJ	-8.866	kg CO_2 eq.
Switchgrass production	3.898	MJ	0.053	MJ	0.271	kg CO_2 eq.
Preprocessing						
Electricity	0.000	MJ	0.000	MJ	0.000	kg CO_2 eq.
Production						
Anhydrous ammonia	9.656	MJ	0.065	MJ	0.484	kg CO_2 eq.
Corn steep liquor	1.588	MJ	0.021	MJ	0.117	kg CO_2 eq.
Diammonium phosphate	0.377	MJ	0.016	MJ	0.034	kg CO_2 eq.
Enzyme	0.000	MJ	0.000	MJ	0.000	kg CO_2 eq.
Gasoline	1.193	MJ	0.003	MJ	0.015	kg CO_2 eq.
Glucose syrup	0.461	MJ	0.009	MJ	0.028	kg CO_2 eq.
Sulfuric acid	1.088	MJ	0.054	MJ	0.067	kg CO_2 eq.
Water	1.058	MJ	0.044	MJ	0.082	kg CO_2 eq.
Ash	0.556	MJ	0.022	MJ	0.088	kg CO_2 eq.
Brine	0.000	MJ	0.000	MJ	0.000	kg CO_2 eq.
Process emissions	-		-		7.355	kg CO_2 eq.
Total	**19.874**	**MJ**	**85.795**	**MJ**	**-0.327**	**kg CO_2 eq.**
per kg ethanol	19.828	MJ	85.598	MJ	-0.330	kg CO_2 eq.
per kWh electricity	2.664	MJ	11.498	MJ	0.159	kg CO_2 eq.

Inventory *CS-LHW*

Products	Total		Normalized	
Ethanol	14009	kg	1.000	kg
Electricity	-4949	kWh	-0.353	kWh
Agriculture				
Corn stover growth (carbon sequestration)	136797	kg CO_2	9.765	kg CO_2
Corn stover growth (energy content)	1319344	MJ	94.178	MJ
Corn stover production	104167	kg	7.436	kg
Preprocessing				
Electricity	10001	kWh	0.714	kWh
Production				
Anhydrous ammonia	826	kg	0.059	kg
Corn steep liquor	1608	kg	0.115	kg
Diammonium phosphate	183	kg	0.013	kg
Enzyme	0	kg	0.000	kg
Gasoline	292	kg	0.021	kg
Glucose syrup	3048	kg	0.218	kg
Sulfuric acid	0	kg	0.000	kg
Water	193007	kg	13.777	kg
Ash	6332	kg	0.452	kg
Brine	6910	kg	0.493	kg
Process emissions	115565	kg CO_2	8.249	kg CO_2

Results *CS-LHW*

Products				
Ethanol	1.000	kg	26.800	MJ
Electricity	-0.361	kWh	-1.298	MJ

	NREU		REU		GHG	
Agriculture						
Corn stover growth	-		94.178	MJ	-9.765	kg CO_2 eq.
Corn stover production	6.148	MJ	0.106	MJ	0.433	kg CO_2 eq.
Preprocessing						
Electricity	3.557	MJ	0.321	MJ	0.175	kg CO_2 eq.
Production						
Anhydrous ammonia	2.458	MJ	0.017	MJ	0.123	kg CO_2 eq.
Corn steep liquor	1.254	MJ	0.017	MJ	0.092	kg CO_2 eq.
Diammonium phosphate	0.279	MJ	0.012	MJ	0.025	kg CO_2 eq.
Enzyme	0.000	MJ	0.000	MJ	0.000	kg CO_2 eq.
Gasoline	1.193	MJ	0.003	MJ	0.015	kg CO_2 eq.
Glucose syrup	0.551	MJ	0.011	MJ	0.034	kg CO_2 eq.
Sulfuric acid	0.000	MJ	0.000	MJ	0.000	kg CO_2 eq.
Water	1.158	MJ	0.048	MJ	0.090	kg CO_2 eq.
Ash	0.940	MJ	0.038	MJ	0.148	kg CO_2 eq.
Brine	0.000	MJ	0.000	MJ	0.000	kg CO_2 eq.
Process emissions	-		-		8.249	kg CO_2 eq.
Electricity credit	-	MJ	-	MJ	-	kg CO_2 eq.
Total	**17.538**	**MJ**	**94.751**	**MJ**	**-0.381**	**kg CO_2 eq.**

Inventory

SW-LHW

Products	Total		Normalized	
Ethanol	13864	kg	1.000	kg
Electricity	-11852	kWh	-0.855	kWh
Agriculture				
Switchgrass growth (carbon sequestration)	146171	kg CO_2	10.543	kg CO_2
Switchgrass growth (energy content)	1409749	MJ	101.687	MJ
Switchgrass production	104167	kg	7.514	kg
Preprocessing				
Electricity	10001	kWh	0.721	kWh
Production				
Anhydrous ammonia	912	kg	0.066	kg
Corn steep liquor	1604	kg	0.116	kg
Diammonium phosphate	181	kg	0.013	kg
Enzyme	0	kg	0.000	kg
Gasoline	289	kg	0.021	kg
Glucose syrup	3010	kg	0.217	kg
Sulfuric acid	0	kg	0.000	kg
Water	207963	kg	15.001	kg
Ash	284	kg	0.020	kg
Brine	7776	kg	0.561	kg
Process emissions	125322	kg CO_2	9.040	kg CO_2

Results

SW-LHW | System expansion

Products				
Ethanol	1.000	kg	26.800	MJ
Electricity	0.134	kWh	0.481	MJ

	NREU		REU		GHG	
Agriculture						
Switchgrass growth	-		101.687	MJ	-10.543	kg CO_2 eq.
Switchgrass production	4.636	MJ	0.064	MJ	0.322	kg CO_2 eq.
Preprocessing						
Electricity	0.000	MJ	0.000	MJ	0.000	kg CO_2 eq.
Production						
Anhydrous ammonia	2.742	MJ	0.018	MJ	0.138	kg CO_2 eq.
Corn steep liquor	1.264	MJ	0.017	MJ	0.093	kg CO_2 eq.
Diammonium phosphate	0.280	MJ	0.012	MJ	0.025	kg CO_2 eq.
Enzyme	0.000	MJ	0.000	MJ	0.000	kg CO_2 eq.
Gasoline	1.193	MJ	0.003	MJ	0.015	kg CO_2 eq.
Glucose syrup	0.550	MJ	0.011	MJ	0.034	kg CO_2 eq.
Sulfuric acid	0.000	MJ	0.000	MJ	0.000	kg CO_2 eq.
Water	1.261	MJ	0.052	MJ	0.097	kg CO_2 eq.
Ash	0.043	MJ	0.002	MJ	0.007	kg CO_2 eq.
Brine	0.000	MJ	0.000	MJ	0.000	kg CO_2 eq.
Process emissions	-		-		9.040	kg CO_2 eq.
Electricity credit	-1.317	MJ	-0.119	MJ	-0.065	kg CO_2 eq.
Total	**10.651**	**MJ**	**101.747**	**MJ**	**-0.838**	**kg CO_2 eq.**

Results   *SW-LHW | Energy content based allocation*

Products						
Ethanol	1.000	kg	26.800	MJ		
Electricity	0.134	kWh	0.481	MJ		

	NREU		REU		GHG	
Agriculture						
Switchgrass growth	-		101.687	MJ	-10.543	kg CO_2 eq.
Switchgrass production	4.636	MJ	0.064	MJ	0.322	kg CO_2 eq.
Preprocessing						
Electricity	0.000	MJ	0.000	MJ	0.000	kg CO_2 eq.
Production						
Anhydrous ammonia	2.742	MJ	0.018	MJ	0.138	kg CO_2 eq.
Corn steep liquor	1.264	MJ	0.017	MJ	0.093	kg CO_2 eq.
Diammonium phosphate	0.280	MJ	0.012	MJ	0.025	kg CO_2 eq.
Enzyme	0.000	MJ	0.000	MJ	0.000	kg CO_2 eq.
Gasoline	1.193	MJ	0.003	MJ	0.015	kg CO_2 eq.
Glucose syrup	0.550	MJ	0.011	MJ	0.034	kg CO_2 eq.
Sulfuric acid	0.000	MJ	0.000	MJ	0.000	kg CO_2 eq.
Water	1.261	MJ	0.052	MJ	0.097	kg CO_2 eq.
Ash	0.043	MJ	0.002	MJ	0.007	kg CO_2 eq.
Brine	0.000	MJ	0.000	MJ	0.000	kg CO_2 eq.
Process emissions	-		-		9.040	kg CO_2 eq.
Electricity credit	0.000	MJ	0.000	MJ	0.000	kg CO_2 eq.
Total	**11.969**	**MJ**	**101.866**	**MJ**	**-0.774**	**kg CO_2 eq.**
per kg ethanol	11.758	MJ	100.071	MJ	-0.786	kg CO_2 eq.
per kWh electricity	1.579	MJ	13.442	MJ	0.096	kg CO_2 eq.

Appendix V: Overview of reviewed LCA studies

Table A-III: Overview of reviewed LCA studies (part 1)

ID	Reference	Biomass	Pretreatment	Reporting[a]	Process configurations	System boundaries
1	Bai et al. (2010)	Switchgrass	AFEX	Implicit	SSCF	Well-to-wheel
2	Borrion et al. (2012a)	Wheat straw	Acid	Implicit, based on Aden et al. (2002)	SSCF	Well-to-wheel
3	Bright and Stromman (2009)	Hardwood chips	Acid	Implicit, based on Wooley et al. (1999)	SSCF	Well-to-gate
4	González-García et al. (2009b)	Flax shives	Acid	Implicit, based on Aden et al. (2002)	Co-fermentation	Well-to-wheel
5	González-García et al. (2009a)	Brassica carinata	Acid	Implicit, based on Aden et al. (2002)	Co-fermentation	Well-to-wheel
6	González-García et al. (2010)	Poplar	Acid	Implicit, based on Aden et al. (2002)	Co-fermentation	Well-to-wheel
7	González-García et al. (2010b)	Alfalfa stems	Acid	Implicit, based on Aden et al. (2002)	Co-fermentation	Well-to-wheel
8	González-García et al. (2010a)	Alfalfa stems	Acid	Implicit, based on Aden et al. (2002)	Co-fermentation	Well-to-wheel
8	González-García et al. (2010a)	E. mustard	Acid	Implicit, based on Aden et al. (2002)	Co-fermentation	Well-to-wheel
8	González-García et al. (2010a)	Poplar	Acid	Implicit, based on Aden et al. (2002)	Co-fermentation	Well-to-wheel
8	González-García et al. (2010a)	Flax	Acid	Implicit, based on Aden et al. (2002)	Co-fermentation	Well-to-wheel
8	González-García et al. (2010a)	Hemp	Acid	Implicit, based on Aden et al. (2002)	Co-fermentation	Well-to-wheel
9	González-García et al. (2012)	Black locust	Acid	Implicit, based on Aden et al. (2002)	Co-fermentation	Well-to-gate
9	González-García et al. (2012)	Poplar	Acid	Implicit, based on Aden et al. (2002)	Co-fermentation	Well-to-gate
9	González-García et al. (2012)	Eucalyptus	Acid	Implicit, based on Aden et al. (2002)	Co-fermentation	Well-to-gate
10	González-García et al. (2012)	Eucalyptus	Acid	Implicit, based on Aden et al. (2002)	Co-fermentation	Well-to-wheel
11	Hsu et al. (2010)	Corn stover, wheat straw, switchgrass, forest residues	Acid	Implicit, based on Aden et al. (2002) and GREET model (2012)	–	Well-to-wheel
12	Kalogo et al. (2007)	Municipal solid waste	–	–	SSF	Well-to-wheel
13	Kaufman et al. (2010)	Corn stover	Acid	Implicit, based on Aden et al. (2002)	–	Well-to-gate
14	Kemppainen and Shonnaard (2005)	Upper Michigan Timber	Acid	Explicit, from Wooley et al. (1999)	SSCF	Well-to-gate
14	Kemppainen and Shonnaard (2005)	Newsprint	Acid	Explicit, from Wooley et al. (1999)	SSCF	Well-to-gate
15	Kumar and Murthy (2012)	Grass straw	Various: dilute acid, dilute alkali, hot water, steam explosion	Explicit, extensive description.	SSCoF	Well-to-gate
16	Lavigne and Powers (2007)	Corn stover	–	Implicit, based on GREET model (2012)	–	Well-to-gate
17	Luo et al. (2009)	Corn stover	Acid	Implicit, based on Aden et al. (2002)	Co-fermentation	Well-to-gate

ID	Reference	Biomass	Pretreatment	Reporting[a]	Process configurations	System boundaries
18	MacLean and Spatari (2009)	Switchgrass	Acid, AFEX	Explicit, based on Aden et al. (2002)	SSCF, CBP	Well-to-gate
19	McKechnie et al. (2011)	Poplar	Steam explosion	Explicit, based on Aden et al. (2002)	SSCF	Well-to-gate
20	Mu et al. (2010)	Poplar wood chips, corn stover, waste paper, wheat straw	Acid	Explicit, based on Aden et al. (2002)	SSCF	Well-to-wheel
21	Roy and Dutta (2012)	Wheat straw	–	–	–	Well-to-gate
22	Sánchez-Segado (2010)	Carob pod	–	Implicit	–	Well-to-gate
23	Schmitt et al. (2012)	Yard waste	Steam explosion	Explicit, experimental based, model from Aden et al. (2002)	SSF	Well-to-gate
23	Schmitt et al. (2012)	Mixed waste paper	Acid	Explicit, experimental based, model from Aden et al. (2002)	SSF	Well-to-gate
23	Schmitt et al. (2012)	Municipal solid waste	Acid	Explicit, experimental based, model from Aden et al. (2002)	SSF	Well-to-gate
24	Slade et al. (2009)	Spruce	Two-stage dilute acid and catalysed steam pretreatment (with SO2) as reference.	Explicit (mass balance), reference using Aspen model based on Sassner et al. (2008)	SSF	Well-to-gate
24	Slade et al. (2009)	Straw	Two-stage dilute acid and catalysed steam pretreatment (with SO2) as reference.	Explicit (mass balance), reference using Aspen model based on Sassner et al. (2008)	SSF	Well-to-gate
25	Spatari et al. (2005)	Switchgrass	Acid	Explicit, based on Sheehan et al. (2004)	Co-fermentation	Well-to-wheel
25	Spatari et al. (2005)	Corn stover	Acid	Explicit, based on Sheehan et al. (2004)	Co-fermentation	Well-to-wheel
26	Spatari et al. (2010)	Switchgrass, corn stover	Acid, AFEX	Explicit, model	SSCF, CBP	Well-to-gate
27	Stephenson et al. (2010)	Willow	Steam explosion	Explicit, based on Aden et al. (2002)	SSF	Well-to-wheel
28	Veláquez-Arredondo et al. (2010)	Banana residues	Acid	Explicit	–	Well-to-gate
29	Wang et al. (2011)	Corn stover	–	–	–	Well-to-wheel
30	Zhang et al. (2010)	Hard wood residues, corn stover	Acid	Implicit	Co-fermentation	Well-to-wheel
30	Zhang et al. (2010)	Municipal solid waste	Acid	Implicit	SSF	Well-to-wheel

[a] The way pretreatment is handled in the study. Pretreatment can be described extensively with relevant process parameters and way of calculation which is denoted as explicit. Other studies only mention that the pretreatment data is obtained for a certain study, this is denoted as implicit.

Table A-III: Overview of reviewed LCA studies (part 2)

ID	Paper	NREU (MJ/kg)		Energy Use from paper		Unit	GHG (kg CO$_2$ eq. /kg)		GHG from paper		Unit	Notes
1	Bai et al. (2010)						1.35	1.22	0.0814	0.0896	kg CO$_2$ eq/km	E85; 10.10 km/kg
2	Borrion et al. (2012a)	65.4		146.9		g oil eq/km	0.94		88.1		g CO$_2$ eq/km	E85; 10.64 km/kg
3	Bright and Stromman (2009)						0.58	0.81	21.7	30.185	g CO$_2$ eq/MJ	Best case; worst case is +39.1%
4	González-García et al. (2009b)						-0.37	4.03	-0.367	4.03	kg CO$_2$ eq/kg	Range from different allocation methods
5	González-García et al. (2009a)						-4.84		-4.84		kg CO$_2$ eq/kg	E85
6	González-García et al. (2010)	8.15		0.84		kg coal eq/km[a]	0.97		0.096		kg CO$_2$ eq/km	7.78 km/L
7	González-García et al. (2010b)	16.19		1.67		kg coal eq/km[a]	-0.27		-0.027		kg CO$_2$ eq/km	7.78 km/L
8	González-García et al. (2010a)	21.91		2.1		kg coal eq/km[a]	0.34		0.031		kg CO$_2$ eq/km	E85; 8.29 km/L
8	González-García et al. (2010a)	14.61		1.4		kg coal eq/km[a]	-1.27		-0.117		kg CO$_2$ eq/km	E85;8.29 km/L
8	González-García et al. (2010a)	15.65		1.5		kg coal eq/km[a]	1.36		0.125		kg CO$_2$ eq/km	E85; 8.29 km/L
8	González-García et al. (2010a)	25.04		2.4		kg coal eq/km[a]	1.73		0.159		kg CO$_2$ eq/km	E85; 8.29 km/L
8	González-García et al. (2010a)	18.78		1.8		kg coal eq/km[a]	2.47		0.227		kg CO$_2$ eq/km	E85; 8.29 km/L
9	González-García et al. (2012)	1.17		1.22		kg coal eq/kg[a]	-1.83		-1.83		kg CO$_2$ eq/kg	
9	González-García et al. (2012)	6.75		7.03		kg coal eq/kg[a]	-0.62		-0.619		kg CO$_2$ eq/kg	
9	González-García et al. (2012)	7.48		7.79		kg coal eq/kg[a]	-0.40		-0.397		kg CO$_2$ eq/kg	
10	González-García et al. (2012)	8.44		34.8		g coal eq/km	1.36		0.135		kg CO$_2$ eq/km	10.10 km/kg fuel
11	Hsu et al. (2010)	2.68	13.42	0.1	0.5	MJ/MJ	0.64	2.20	0.024	0.082	kg CO$_2$ eq/MJ	Data obtained from figure
12	Kalogo et al. (2007)			1767	2528	kJ/km			54	119	g CO$_2$ eq/km	E85
13	Kaufman et al. (2010)						0.40	1.07	15	40	g CO$_2$/MJ	Range dependend on allocation method

ID	Paper	NREU (MJ/kg)		Energy Use from paper		Unit	GHG (kg CO$_2$ eq. /kg)		GHG from paper		Unit	Notes
14	Kemppainen and Shonnaard (2005)	3.76		0.14		fossil energy per energy content	0.25		0.196		kg CO$_2$ eq/L	
14	Kemppainen and Shonnaard (2005)	6.48		0.27		fossil energy per energy content	0.97		0.769		kg CO$_2$ eq/L	
15	Kumar and Murthy (2012)	13.29	31.00	10.5	24.49	net energy value (MJ/ L)	-1.49	-0.35	-555.4	-131	kg CO$_2$ eq/10 GJ	Range depend on pretreatment technology
16	Lavigne and Powers (2007)	3.29		2.6		MJ/L						
17	Luo et al. (2009)	24.68	30.42	24.68	30.42	MJ/L						
18	MacLean and Spatari (2009)	4.56	8.32	0.17	0.31	MJ/MJ	0.40	0.81	15	30	g CO$_2$ eq/MJ	Data obtained from figure; well-to-tank
19	McKechnie et al. (2011)						-3.05	-0.46	-113.6	-17.3	g CO$_2$ eq/MJ	
20	Mu et al. (2010)	-6.96	-2.53	-5.5	-2	MJ/L	-0.48	-0.23	-0.38	-0.18	kg CO$_2$ eq/L	Data obtained from figure
21	Roy and Dutta (2012)	18.99		15		MJ/L	1.15		0.91		kg CO$_2$ eq/L	Data obtained from abstract
22	Sánchez-Segado (2010)	14.36		14.36		MJ/kg	0.72		0.72		kg CO$_2$ eq/kg	
23	Schmitt et al. (2012)	0.69		0.546		MJ/L	1.17		928		g CO$_2$ eq/L	
23	Schmitt et al. (2012)	1.08		0.852		MJ/L	1.37		1080		g CO$_2$ eq/L	
23	Schmitt et al. (2012)	7.57		5.98		MJ/L	1.53		1210		g CO$_2$ eq/L	
24	Slade et al. (2009)						0.32	1.15	12	43	kg CO$_2$ eq/GJ	Data obtained from figure
24	Slade et al. (2009)						0.30	0.97	11	36	kg CO$_2$ eq/GJ	Data obtained from figure
25	Spatari et al. (2005)						0.62		489		g CO$_2$ eq/L	Well-to-wheel
25	Spatari et al. (2005)						0.42		330		g CO$_2$ eq/L	Well-to-wheel
26	Spatari et al. (2010)	9.62	11.77	7.6	9.3	MJ/L	0.75	1.00	590	790	g CO$_2$ eq/L	

ID	Paper	NREU (MJ/kg)		Energy Use from paper		Unit	GHG (kg CO_2 eq. /kg)		GHG from paper		Unit	Notes
27	Stephenson et al. (2010)	5.20	6.30	5.2	6.3	GJ/tonne	0.27	0.34	271	342	kg CO_2 eq/tonne	
28	Veláquez-Arredondo et al. (2010)	13.96	16.61	1396 4	1661 3	kJ/kg						
29	Wang et al. (2011)						0.13	0.19	5	7	g CO_2/MJ	
30	Zhang et al. (2010)	2.15	4.56	0.08	0.17	MJ petr/MJ fuel	-0.16	0.50	-5.9	18.6	g CO_2 eq per MJ	
30	Zhang et al. (2010)	0.27		0.01		MJ petr/MJ fuel	1.08		40.2		g CO_2 eq per MJ	

[a] Initial conversion of the kg coal equivalent to MJ result in unexpected high values. After personal communication with the author it became clear that the conversion factors used where 47.575 kg coal eq/kg for the crude oil and 49.548 kg coal eq/kg for the natural gas, instead these conversion factors need to be approximately 25 times smaller. In order to calculate the correct values, the initial values are multiplied with 0.04.

Sustainability assessment of second generation bioethanol production: Model-based life cycle assessment of various biochemical conversion paths

Lignocellulosic biomass is of increasing importance for the bio-economy in providing feedstock for sustainable energy carriers and chemicals. Main challenge is the recalcitrant behavior of lignocellulosic biomass that requires pretreatment before subsequent hydrolysis and fermentation. Pretreatment can be performed in numerous ways, each especially suitable for certain types of biomass and coming with distinct advantages and disadvantages.

In order to determine the environmental performance of second generation bioethanol, the production chain was studied using life cycle assessment (LCA) based on a recent process model from NREL. The LCA results were shown especially sensitive toward the pretreatment temperature and acid loading, and hydrolysis enzyme loading and conversion efficiencies. Further adaptations in the model were made to represent experimental pretreatment studies of corn stover and switchgrass.

Wouter Terlouw, master student Energy Science at Utrecht University, has a background in chemistry. He has experience in energy related research, natural science research, data analysis and education. This thesis was written as academic research for his masters.