MSc Program
Environmental Technology & International Affairs

Meta Study to Assess the Sustainability of Second-Generation Biofuels: Emphasis on Residues and Wastes

A Master's Thesis submitted for the degree of
"Master of Science"

supervised by
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Vienna, 28.05.2013

Affidavit

I, **SHRUTI AVINASH ATHAVALE**, hereby declare

1. that I am the sole author of the present Master's Thesis, "META STUDY TO ASSESS THE SUSTAINABILITY OF SECOND-GENERATION BIOFUELS: EMPHASIS ON RESIDUES AND WASTES", 79 pages, bound, and that I have not used any source or tool other than those referenced or any other illicit aid or tool, and
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Abstract

Due to concerns about climate change and the growing fear of dwindling fossil fuel reserves, governments all over the world have committed themselves to search for an alternative, “greener” fuel source. Biofuels have been heralded as a panacea to climate change, but recent studies demonstrate that the costs of biofuel production, namely the harmful environmental impact of the process, may outweigh the benefits. This Master's thesis aims to provide a comparison of studies on first- and second-generation biofuels in order to assess their environmental, social, and economic sustainability. The numerous technical barriers hindering the commercialization of lignocellulosic biofuels are addressed and the benefits of using agricultural and forestry residues for biofuel production are analyzed. By means of a material flow analysis, the CO_2 emissions resulting from the use of gasoline and bioethanol at the stage-of-use are compared. It is shown that the combustion of bioethanol results in lower CO_2 emissions than those from the combustion of gasoline. Despite these favorable results, it remains to be seen if biofuels are viable, when the entire life-cycle, from feedstock cultivation to fuel production, is taken into consideration.

Acknowledgements

First and foremost, I would like to thank my thesis supervisor Professor Paul H. Brunner for his guidance, patience, and enthusiasm.

Furthermore, I would like to express my deepest gratitude to my parents and my brother for their continuous support throughout my studies.

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List of Abbreviations and Acronyms

Ammonia Freeze Explosion (AFEX)

Annum (a)

Carbon Dioxide (CO_2)

Carbon Monoxide (CO)

Clean Development Mechanism (CDM)

Compare Following (cf.)

European Union (EU)

Fisher-Tropsch Synthesis (FTS)

Gasoline Gallon Equivalent (GGE)

Genetically Modified Organism (GMO)

Gigajoule (Gj)

Gram (g)

Greenhouse Gas (GHG)

Hectare (ha)

Hydrogen (H_2)

Lower Heating Value (H_u)

Kilogram (kg)

Material Flow Analysis (MFA)

Megaton (Mt)

Methane (CH_4)

Microgram (µg)

Million Tons of Oil Equivalent (Mtoe)

Nitrous Oxide (N_20)

No Date (n.d.)

No Page (n.p.)

Refuse-Derived Fuel (RDF)

Renewable Energy Directive (RED)

Soil Organic Content (SOC)

Square Meter (m^2)

Substance Flow Analysis (STAN)

Sulfur Oxide (SO_x)

Teragram (Tg)

Ton (t)

United Nations (UN)

United States of America (U.S.)

Year (yr)

1. Introduction

Recently, climate change and energy scarcity seem to be on everyone's mind. Countries are now slowly turning towards cleaner, renewable energy sources to meet growing energy demands, without increasing emissions of greenhouse gases. Man's dependence upon scarce resources, especially fossil fuels, is one of the main reasons we are facing climate issues. Fossil fuels, which include oil, coal, and natural gas, contribute to approximately 86% of total world energy supply (see EIA 2013: n.p.). Reducing carbon dioxide (CO_2) emissions, especially those produced as a result of fossil fuel burning, is an important strategy of many governments to prevent global warming (see Annex 1). Nations have become increasingly aware of the challenges and difficulties that come with a strong dependence on fossil fuels and non-renewable resources. Due to the asymmetrical distribution of oil and gas reserves, dependency on another nation is seen as a weakness, a weakness that can be easily exploited. Competition over scarce resources, the undeniable link between fossil fuel consumption and climate change, and the search for a safer, alternate fuel source have prompted the interest in biofuels.

Biofuels have gained increasing popularity, because they are supposed to have a significantly lower global warming effect than fossil fuels and have the potential of reducing dependency on oil import. Furthermore, many European countries believe that the production of biofuels would help reduce the problem of food overproduction in agriculture (cf. Rose 1994: 63). In this context, many countries have begun to implement far-reaching energy legislations, which put an emphasis on expanding the biofuel market. The Renewable Energy Directive (RED) of the European Union (EU) (Directive 2009/28/EC) aims at the promotion of the use of energy sources and sets a 10% target of renewable energies in road transport by 2020. It has been projected that the majority share of road transport energy will be taken up by biofuels and thus biofuels have become an integral part of the EU energy strategy for the future. In doing so, the EU considers the effect of biofuels on greenhouse gas (GHG) emission mitigation, energy supply security and the belief that biofuels will bring economic benefits to the member states of the European Union. In 1962, Rudolph Diesel stated, *"The use of vegetable oils for engine fuels may seem insignificant today, but such oils may become in the course of time as important as the petroleum and coal tar products of the present time." (Diesel News 2008: n.p.)* However, many scientists are quick to point out that despite the many benefits biofuels seem to offer at first glance, they have hidden costs that could prove to be environmentally prohibitive. It remains to be seen whether biofuels will be the answer to all our energy questions, but it is sure to be a driving force in many future energy legislations.

1.1. Objective and Research Questions

The goal of this thesis is to address the sustainability issues of biofuels based on an evaluation of existing studies. In particular second-generation biofuels are investigated, an overview of the technical barriers towards full commercialization and widespread use of biofuels is provided, and a simple method of comparison between the relative benefits of using fossil fuels versus biofuels is offered. Furthermore, the advantages and disadvantages of using agricultural residues and crop wastes as biofuel feedstocks are addressed.

This thesis aims to answer the following research questions:

- Taking into consideration the demands made on water, nutrients, and land usage, are second-generation biofuels truly more sustainable than first-generation biofuels?
- What are the limiting factors preventing the expansion of the biofuel market?
- Would using agricultural residues and wastes improve the sustainability of biofuels?
- What role do agricultural residues play in the maintenance of soil quality and balance?
- How much waste is produced from a single field?
- What agricultural residues are particularly suitable for the production of biofuels?
- How much energy can be obtained from agricultural residues?
- Does the use of bioethanol in a passenger vehicle result in lower CO_2 emissions than from the use of gasoline?

1.2. Methodology

This thesis is primarily a meta study, which focuses on collecting contrasting and overlapping results from different studies, with the goal of drawing conclusions, identifying commonalities and other relationships which may have been previously overlooked. A number of steps were involved in conducting this meta study: First, a literature review was undertaken in order to search for relevant articles, books, reports, and research papers on the current state of the art information on biofuels. This required filtering through a large amount of available literature to find relevant articles and studies on first- and second-generation biofuels. Online internet searches, library resources, online journal websites and databases were the primary data sources. The second and third steps included the development of an evaluation scheme in order to identify the objective of some selected studies, to compare their systems' boundaries, methodological approaches, and their results. The fourth step involved drawing conclusions regarding the available studies and comparing the benefits of using biofuels versus fossil fuels. Fifth step included conducting a material flow analysis (MFA) to depict and compare various processes, namely the carbon dioxide flows for fossil fuels and second-generation biofuels. This MFA should help answer the research questions posed in chapter 1.1. In order to conduct the meta study, a software called STAN, provided by the Technical University of Vienna's institutes for Resource and Waste Management, and Water Quality, was used. Last step included pointing out some future directions that had been neglected so far and that seemed worth pursuing according to the results of the literature review.

1.3. Terms and Definitions

In this section, I will define a number of terms and concepts that are important for the understanding of the content that follows. Biofuel is a term used to describe all types of fuel derived from biomass feedstock or biological materials (see Srirangan et al. 2012: 172). Biofuels can be produced using feedstock derived from traditional agricultural crops (first-generation biofuels), lignocellulosic crops and agricultural residues (second-generation), microscopic organisms (third-generation), or animal food and solid wastes (fourth-generation) (see Figure 1). Further details on the differentiation between the various biofuel generations can be found in the following chapters.

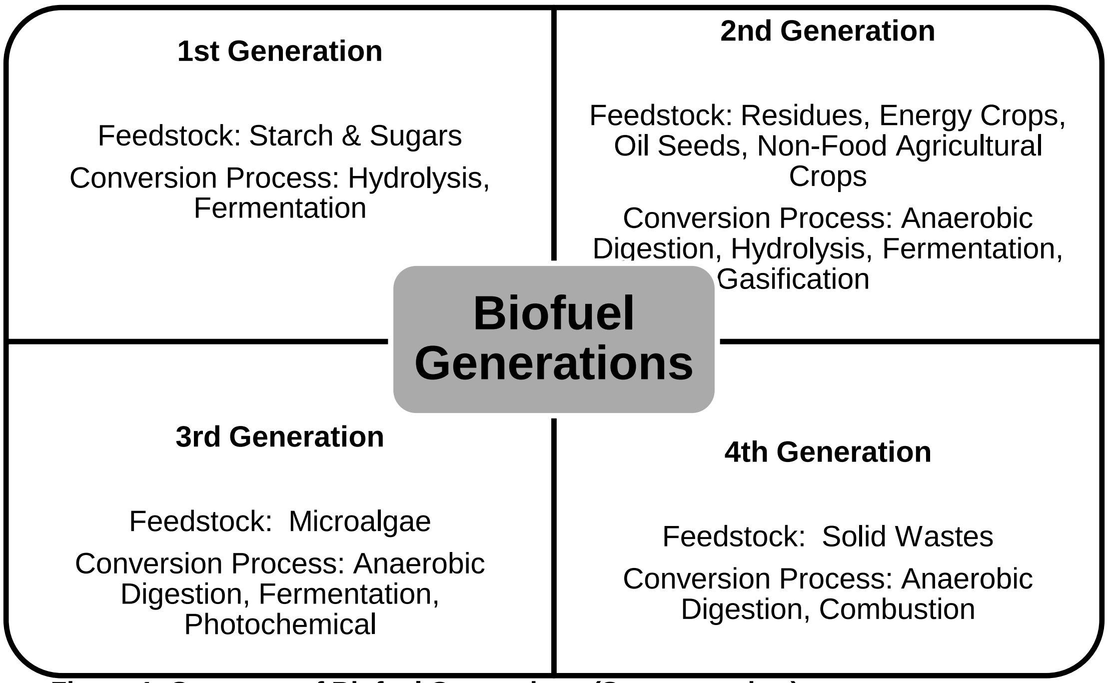

Figure 1: Summary of Biofuel Generations (Source: author)

Biomass generally includes five basic categories of material, namely (a) virgin wood from forestry, (b) energy crops which are high-yield crops grown specifically for energy production, (c) agricultural and crop residues from agriculture harvesting or processing methods, (d) food waste, and (e) industrial waste from manufacturing and other industrial processes (cf. BEC 2011: n.p.). Biofuels can be subdivided into solid, liquid, and gaseous biofuels, which vary depending on their chemical properties, physical characteristics, and production technologies.

1.3.1. Solid Biofuels

Solid biofuels have been used from the dawn of civilization and are therefore the most common. The main solid biofuels are the following (cf. Petrou/Pappis 2009: 1056):

- Wood: this group includes wood scraps and chips from forests as well as agricultural and forest residues. The water content can vary widely, thus affecting the heating value and the applications of the biomass (co-generation of power, central heating systems, or cement industry).

- Refuse-Derived Fuel (RDF): the fraction of fuel produced from municipal solid waste after mechanical and biochemical treatment that primarily contains paper and plastic residues.
- Pellets: produced from a thermo-mechanical or physicochemical process of compaction of fine pieces of biomass, mainly forest or agricultural residues.
- Briquettes: produced from virgin, untreated biomass through a specific thermo-mechanical process. Briquettes only differ from pellets due to their size and both usually have the same application.
- Industrial wastes: this group contains by-products of various industrial processes and is therefore a rather heterogenous group, including biomass from the wood industry, cotton industry, or from agriculture.

1.3.2. Liquid Biofuels

Liquid biofuels are usually divided into natural biochemical liquefaction biofuels (e.g. biodiesel) and synthetic oxygenated liquid fuels (e.g. biomethanol and bioethanol).

- Bioethanol (ethyl alcohol, CH_3-CH_2-OH): a fuel source derived from biological feedstock that contains significant amounts of sugar or materials that can be converted into sugar (cf. Petrou/Pappis 2009: 1056). Polysaccharides polymers are broken down into monomeric sugars which are then fermented into ethanol using enzymes. Lignocellulosic biomass, including agricultural residues and herbaceous crops, has been considered a potential source for ethanol production, but it is still under development. Bioethanol can be produced via three processes: (i) hydrolysis of sugars to glucose, (ii) fermentation of glucose to produce ethanol and carbon dioxide, and (iii) thermo-chemical process where dilute ethanol is distilled to produce absolute ethanol (see Jegannathan et al. 2009: 2164). Bioethanol is commonly produced from wheat, corn, sorghum and agricultural residues left behind after the harvest.
- Biobutanol (butyl alcohol, C_4H_9OH: an alcohol-based fuel that can be produced from a variety of biomass feedstocks via the fermentation of sugars into butanol. Biobutanol is considered to be more economically viable than ethanol, because it is chemically more similar to gasoline than ethanol and therefore can be more easily integrated into the existing internal combustion engines (see BioButanol 2013: n.p.). Furthermore, biobutanol is less volatile and explosive than bioethanol which makes it safer to handle.

Sugarcane, sorghum, miscanthus, and switchgrass can all be used to produce biobutanol.

- Biodiesel: *"It is defined as monoalkyl esters of long-chain fatty acids derived from renewable feedstocks, such as vegetable oils and animal fats, or other triglyceride-bearing biomass, such as microalgae, for use in compression ignition engines." (Petrou/Pappis 2009: 1056)* High-quality biodiesel fuel can be produced from Jatropha oil, sunflower oil, or jojoba oil.

1.3.3. Gaseous Biofuels

Gaseous biofuels (biogas) are the least commonly used biofuels, mainly due to limited technological capacity, and involve a thermal (pyrolysis) or microbial degradation (digestion) of biomass substances (see Petrou/Pappis 2009: 1056). As a result of these processes, methane (CH_4), hydrogen (H_2), carbon monoxide (CO), or carbon dioxide (CO_2) are produced, which have to be captured in order to be further utilized. Wood, forest and agricultural residues, as well as waste and manure can be used as raw materials in the gasification process.

2. First-Generation Biofuels

The use of biofuels has become an important topic on the political agenda ever since the international oil crises of 1972 and 1979, but it only really gained momentum in the late 1990s and early 2000s due to concerns about climate change (see Figure 2 for a graph depicting the growth of some popular biofuels). As the demand for oil continues to increase and supplies become more difficult to extract and the expansion of electric vehicles onto the world market remains slow, turning to biofuels is one of the few feasible options for transport fuel. First-generation biofuels, produced from sugar, starch and vegetable oil, can be converted into fuel through relatively simple, well-established technologies like fermentation and distillation. Currently, there are three types of liquid and gaseous biofuels that are on the world market (see IEA 2008: 16): (i) bioethanol, used as a gasoline substitute in spark ignition engines; (ii) biomethane, a product that is similar to the already commercialized natural gas, which can be used in vehicles designed to be fuelled with compressed natural gas; and (iii) biodiesel, used as a diesel fuel substitute in the standard compression ignition engines. *"All together, biofuels currently provide over 1.5% of the world total transport fuels (34 Mtoe in 2007 on an energy basis) (...) and the crops grown for biomass feedstock take up less than 2% of the world's arable land." (IEA 2008: 16)*

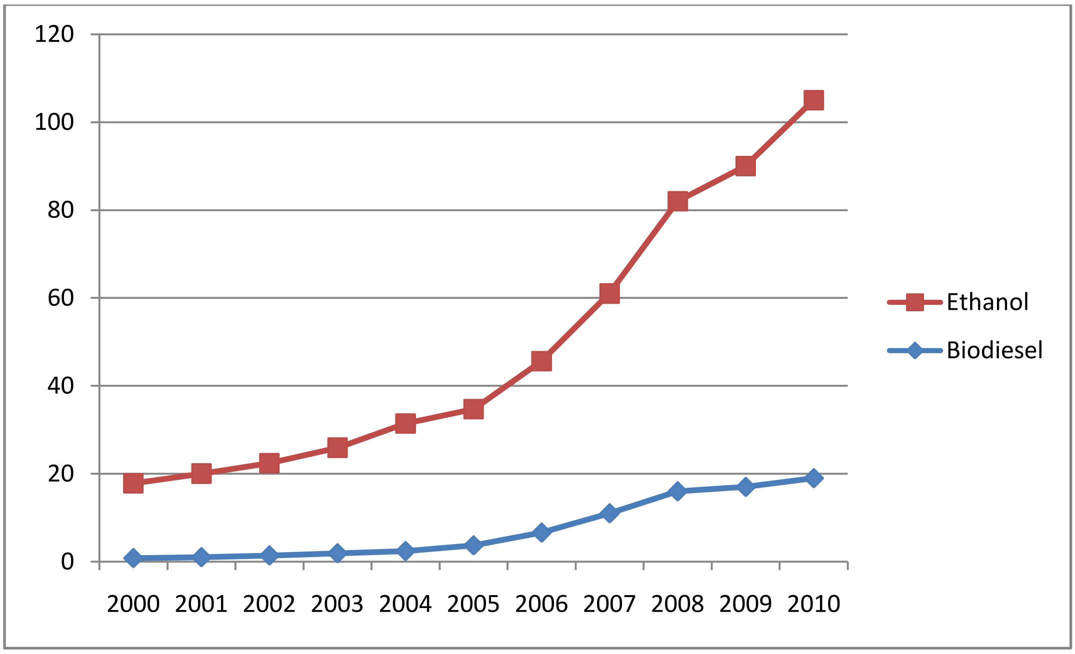

Figure 2: Ethanol and Biodiesel Production 2000-2010 (adapted from REN21 2011: 32)

Even though biofuels are made from animals or plants, and are thus, in principle, a renewable source of energy, they are not as environmentally friendly as they seem at first glance. In order to grow, plants absorb carbon dioxide and water and produce oxygen and glucose through a process called photosynthesis, $6CO_2 + 6H_2O + hv$ (sunlight) $\rightarrow C_6H_{12}O_6 + 6O_2$. When the feedstock is used as a fuel source, it is burnt and the carbon dioxide that was first in it is returned to the atmosphere with no net change in the carbon balance. The greenhouse gas savings depend not only on the source of biomass, but also on its land use and fertilizer input.

First-generation biofuels have especially had to bear the brunt of criticism from the moment they were touted as being a viable renewable energy source. Among other problems, the production of biofuels requires a large amount of land, water, fertilizers, and high energy for the conversion and refinery processes, leading to an increased output of carbon dioxide emissions. Furthermore, these biofuels are produced from food crops such as grains and sugar beet, thereby intensifying the food-versus-fuel debate. Ethical and moral questions are raised when edible biomass products are converted into biofuels, especially since millions of people suffer from hunger and malnutrition. Jean Ziegler, the United Nations Special Rapporteur on the right to food, once said, *"It is a crime against humanity to convert agricultural productive soil into soil which produces food stuff that will be burned into biofuel" (UN News Centre 2007: n.p.)*. He also stated that converting crops such as wheat, sugar, and maize into fuels was the reason for the higher-than-normal prices of food, water, and land. Increasing food prices would have a catastrophic effect on the world's poorest, as developing countries would no longer be able to afford the import of food to feed their populations. Ziegler argued that biofuels would lead to *"further hunger in a world where an estimated 854 million people – 1 out of 6 – already suffer from the scourge; 100,000 people die from hunger or its immediate consequences every day; and every five seconds, a child dies from hunger" (UN News Centre 2007: n.p.).*

Another disadvantage of first-generation biofuels is the increase in fertilizer use needed to produce vast amounts of food crops for energy purposes. Fertilizer application results in harmful nitrous oxide (N_2O) emissions, a greenhouse gas that has nearly 300 times the global warming potential of an equal mass of CO_2 (cf. Crutzen et al. 2008: 389), into the atmosphere, which negatively contributes to the formation of stratospheric ozone. According to Crutzen et al., the amount of CO_2 that could potentially be saved through the use of biofuels would be counteracted by the increased input of fertilizers and land use changes. Additional emissions through direct and indirect land use changes are a major problem of first-generation biofuels. In order to cultivate biofuel feedstocks, land has to be cleared and made suitable for crops - a process that involves disturbing and releasing the carbon stored in previously undisturbed natural soils and forests. The GHG emissions from direct land use changes depend on the characteristics of the plant itself, the location and the existing ecosystem. In countries like Indonesia and Malaysia, where palm oil is already extensively grown for the food industry, further demand for biofuel production could lead to increased deforestation. *"[E]ven if biofuels [sic!] crops are not grown on biodiverse land directly, using available cropland to cultivate feedstocks can divert food production to other area, encourag[ing] deforestation elsewhere." (BirdLife 2013: n.p.)* This diversion can lead to an effect called indirect land use, which means valuable ecosystems and wildlife habitats will be threatened in order to make room for cropland to cultivate energy feedstock. Clearing forests, thereby leading to higher CO_2 emissions, in order to plant food crops for energy is a roundabout way of solving current environment-related issues.

Large-scale cultivation of food crops usually involves the heavy use of fertilizers and water, which can have negative effects on nearby water bodies. Water pollution, ecotoxicity, and eutrophication resulting from runoff processes are only some examples of dangers that must be considered when assessing the sustainability of biofuels. Additionally, extensive irrigation is needed in order to guarantee the growth of food crops and that could jeopardize the already scarce global water resources. Furthermore, deforestation would cause a change in the soil's water-holding capacity, thereby affecting evapotranspiration processes, which could have a further widespread effect on the local environment.

To summarize, it has been established that first-generation biofuels provide considerably fewer benefits than previously expected. The other concern is that the production of biofuels contributes to higher food prices due to direct competition with food crops, to limited GHG reduction benefits, to competition for scarce water resources, and to increased deforestation (see IEA 2008: 14). One solution to limit the damage done by first-generation biofuels would be to

> *"set environmental criteria (...) that would limit certain kinds of biofuels - both for production and imports. Recent proposals along these lines could conceivably exclude biofuels based on corn, rapeseed and palm oil [note from the author:*

because they demonstrate negative GHG reduction], which would mean a very substantial reduction in current production" (IEA 2008: 20).

It is becoming increasingly clear that the potential of first-generation biofuels to aid in climate change mitigation, GHG reductions and economic growth is limited, and this has pumped up the interest in the development of biofuels from non-food feedstock, namely second-generation biofuels.

3. Second-Generation Biofuels

Ever since the first-generation biofuels came under heavy fire, scientific attention turned towards second-generation biofuels, which can be produced from non-food feedstock, such as energy crops and agricultural or crop residues. Much work is needed to reduce costs and improve the performance of the existing conversion methods (from feedstock to finished fuel) in order to make wide-scale use of biofuels a possibility. However, before these biofuels can become economically viable, studies to accurately assess their technical feasibility and effect on climate change mitigation will have to be conducted. Currently, the production of second-generation biofuels remains non-commercial and only a few testing and pilot facilities exist. *“When commercialized, the cost of second generation biofuels has the potential to be more comparable with standard petrol (…) [and] diesel, and would be [the] most cost effective route to renewable, low carbon energy for road transport.” (Naik et al. 2010: 579)* In this chapter, a detailed description of second-generation feedstocks, the production process, and the barriers to commercialization will be provided.

3.1. Feedstock Possibilities

Lignocellulosic biomass is an abundant, renewable feedstock *"with an estimated annual worldwide production of 10-50 billion dry tonnes though only a small portion of this (…) [can] be used in practice. This includes cereal straw, wheat chaff, rice husks, corn cobs, corn stover, sugarcane, bagasse, nut shells, forest harvest residues, wood process residues" (IEA 2008: 35).* The processing of lignocellulosic materials has been proven to be more complex than for the first-generation feedstocks due to the high variation in the biomass sample - the higher the homogeneity of feedstock, the easier the production of biofuels. Furthermore, the different chemical composition of the biomass, for example the ratio of cellulose to lignin, can make some feedstocks more preferable to others (see Annex 2 for information on the chemical composition of various biomass feedstocks). For example, perennial grasses like switchgrass contain much lower levels of lignin than woody biomass. Second-generation feedstocks can be subdivided into four main categories: energy crops, oilseed species, agricultural crops, and agricultural or forest residues and wastes. Please note that the last category will be covered separately in chapter five of this thesis.

3.1.1. Energy Crops

Energy crops grown specifically for a feedstock source for biofuel production differ widely in their chemical and physical characteristics and can be grouped into grassy and woody crops (see Carriquiry et al. 2010: 8). As additional land is needed for energy crop production, the food-versus-fuel aspect is hotly debated. To limit the negative impacts of biofuel production, woody or grassy crops should not be grown on land where food crop production (arable land) is viable, but only on degraded lands.

3.1.1.1 Perennial Forage Crops

Perennial forage crops such as switchgrass (*Panicum virgatum L.),* reed canary grass (*Phalaris arundinacea L*.), miscanthus (Miscanthus giganteus), Napier grass (*Pennisetum purpureum Schumach.),* and Bermuda grass (*Cynodon dactylon*) have shown to be promising due to their high yields and climate tolerance. Some of these crops will be described in detail below.

Switchgrass is a prairie grass that needs relatively low water and nutritional input and can adapt to low quality land, thus preventing a possible conflict with arable land for food production. It has demonstrated the ability to improve soil quality and sequester carbon, thereby increasing the potential for its use as a biofuel feedstock (see Hartman et al. 2011: 3416). *“Switchgrass can yield almost twice as much ethanol as corn. Genetic and breeding research will improve its biomass yield and its ability to recycle carbon as a renewable energy crop.” (BOARD 2008: 24)*

Reed canary grass has been used mostly for hay and forage and it is best suited to temperate regions. Miscanthus is a native Asian grass and has high tolerance to cold temperature and thus could be grown in mountainous regions of Europe (see Carriquiry et al. 2010: 9).

Bermuda grass is a popular forage crop and perennial grass common in North Africa, Asia, Australia, Southern United States, and Southern Europe. *"It has short greygreen [sic!] blades with rough edges, erect stems of 1–30 cm in length, and a deep root system that can penetrate 2 m into the ground, though most of the root mass is less than 60 cm under the ground surface." (Xu et al. 2011: 7613)* Despite its widespread distribution, Bermuda grass yield is dependent on specific growing conditions especially with regard to soil type (high nitrogen rates are very advantageous), temperature (optimal growth between 24 to 37°C) (297K to 310K) and precipitation. Applying high nutrient loading to marginal lands to improve Bermuda grass growth could result in ground and surface water pollution. Due to its high carbohydrate content, it is especially favorable for the production of bioethanol. Genetic modifications to change the sensitivity to nutrient demand could help make Bermuda grass a viable lignocellulosic biomass feedstock option. Bermuda grass can be grown in weathered soils, but that may result in releasing an invasive foreign species in wetland areas. However, one of the main disadvantages of Bermuda grass is the high ash content (33%) – ash disposal after energy recovery is neither cost effective due to the high landfill costs, nor is the process easy. Ash has often been used in concrete production, in waste stabilization processes, and as a fertilizer, but such alternative uses require strict adherence to laws regulating the chemical composition of ash.

3.1.1.2 Woody Energy Crops

"Of the diverse array of available lignocelluloses, trees are one of the better feedstock options, partly due to their higher cellulose density and compositional uniformity. Moreover, trees possess a lignocellulosic energy conversion factor of 16 (compared to one and eight for corn and sugarcane, respectively), and can be grown on marginal land, thereby minimizing encroachment on food crop terrain." (McIntosh et al. 2012: 264)

Woody energy crops have shown to have relatively wide geographical distribution and relatively low levels of nutrient and water input when compared with the grassy crops. Eucalyptus, poplar trees, willows, sycamore, and southern pines are some short-rotation forest species currently being considered for potential lignocellulosic biomass (see IEA 2008: 37). Most of these crops can grow quickly in a plantation environment and can be utilized for fuel production purposes even when the trees are young (see BOARD 2008: 22). The Poplar tree can grow in several temperature climates and at high density, making it especially popular for biofuel production (see Simmons et al. 2008: 242).

3.1.2. Oilseed Species

There are several different oilseed species that could be used for biofuel production, but scientists believe that Jatropha (*Jatropha curcas L.*) might be the best choice. Jatropha, a non-edible low-growing plant that is native to tropical America, has shown high potential for biodiesel production. It can grow in semi-arid conditions and on degraded lands and produces seeds with an oil content of 30-40% - perfect for the production of biodiesel. Scientists are still debating whether Jatropha plants can be sustained on dry lands without high nutritional and water inputs (see Carriquiry et al. 2010: 8; cf. Ovando-Medina et al. 2009: 1037).

3.1.3. Agricultural Crops

Cassava and sorghum (*Sorghum* bicolor *L. Moench*) are two examples of agricultural crops that are under consideration for their potential as biofuel feedstocks. Cassava is a perennial plant in tropical and subtropical countries in South Asia and it possesses a high amount of starch, making it a possible alternative to sugarcane or corn for the production of bioethanol (see Srirangan et al. 2012: 174). Sorghum is one of the most widely grown cereal crops in the world and has received scientific attention due to its high productivity and drought-tolerance.

The following table provides an overview of the composition of common lignocellulosic feedstocks.

Table 1: Average Composition of Common Lignocellulosic Materials (cf. SDSU 2007: 8-9; Sannigrahi/Ragauskas 2010: 214)

Lignocellulosic Materials	Cellulose (% of dry matter)	Hemicellulose (% of dry matter)	Lignin (% of dry matter)	Ash (% of dry matter)
Switchgrass	37	29	19	6
Reed Canary Grass	24	36	~32	8
Miscanthus	43	24	19	2
Forage Sorghum	34	17	16	5
Wheat Straw	38	29	15	6
Barley Straw	42	28	~19	11

Rye Straw	31	25	~38	6
Eucalyptus	48	13	27	~12
Jatropha Shells	34	10	12	15
Bermuda Grass	25	36	6	~33
Bagasse	44	29	22	5

3.1.4. Composition of Lignocellulose

Second-generation biofuels are differentiated from other biofuels on the basis of their composition and use. Lignocellulose, the defining component of second-generation biofuels, is the scientific term used for biomass from fibrous or woody plant material and is primarily composed of a complex, linked matrix of cellulose, hemicellulose, and lignin polymers (see Figure 3 for details). Most lignocellulosic biomass samples also contain small quantities of ash and other compounds like resins and fats. The content of each component varies strongly from species to species, but the *"combined mass of cellulose and hemicellulose in the plant material (...) is typically 50-75% of the total dry mass with the remainder consisting of lignin" (IEA 2008: 35).* Biomass feedstock composition is also affected by the method of harvest, storage, harvest timing, and crop maturity.

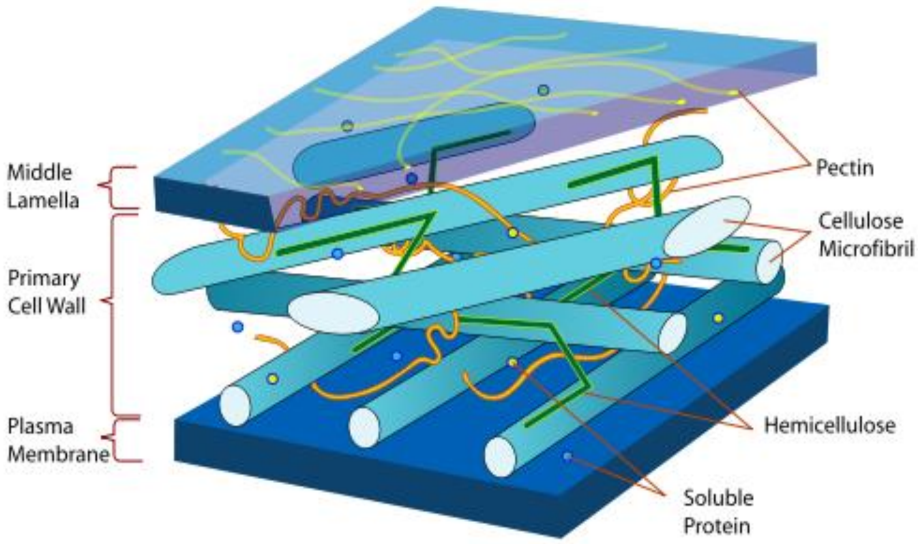

Figure 3: Plant Cell Wall Structure (Wikimedia Commons 2007a: n.p.)

- Cellulose $(C_6H_{10}O_5)_n$ is a straight and stiff molecule made up of a linear chain of approximately ten thousand linked D-glucose units. It makes up approximately 30–50% of total feedstock dry matter (see SDSU 2007: 6).

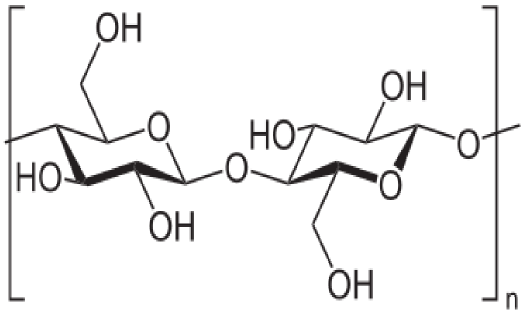

Figure 4: Cellulose (Wikimedia Commons 2007b: n.p.)

- Hemicellulose is a branched polymer containing C5 sugars, such as xylose $(C_5H_{10}O_5)$ and arabinose, and C6 sugars, like galactose, glucose $(C_6H_{12}O_6)$, and mannose, of approximately 200 units. It makes up about 20–40% of total feedstock dry matter.

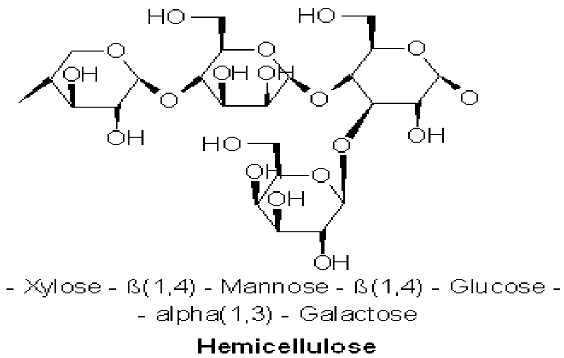

Figure 5: Hemicellulose (Wikimedia Commons 2006: n.p.)

- Lignin is a three-dimensional branched polymer consisting of phenolic units (cf. IEA 2008: 35). It makes up about 15–25% of total feedstock dry matter. The molecular formula can differ from plant to plant, but usually takes the following forms: $C_9H_{10}O_2$, $C_{10}H_{12}O_3$, or $C_{11}H_{14}O_4$.

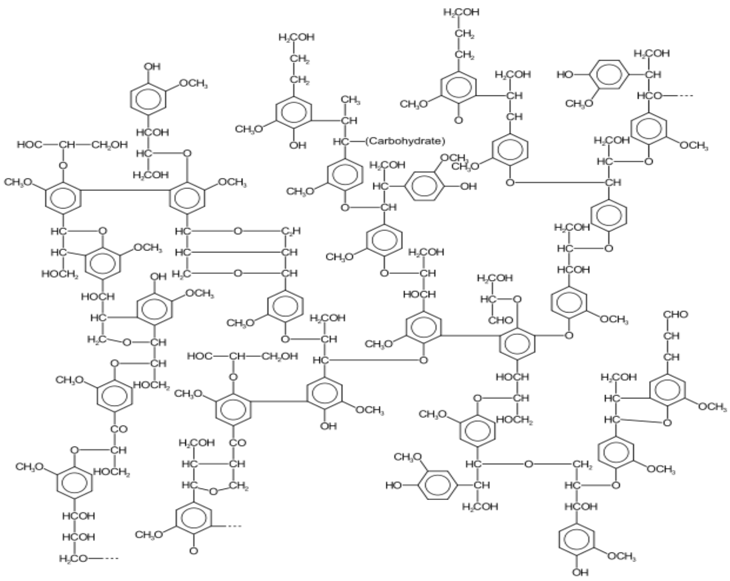

Figure 6: Lignin Structure (Wikimedia Commons 2007c: n.p.)

- Ash usually makes up about 3-10% of total feedstock dry matter and is the residue that remains after combustion. *"It is composed of minerals such as silicon, aluminium, calcium, magnesium, potassium, and sodium." (SDSU 2007: 6)*
- Other compounds (also known as extractives): such as fats, phenolics, salts, minerals, nitrogenous material, chlorophyll, waxes and resins are common components of lignocellulosic biomass feedstock.

3.1.5. Combustion of Biomass

Biomass can be converted into liquid fuel or be burned directly in order to utilize the energy contained in it. Direct combustion of biomass is an effective method to produce heat or electricity. Many countries in the Caribbean burn bagasse to produce heat and bagasse is also the primary fuel source for sugar mills in the region. The calorific value, physical properties, and the chemical content of the biomass, especially, heavy metals, toxic compounds, and water, can affect the thermal conversion of biomass. Such characteristics impact not only the design and construction of the combustion plant, but also the after-treatment of emissions and ash disposal. On a larger scale, the combustion of biomass results in additional costs for the fuel refinery: in order to minimize local air pollution, expensive flue gas cleaning is usually required by law. Biomass combustion has both advantages and disadvantages: biomass is a relatively cheap fuel source that reduces reliance on fossil fuels, but the fuel quality varies depending on the feedstock and the logistics of fuel storage complicate the process.

3.2. Production of Biofuels

Plant biomass is one of the most abundant biological resources available and could prove to be a sustainable source of liquid fuel. However, the biggest current obstacle to the large-scale production of biofuels is the lack of technology for the efficient conversion of lignocellulosic biomass to liquid fuel. Due to this technological obstacle, first-generation biofuels are considered to be more favorable for liquid fuel production, due primarily to their chemical structure which can be more effectively processed. *"The total biomass production on earth is approximately 100 billion tones [sic!] (…) of land biomass per annum and 50 billion tones [sic!] of aquatic biomass." (Naik et al. 2010: 579)* Only a part of the land biomass is used in the production of food, feed, or energy, while the rest is discarded as residues or wastes. The possibilities for the use of unused biomass will be treated in chapter five of this thesis.

The plant in which biofuel is produced is very similar to today's petroleum refineries that are capable of producing multiple products and fuel types from petroleum. A biorefinery is a *"facility that integrates biomass conversion processes and equipment to produce fuels, power, and chemicals from biomass" (NSF 2008: 23)* and is considered to be the most promising route for the emerging biofuel industry. Through the production of several products from multiple feedstocks, biorefineries can utilize the different components of biomass samples and intermediates to optimize the final products, thereby enhancing profitability and maximizing returns. *"A biorefinery might, for example, produce one or several low-volume, but high-value, chemical products and a low-value, but high-volume liquid transportation fuel, while generating electricity and process heat for its own use, and perhaps enough for sale of electricity." (NSF 2008: 23)* State of the art biorefineries should have a tightly linked system of processes to minimize unnecessary energy losses and decrease equipment size and space.

The net calorific value (MJ/kg_{fuel}) of biomass can be calculated using the elemental composition, the water content, and the Boie-Formula (see Ortner 2012: 77-78).

$$\mathrm{Hu} = 34.8 * \mathrm{C} + 93.9 * \mathrm{H} + 6.3 * \mathrm{N} + 10.5 * \mathrm{S} - 10.5 * \mathrm{O} - 2.5 * \mathrm{Water}$$

The lower heating value (H_u), i.e. net calorific value, is defined as the *"quantity of heat released when the biofuel is burned completely and the water in the flue gas after combustion is not condensed"* (Ortner 2012: 75). The water content in the biomass can be calculated by dividing the mass of water in the biomass by the mass of the raw material itself. The table below provides information on the net calorific value of some common biomass samples and popular fossil fuels.

Table 2: Net Calorific Value of Various Biomass and Fossil Fuel Samples (see Ortner 2012: 77-78)

Biomass Sample	**Net Calorific Value MJ/kg (dry matter)**
Rye Straw	17.4
Wheat Straw	17.2
Maize Straw	17.7
Short-rotation Poplar	18.5
Short-rotation Willow	18.4
Barley Straw	17.5
Bark	19.2
Rape (grain)	26.5
Miscanthus	17.6
Fossil Fuel Sample	
Coal (Anthracite)	29.7
Coal (Lignite)	20.6
Heavy Fuel Oil	41.2
Wood	21.7

There are two main methods currently available for producing biofuels from lignocellulosic biomass, namely thermochemical processing and biochemical processing. *"Substantial amounts of CO_2, waste water effluent[,] and solid residue consisting of lignin, leftover carbohydrates, proteins[,] and cells are also formed in the process. About one third of the initial raw feedstock material by weight ends up* *in this residue." (IEA 2008: 45)* The combustion of residues could produce large amounts of heat and electricity, due to the high energy content, for use in the biorefinery itself.

3.2.1. Thermochemical Processing

Thermochemical conversion involves the heating of biomass at different concentrations of oxygen.

i. The gasification process involves reacting biomass with air, oxygen, or steam, at temperatures of 600-900°C (873-1173 K), to produce syngas, a gaseous mixture of CO, CO_2, H_2, CH_4, and N_2 (cf. NSF 2008: 98). One of the benefits of this by-product is that syngas can be converted to electric power, steam or hydrogen and then it can be used to power the biorefinery itself; the useful integration and utilization of such side products is a key element in sustaining the biofuel market. However,

> *"[s]ignificant technical hurdles remain to be overcome, particularly regarding biomass-derived syngas clean-up requirements and associated char build-up problems. This is critically important because impurities in the syngas can poison the catalysts of the FT process and could therefore render the process uneconomic." (IEA 2008: 57-58)*

The Fisher-Tropsch Synthesis (FTS) method then converts the syngas, produced by biomass gasification, into liquid fuel (i.e. FT-oil or green motor fuel), which can then be directly used as a transport fuel. *"The major drawback of FTS (…) is the polymerization (…) process which yields very high molecular mass waxes[,] which need to be hydrocracked to produce green diesel." (Naik et al. 2010: 591)* The FTS process can be characterized through the following set of reactions, where carbon monoxide and hydrogen are produced from the gasification of biomass into several different liquid hydrocarbons:

$(2n + 1)H_2 + nCO \rightarrow C_nH(2n+2) + nH_2O$ where n is the positive integer representing the length of the hydrocarbon chain.

ii. Another thermal conversion method, that requires a catalyst, is liquefaction, which produces water insoluble oils of high viscosity. Catalysts such as sodium carbonate or potassium carbonate help break down cellulose and hemicellulose into smaller parts, so that they can burn more quickly. This process takes place at high pressures (120-200 atm), but lower temperatures (300-400ºC or 573-673 K) than in gasification (see NSF 2008: 34). At the end of the process, a liquid similar to heavy fuel oil is left (bio-oil), which is rather difficult to handle and must be treated with organic solvents (i.e. acetone or ethyl acetate). These solvents are easy to recover and reuse in another conversion cycle. Liquefaction bio-oil has a significantly lower oxygen content than the fast pyrolysis bio-oil, making it a more attractive fuel (cf. NSF 2008: 37).

iii. A further thermal conversion method is pyrolysis or the thermal degradation of biomass by heat without oxygen that results in the production of charcoal, fuel gaseous products, and bio-oil (see Naik et al. 2010: 589). Bio-oil is a dark viscous, highly corrosive compound that is often used as a fuel for furnaces or boilers. The Pyrolysis process produces liquid oil as an end-product and can be subdivided into three classes, depending on the different operating conditions (cf. Naik et al. 2010: 590):

- Conventional pyrolysis is normally used for large pieces of wood and occurs at a slow heating rate (0.1- 1 K/s).
- Flash pyrolysis occurs at very high temperatures (1050-1300 K) and fast heating rates (higher than 1000 K/s) and requires very small particles to function. This process has also been proven to have higher efficiency than other pyrolysis methods.
- Very high temperatures (850-1250 K) and quick heating rates (10-200 K/s) are needed for fast pyrolysis. This process requires relatively small particles and is generally used for the production of gaseous or liquid products with bio-oil and char as common reaction products (see NSF 2008: 32).

The bio-oil produced in the pyrolysis processing is then cleaned to removed particulates and ash, before it undergoes hydrotreating and hydrocracking processing. At the end, the total oxygen content has been reduced, and the bio-oil can be used as a transport fuel.

Figure 7 provides an overview of the thermochemical processing of biofuels and its various components.

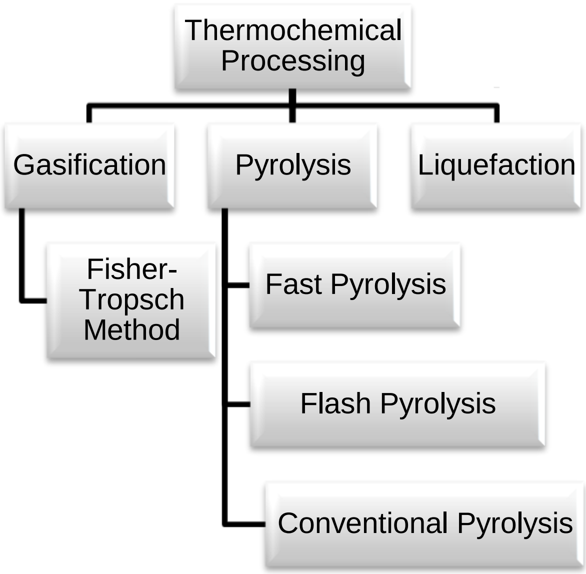

Figure 7: Summary of the Thermochemical Processing of Lignocellulosic Biomass (Source: author)

3.2.2. Biochemical Processing

The conversion of lignocellulosic biomass comprises three main steps: pretreatment of biomass, hydrolysis, and fermentation or distillation.

> *"Process steps also include feedstock harvesting, handling, recovery and transport; comminution of the biomass to give small and homogeneous particles; fractionation of the polymers; separation of the solid lignin component; and end product recovery. The cellulose undergoes enzymatic hydrolysis to produce hexoses such as glucose. Pentoses, mainly xylose, are produced from the hemicellulose, thereby fully utilizing the feedstock." (IEA 2008: 44)*

The distinct steps will be covered in more detail over the course of this chapter and a summary is provided in Figure 9.

Biological conversion methods are much simpler than thermal methods and have therefore been used more widely. Lignocellulosic biomass consists of four main structural units, namely cellulose microfibrils, hemicelluloses (polymers made of xylose and arabinose), pectins, and lignins (large poly-aromatic compounds) (cf.

Naik et al. 2010: 591). Lignin is an integral part of most biomass feedstock, because it fills the empty space in the cell wall between the cellulose, hemicellulose, and pectin parts, thereby adding to the structural stability of the material through cross-linking polysaccharides (cf. DOE 2006: 41). These chemical properties interfere with the enzymatic conversion of biomass and therefore the degradation of lignin is a prerequisite for the production of biofuels. The higher the plant lignin content, the higher the interference with the release and hydrolysis of polysaccharides, the main constituents of liquid fuel, especially of bioethanol. All three complex structures have to be broken down into simple sugars such as glucose, before they can be distilled or fermented. Converting lignocellulosic biomass to alcohol is more difficult than the conversion of starch-based feedstocks, mainly due to the rigidity of lignocellulose.

In order to weaken the individual lignocellulose fibers, a pretreatment process is carried out, thereby preparing the biomass for further processes. An ideal pretreatment has the following objectives: maximize the yields of hexose and pentose sugars, minimize the production of process-inhibiting chemicals, facilitate the separation of lignin from the biomass sample, and have low energy requirements (cf. IEA 2008: 46). Additionally, pretreatment effectively separates xylose (a sugar extracted from woody materials) from the cellulosic structure. In order to increase the efficiency of the subsequent steps, both physical and chemical pretreatment is applied to the biomass: the lignocellulosic biomass is ground and reduced and then the chemical treatment breaks down chemical barriers so that enzymes have a clear pathway for microbial degradation. Available pretreatment techniques include, but are not limited to, steam explosion, acid hydrolysis, alkaline wet oxidation, ammonia freeze explosion (AFEX), ozonolysis and organosolv (see Harmsen et al. 2010: 21-27; IEA 2008: 47).

3.2.2.1. Pretreatment

Pretreatment methods can be classified into four sub-sections (cf. IEA 2008: 47): biological (using fungi to degrade the hemicellulose and lignin), chemical (to reduce cellulose crystallinity and polymerization while maintaining the fibre integrity), combination (such as organosolv treatments), and physical (mechanical breakdown of biomass into smaller particles to reduce surface area to make it more accessible to enzyme attack). An ideal pretreatment successfully separates cellulose from the rest of the biomass (see Figure 8), while minimizing the formation of by-products that would inhibit the subsequent processes, in order to minimize costs and toxic products, such as furfural (from five-carbon sugars like xylose) or hydroxymethylfurfural (from six-carbon sugars like glucose) (see Dehkhoda et al. 2009: 310). The choice of pretreatment depends primarily on the composition of the particular biomass sample and the byproducts produced as a result of this treatment.

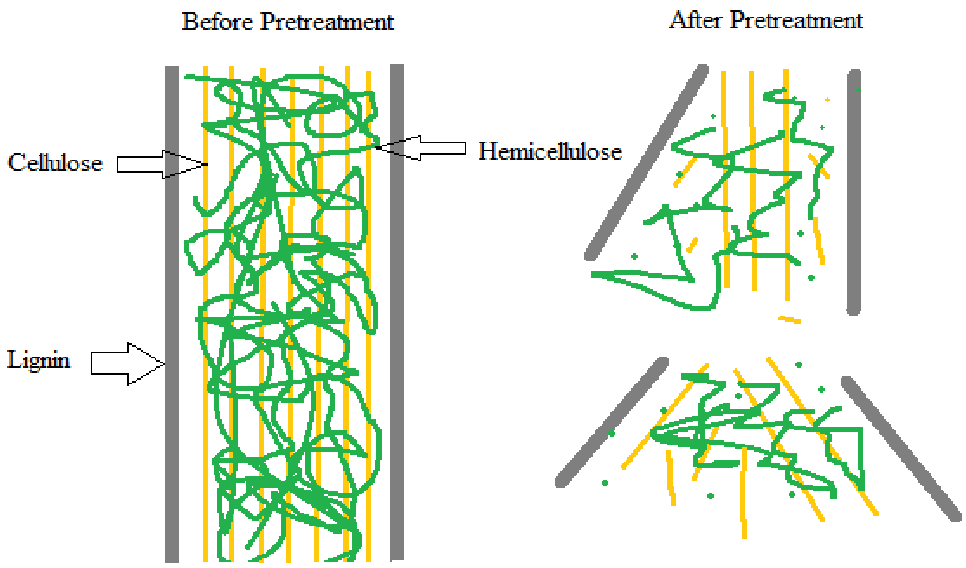

Figure 8: Pretreatment Process (Source: author)

Biological Pretreatment:

Scientists have found considerable evidence that microorganisms such as wood-degrading fungi, especially brown-, white-, or soft-rot fungi, could be used to breakdown lignin in the lignocellulosic biomass sample, making the biomass more flexible and easier to convert into liquid biofuel. *"Brown rots mainly attack cellulose, whereas white and soft rots attack both cellulose and lignin. Lignin degradation by white-rot fungi occurs through the action of lignin-degrading enzymes such as peroxidases and laccase." (Kumar et al. 2009: 3723)* A biological process such as this one could eliminate the need for energy-intensive pretreatment steps such as steam explosion. However, biological pretreatment is usually not economically viable due to the long residence time (approximately two to eight weeks) needed for fungi to effectively break down the feedstock which slows down subsequent steps. In order to minimize overall energy input, an initial biological pretreatment could be followed by a chemical or physical pretreatment.

Chemical Pretreatment:

i. Acid hydrolysis is a process where chemical bonds between molecular units are separated by the addition of water and accelerated by a catalyst, in this case, an acid.
ii. Ozonolysis or ozone treatment is a method that uses ozone molecules to cleave the aromatic ring structure of lignin, leaving hemicellulosic and cellulosic units nearly untouched. One of its benefits is that it can be used to treat many different feedstocks, including bagasse, wheat straw, and poplar sawdust (see Harmsen et al. 2010: 25).

Combination Pretreatment:

Oraganosolv pretreatment is one of the more expensive methods at present, but provides some valuable by-products (e.g. cellulosic fibers and solid lignin), which could make the process more promising for the biorefining of lignocellulosic feedstock. This method involves the extraction of lignin from the feedstock with the help of organic solvents (e.g. glycerol, dimethylsulfoxide or phenols) or their aqueous solutions. One advantages is that these solvents can be recovered through distillation and recycled for the next use, thereby minimizing wastes and reducing costs over the long-term (cf. Zhao et al. 2009: 816).

Physical Pretreatment:

i. Mechanical extraction is a method which recovers crude vegetable oils from the seeds of various plants by applying a mechanical pressure using a screw press. These seeds can either be pre-pressed, so that only part of the oil is recovered and the rest has to be gained through solvent extraction, or fully-pressed, where all the oil is recovered in the step. Full pressing is usually applied for seeds with a high oil content (approximately 30-40%) (see Naik et al. 2010: 588).
ii. When biomass, especially forestry and agricultural residues, arrives at a treatment plant it is often difficult to use as biofuels because of the uneven size. By processing biomass into briquettes, densely packed material compacted into a cylindrical form, they can be treated more easily. This densification process can take place in two ways, either through maceration (i.e. grinding or pulverizing) or through pressing.

- Distillation, a highly energy-intensive process, is the most commonly used method to extract essential oils by evaporating the volatile parts of a blend to separate them from the less volatile parts.
- The steam explosion process is a physicochemical method that works as follows: the biomass sample is placed in a pressurized container and briefly vaporized at high temperature (473–543 K) and pressure (14–16 bar) (see Naik et al. 2010: 592). The pressure in the container is then suddenly dropped, exposing the material to normal atmospheric pressure, thereby causing an explosion which separates the hemicellulose and lignin from the rest of the biomass.

> *"The crystalline cellulose remains solid after the pretreatment and later breaks down to glucose by the enzymatic hydrolysis process. The glucose is further fermented to alcohol and the hemicellulose fraction is converted to xylose. The conversion of xylose to ethanol is a difficult process, therefore, pretreatment is necessary to (…) lessen the average polymerization of the cellulose and hemicellulose–lignin sheath that surround (…) [it] and to increase available surface area for the enzyme to attack." (Naik et al. 2010: 592)*

3.2.2.2. Chemical Conversion

The next step in biochemical processing after pretreatment is the chemical conversion of lignocellulosic feedstock, which can be done in the following ways: solvent extraction, chemical hydrolysis, and supercritical water conversion.

i) *"Solvent extraction involves different unit operations: extraction of the oil from the oil seeds using hexane as a solvent; evaporation of the solvent; distillation of the oil–hexane mixture (called miscella); and toasting of the de-oiled meal." (Naik et al. 2010: 592)* The desired end-product is selectively removed from the biomass sample by allowing it to dissolve into the solvent and then recovering it. The extracted component is then used for hydrolysis and fermentation for biofuel production.

ii) Hydrolysis uses specific cellulase enzymes to break down the lignocellulosic mass to produce sugars, including glucose. This process has relatively low costs compared to acid or alkaline hydrolysis because of the milder operating conditions (lower pH and temperatures) (see Sun/Cheng 2002: 6). Hydrolysis reactions are typically carried out at temperatures ranging from 370-570 K depending on the chemical structure and nature of the polysaccharides (cellulose is harder to hydrolyze due to its rigid crystalline nature). Temperatures outside the stated bounds produce toxic products like furfural (see NSF 2008: 72).

iii) Supercritical processing of biomass is in many cases preferred to the other chemical conversion methods due to the lack of catalytic products and process speed. This process is capable of converting biomass into a mixture of oils, alcohols, sugars (glucose, xylose, and oligosaccharide), gases, and acids (cf. Naik et al. 2010: 592). However, supercritical processing is a costly method due to the high-pressure reactor, which needs to sustain sufficiently high temperatures, so that it can effectively convert biomass to liquid fuel and gaseous side-products.

3.2.2.3. Fermentation and Distillation

The last step in biochemical processing is the fermentation and distillation of the separated sugars into liquid fuel. Once the sugars contained in the lignocellulosic biomass are released during pretreatment and chemical conversion, they can be fermented into ethanol.

$C_6H_{12}O_6$ (glucose) → 2 C_2H_5OH (ethanol) + 2 CO_2 (carbon dioxide)

Liquid biofuels can be produced using biological catalysts (e.g. yeast), which perform the conversion in anoxic conditions (anaerobic process), or chemical catalysts (e.g. homogeneous acids). One advantage of chemical catalysts is that they can function at slightly higher temperatures and over a broader set of operating conditions than biological catalysts, which are very selective for fermentation reactions (see NSF 2008: 17). Fermentation requires a high degree of feedstock selectivity for an efficient conversion into liquid fuel: *"high preference for C6 compared to C5 sugars, and high sensitivity to the presence of contaminants inhibitory to the organisms [note from the author: in this case, catalysts]." (NSF 2008: 83)* Scientists are currently working on developing more cost effective processes which would be able to co-ferment C5 and C6 sugars together to minimize costs (see IEA 2008: 53). Another advantage of chemical catalysts is that they are cheaper and can be easily separated from acqueous solvents once the fuel is produced. *"The majority of biological catalyst-based processes require feedstocks* *to be sterilized prior to enzymatic conversion. No sterilization step is required for chemical conversion." (NSF 2008: 17)* Biorefineries will likely use a combination of chemical and biological catalysts to make biofuels more affordable.

The final step toward liquid fuel is distillation, meaning the separation of fermented ethanol and water into individual parts.

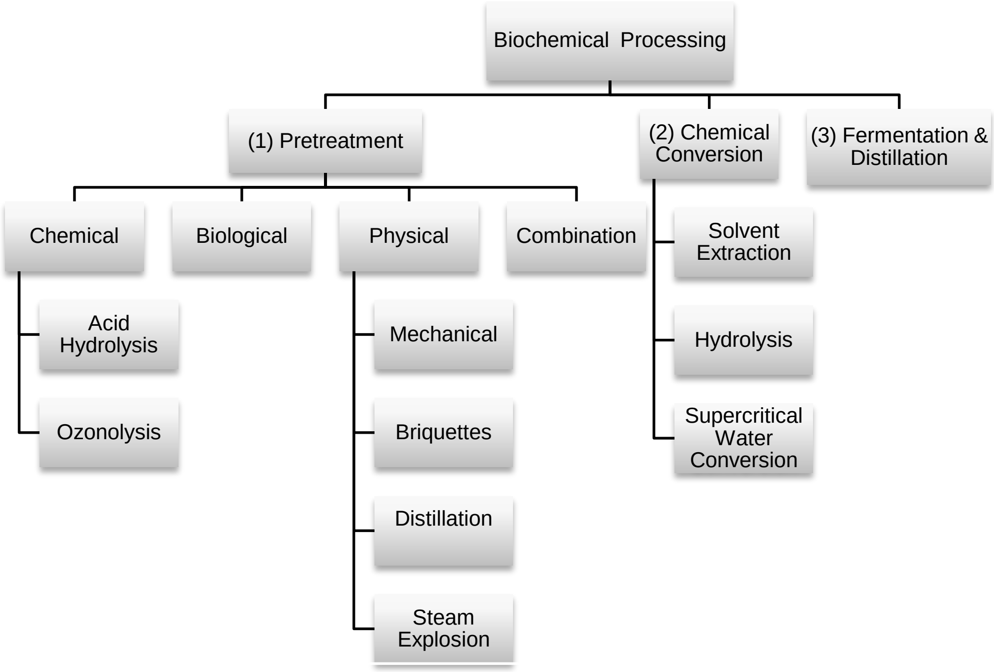

Figure 9: Summary of the Biochemical Processing of Lignocellulosic Biomass (Source: author)

3.2.3. Barriers for the Production of Lignocellulosic-Based Biofuels

Despite the many environmental advantages that second-generation biofuels have over first-generation ones, the latter are much easier to produce due to the chemical structure of the biomass. Lignocellulosic biomass is rigid and harder to convert as a result of the tight structure of the cellulose and hemicellulose content. Cellulase enzymes have a harder time breaking down the bonds, than in starch- or sugar-based biomass, in order for the biomass to be subsequently converted into liquid fuel. *"Cellulose fibers are embedded in a covalently joined matrix of pectin, lignin, and hemicellulose. Each cellulose macrofiber is composed of crystalline bundles of individual chains of cellulose." (Cheng/Timilsina 2011: 3543)* Pretreatment technologies are designed to overcome this barrier, but in many cases the energy input needed is far too high to be cost-effective.

The multiple pretreatment steps require significant capital investment and have very high operating costs. Eliminating these steps would make second-generation biofuels more economical. *"Pretreament technologies (...) are suitable for specific feedstocks and situations as individual pretreatment technologies have different characteristics with varying strengths and weaknesses." (IEA 2008: 48)* The commercialization of lignocellulosic biofuels also suffers from the high costs of cellulase enzymes, obtained from fungi or bacteria, that are used during hydrolysis. These enzymes are a crucial aspect of the process because they have to physically separate cellulose chains from the crystalline fabric for subsequent hydrolysis reactions (cf. DOE 2006: 45). Further research should be undertaken to find suitable low-cost substitutes or to develop low-cost cellulase enzyme production technologies (see Cheng/Timilsina 2011: 3545). Because of the large number of individual processes in the conversion of lignocellulosic biomass, better process integration would have the potential of lowering capital and operating costs, thereby optimizing biofuel production (cf. IEA 2008: 53).

The conversion of lignocellulosic-based biomass results in a number of by-products which must be effectively managed in order for the entire process cycle to be economically viable. One advantage of first-generation biofuels is that during the biofuel production, nearly all the sugars and starch contained in the biomass are converted to liquid fuel (e.g. ethanol). Unfortunately, *"the conversion rate of lignocelluloses to ethanol is much lower, in the range of 30-60% depending on the technologies. Among the three major components of lignocelluloses, cellulose has the highest conversion rate to ethanol, 85-90%; hemicelluloses 30-85%; lignin 0%" (Cheng/Timilsina 2011: 3545).* Due to the low conversion rates of lignocellulose to ethanol, increased pretreatment steps and multiple high-cost enyzme-induced reactions are necessary. Additionally, pretreatment steps like hemicellulose hydrolysis produce products such as hexoses and pentoses (both monosaccharides i.e. building units of basic carbohydrates); cost-effective technologies need to be developed in order to ferment both products (pentoses are much harder to ferment than hexoses) into ethanol. Other consequence of many procedural steps is the separation of cellulose from lignin. Lignin, though difficult to ferment into ethanol, can be used on its own as a fuel during ethanol purification processes (Cheng/Timilsina 2011: 3545).

Before second-generation biofuels can be used extensively, further research is needed to develop energy efficient pretreatment technologies which have a high separation efficiency, to find possible substitutes for cellulase enzymes and to better utilize by-products of the biofuel production cycle. One possibility that is currently being explored is the genetic modification of biomass in order to alter the cell-wall composition to reduce the lignin and increase the cellulose content (cf. DOE 2006: 41). If this is successful, it would eliminate the need for other energy-intensive pretreatment methods making the entire process more cost-effective. Another related possibility would be to develop plants with modified lignin structure so that the lignin can be easily removed during the conversion process.

Catalyst stability is one of the most important aspects when working with biomass feedstocks due to the presence of various impurities such as inorganic salts, ash, phosphorus or sulfur compounds, which can act as inhibitors. Such impurities can decrease the effectiveness of the catalyst or sometimes even permanently damage it (see NSF 2008: 87). Researching the effects that particular impurities have on a catalyst is tricky and the impacts can vary from catalyst to catalyst. Because these catalysts are expensive, better efforts should be made to recycle and reuse them in the following cycle to minimize production costs. However, enzyme recovery and recycling can be difficult since during bio-chemical processes (like hydrolysis), the enzyme binds to the biomass units, making it harder to dislodge while maintaining its structural integrity (see IEA 2008: 52).

Amylases, used in the production of starch-based ethanol production (first-generation biofuels), are much cheaper than the cellulase enzymes needed for lignocellulosic-based ethanol. Finding suitable, highly efficient biological substitutes such as fungi or other microorganisms would help decrease the production costs. An additional area that needs to be developed is the effective utilization of products formed during pretreatment steps. *"Glucose is the main product of enzymatic hydrolysis of cellulose, while xylose is a main product of hemicellulose hydrolysis." (Cheng/Timilsina 2011: 3545)* While the fermentation of glucose to ethanol is fairly simple, the conversion of xylose to ethanol is a multi-step process. The co-fermentation of glucose and xylose has been proposed by some scientists to eliminate the need for separate conversion technologies.

High costs of the production of biofuels from lignocellulosic biomass is a major deterrent to their widespread use. The cost of producing lignocellulosic ethanol is much higher than the costs of producing gasoline or food crop-based ethanol (see Figure 10), because of the complicated pretreatment and multi-step process.

However, the biomass material itself is much cheaper; lignocellulosic materials such as grasses, energy crops, and forestry or agricultural residues are fairly abundant and easy to find in most areas of the world and their use in biofuel production does not conflict with food production.

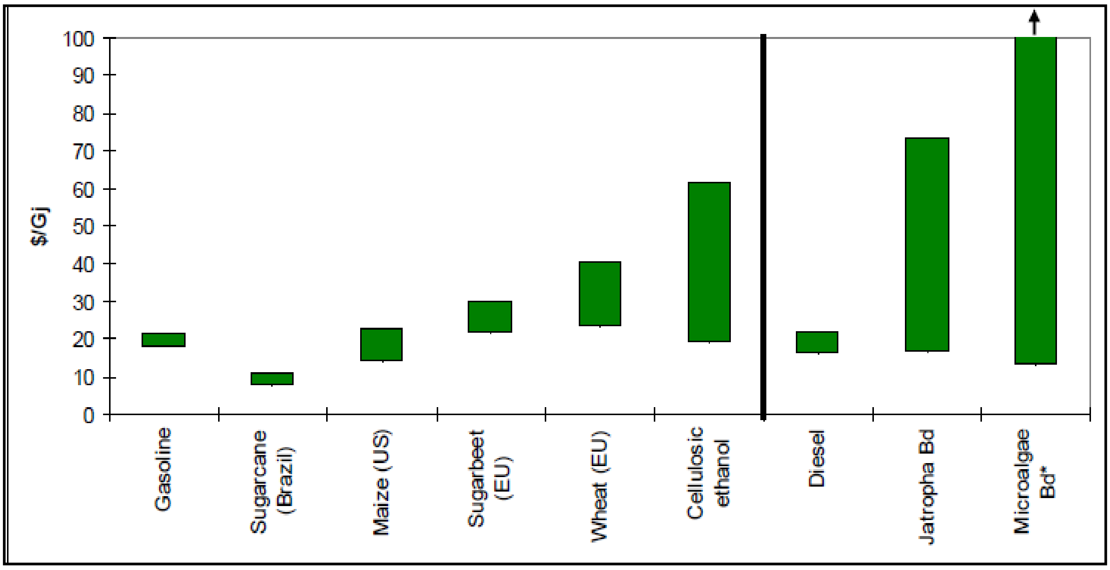

Figure 10: Biofuel Production Costs ($/Gj) from Various Feedstocks (Carriquiry et al. 2010: 33)

If production technologies can be improved and made cost-effective, second-generation biofuels would be able to replace a majority of fossil fuels, thereby making a major contribution to the climate change mitigation efforts. Before this can happen though, further research is needed to effectively manage the by-products of the various production stages, thereby leading to greater economies of scale.

Research not only in the technological improvements, but also in the chemical and physical properties of the biomass would be of great benefit. Additional knowledge about plant cell wall structure and its susceptibility to chemical treatments could lead to the creation of more suitable technologies: *"[M]ore knowledge is needed about the natural organization and structure of polymers and chemicals in plant tissue that affect chemical pretreatment, enzymatic digestibility, and the generation of compounds inhibiting fermentative microorganisms used to produce the final fuel or chemical" (DOE 2006: 40).*

Knowledge of the carbon fixation process of plants could help develop energy crops which capture higher amounts of CO_2 and thereby mitigate climate change. *"Expected significant increases in the ratio of carbon to nitrogen and mineral nutrients would have a beneficial effect on agricultural inputs (e.g., planting,* *fertilizing, cultivating, and harvesting), costs, and sustainability." (DOE 2006: 48)* One of the biggest challenges in biofuel production research will be understanding how to modify cell walls to meet the need of biorefineries, without affecting plant growth and durability: *"Genetic studies have indicated that lignin reductions may cause deleterious changes in plant growth and development. However, lignin possibly may be reduced with or without harmful effects on plant growth if compensating changes could be made in the amount of cell-wall polysaccharides." (DOE 2006: 49)*

Biomass samples are not always chemically similar and the presence of different structural elements means that samples react differently to pretreatment methods, making the conversion process even more complicated. Optimization of biofuel production is dependent upon the maximization of fuel yield from a unit of biomass, while minimizing costs and energy inputs. The plant cell wall, due to its structural importance to the plant itself, is especially problematic to the production process. Long term, any research done to better understand cell-wall composition, its structural components and the roles of various polymers would facilitate the biofuel production cycle (see DOE 2006: 47). Changes in the composition of the cell wall, adjustments to the ratio of monosaccharides and polysaccharides, increasing the content of cellulose and minimizing the content of lignin would help improve the efficieny of biomass conversion.

The logistics of supplying a biorefinery plant with sufficient amount of biomass are complex and sometimes problematic. Feedstock can be stored outside of the biorefinery, but only for a short time to prevent energy loss through processes such as degradation. Such storage facilities can be costly, so making sure only a few days of supply are in storage at any given time is imperative, running the risk of low supply in times of high demand. *"The fibrous nature of ligno-cellulosic biomass and its low energy density (particularly with high moisture content) make it difficult (...) to collect (...) [and] handle. (...) Some forest and crop residues may not be cost competitive because the biomass resource is dispersed over large areas leading to high collection and transport costs." (IEA 2008: 39-40)* Loss of feedstock during harvest and transportation (spillage off a vehicle) is also very common and many times unavoidable. Furthermore, some biomass such as straw and bagasse run the risk of fire (spontaneous combustion) when stored in very high piles. Increased transportation due to limited storage capacity can lead to more frequent vehicle on- and off-loadings contributing to higher local air pollution and deterioration of road infrastructure (see IEA 2008: 41). The variable moisture content of different biomass feedstocks poses an additional difficulty in biofuel production; a biorefinery must be able to adapt its processes to suit the specific characteristics of the feedstock to maximize efficiency and output. Designing a plant with these specifications and parameters is not only extremely difficult, but also costly.

Despite the considerable amount of progress that has been made in improving the lignocellulosic-based biofuel production, a number of challenges remain before second-generation biofuels can be commercially applied. Currently, scientists and technicians have managed to improve the separation efficiency in the pretreatment steps, to lower the costs of enzyme and catalyst production, as well as to develop less energy-intensive technologies. Lignocellulosic biomass-derived fuels will only be marketable if they offer the same characteristics of fossil fuels, namely good mileage, wide availability, and minimum costs, while minimizing impact on vehicle engines and infrastructure. So far, biodiesel and bioethanol have proven to be relatively easy to integrate into the existing transportation infrastructure. Properties such as fuel volatility, heating value, octane value, water tolerance, lubricity, acidity, material compatibility (minimum corrosion and degradation), and minimum environmental damage (e.g. GHG emissions) are crucial elements which will affect the commercialization of biofuels (see NSF 2008: 18-21).

4. Sustainability of Second-Generation Biofuels

Research so far has shown that second-generation biofuels, those produced using non-food crops and purpose-grown energy crops or residues, enjoy certain advantages over many first-generation biofuels. These include the reduced greenhouse gas emissions, their ability to be grown on marginal land so as not to be in conflict with food production, and a more positive energy balance (see IEA 2008: 6). The procurement of sufficient feedstock from within a reasonable distance and the development of conversion technologies to guarantee widespread commercialization of second-generation biofuels are some remaining problems. While research and investment in technology should continue, the sustainability issues of these biofuels should be investigated more closely (see Figure 11 for an overview on the various sustainability issues that will be covered in this chapter). Scientists and environmentalists alike have expressed concerns regarding the growing interest in the production of biofuels. The concept of sustainable energy development is rather recent and can be traced back to the work undertaken by the Brundtland Commission in the 1980s. The Commission's Report of 1987 listed four key elements of sustainable energy:

- *"sufficient growth of energy supplies to meet human needs (including accommodating relatively rapid growth in developing countries);*
- *energy efficiency and conservation measures, in order to minimise waste of primary resources;*
- *addressing public health and safety issues where they arise in the use of energy resources; and*
- *protection of the biosphere and prevention of more localised forms of pollution." (Jefferson 2006: 573)*

It remains to be seen whether lignocellulosic-based biofuel production will fulfill these criteria and provide an answer to our sustainable energy demands.

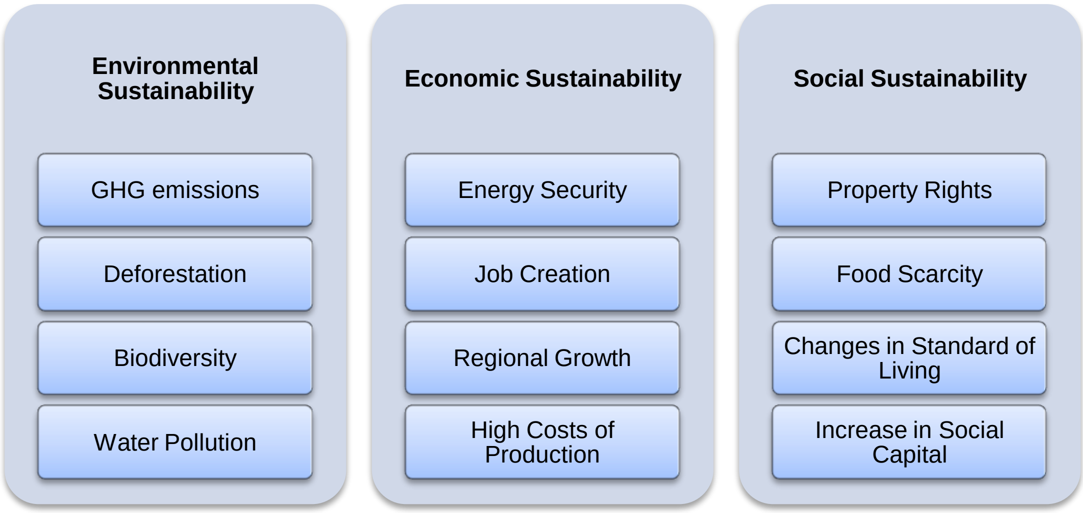

Figure 11: Environmental, Economic, and Social Sustainability of Second-Generation Biofuels (Source: author)

4.1. Environmental Aspects

The environmental sustainability of second-generation biofuels is assessed based on indicators such as GHG emissions, water use, land use changes, biodiversity loss, air emissions and soil quality. These biofuels have the potential to have higher yields per hectare than conventional crops (see Table 3), thereby reducing water and land demand.

Table 3: Yields per Hectare of Common Biomass Feedstocks in the United States, 2011/2012 (see USDA 2013a: 9-22)

Feedstock	Yield in Metric Tons per Hectare (t/ha)
Rye	1.64
Rapeseed	1.65
Oats	2.05
Soybean	2.82
Sorghum	3.43
Barley	3.74
Rice	7.92
Corn	9.24
Miscanthus	10.2
Jatropha	12.5
Switchgrass	12.9

The production of second-generation feedstocks is expected to yield fewer GHG emissions due to fewer land use changes, reduced fertilizer and pesticide inputs if grown on land meant for food production, and *"greater carbon sequestration in soil, plant, and root systems" (Williams et al. 2009: 4765).* However, GHG savings associated with biofuels depend highly on the way it was grown, on which land it is grown and how it is converted from the feedstock to liquid fuel. Depending on the choice of feedstock, second-generation biofuels have the potential to provide benefits such as making use of marginal land, using excess agricultural or forestry residues, and possibly even improving economic conditions in developing regions. However, it is also possible that second-generation biofuels are unsustainable if energy crops start competing for arable land, or if extra water and fertilizer inputs are necessary for their growth.

Despite the fact that lignocellulosic biomass is renewable, mass production of biofuels can lead to an overall increase in emissions due to the complex logistics needed for their cultivation, collection, and transportation (see Singh et al. 2011: 11). Clearing of grasslands or shrubbery to make room for energy crops could also lead to higher emissions. Land use changes could result in the release of natural carbon stocks, for example in forests, which might counter the GHG savings otherwise provided by the substitution of biofuels. *"Several studies find that if emissions related to land-use change caused by biofuel expansion are included, the emissions would be so high that it would take tens to hundreds of years to offset those emissions through the replacement of fossil fuels." (Timilsina/Shrestha 2011: 2063)* Production of second-generation biofuel feedstocks which are incapable of growing on marginal land would increase pressure for arable land, leading to food shortages and higher food prices, a change that would prove to be especially detrimental for poorer countries. The proposal to grow energy crops on marginal land may seem beneficial at first glance, but substantial irrigation may prove to be necessary to maintain their economic viability (see Williams et al. 2009: 4767).

A continuous removal of biomass for fuel production is not sustainable. Furthermore, it seems illogical to assume that increased biomass production on marginal lands will be possible without a surplus of nutrient and water input. More nutrient input will be needed to keep up soil quality to enable future harvests and over-removal of residues could lead to faster soil erosion and decline in soil organic matter. The nitrogen cycle has been strongly affected by human behaviour due primarily to the large-scale non-manure applications (i.e. fertilizers) of nitrogen to soils and crops.

Ammonia, a very volatile substance, is often applied directly to the soil as a fertilizer, where it continues to be a part of the natural nitrogen cycle of nitrification, denitrification, and plant uptake. Large amounts of nitrogen have led to soil acidification, eutrophication of water bodies, an increase in N_2O emissions, and nitrate pollution of drinking water.

The production of energy crops, especially perennial herbaceous ones, are expected to result in lower GHG emissions, because they have the potential of being grown on uncultivated or degraded land, thereby decreasing the need for higher fertilizer inputs. Additionally, they have climate mitigation benefits:

> *"Because dedicated herbaceous energy crops are grown for durations as long as a decade or more per rotation, they provide year-round soil cover and develop deep and complex root systems that sequester significant amount of carbon underground. For example, carbon sequestration rates have been found to be as high as 20-30x greater for perennial grasses such as switchgrass compared to annual row crops like corn." (Williams et al. 2009: 4765)*

Crops such as miscanthus and prairie grasses also have higher nitrogen take up and use per applied amount, meaning that less nitrogen fertilizer would need to be applied, leading to overall lower harmful N_2O emissions. However, nitrogen application rates will depend highly on the feedstock itself, the targeted yield, and the region in which it is grown (cf. Williams et al. 2009: 4766).

Scientists firmly believe that the production of most energy crops will likely have a low impact on soil quality due to the decrease in chemical inputs needed for their production. Additionally, because of the specific year-round growth patterns of energy crops and their root penetration, energy crops could have the potential to enhance soil organic content (SOC) and reduce soil erosion, thereby decreasing the necessity of having a layer of residues to maintain soil structure. Furthermore, *"measured SOC from annually harvested perennial grasses was not found to differ significantly from an undisturbed native grassland, suggesting that perennial feedstocks will not adversely affect soil quality" (Williams et al. 2009: 4767).*

Water use for the growing of crops specifically for fuel production poses one of the biggest challenges. Crop irrigation uses about 70% of the freshwater consumption in most countries and if more water is needed for growing energy crops, this would put a serious strain on the already scarce water resources. *"Energy derived from biomass requires about 70 to 400 times more water than that derived from other energy carriers such as fossil fuels, wind, and solar." (UNEP 2009: 56)* Also, more fertilizers and pesticides could cause additional problems for local water bodies by elevating phosphorus and nitrogen runoffs, resulting in eutrophication or higher nitrate levels in groundwater.

Genetically-modified plants have been proposed to decrease the water and nutrient inputs, but this leads to the spread of genetically modified organisms (GMOs) in environmentally protected sites, causing a loss of biodiversity. In many developing countries, because of the lack of environmental protection standards, farmers continue to clear rainforests to grow energy crops; in Indonesia, the primary cause of deforestation is palm oil plantations (see EAC 2008: 17). Additionally, some of the more promising lignocellulosic feedstocks have been classified as invasive species and therefore, careful and proper management of biofuel plantations would be necessary to avoid unintentional consequences. If energy crop cultivation continues at the expense of natural forest, emissions from deforestation activities will be largely countered by the substitution of biofuels for fossil fuels. There is a high degree of uncertainty regarding the indirect effects of greenhouse gas emissions from harvest, transport, and land use change.

The scale of land use changes for biofuel production will depend primarily on the type of land that is used (marginal versus arable land) as well as the feedstock which is grown (mono- versus poly-cultures). Some studies show that planting of herbaceous energy crops could help improve nutrient cycling processes in degraded soils. Herbaceous energy crops, especially switchgrass and miscanthus, offer cover for small mammals, while some prairie grasses support pollination activities thereby enhancing local biodiversity and aiding in landscape restoration (see Williams et al. 2009: 4768).

The use of agricultural or forestry residues for use as a feedstock may prove to be very promising because they do not have to be produced, but rather diverted from other streams of use. Crop residues are a co-product of existing production systems and thus the resulting GHG emissions are a direct output of these systems and not of residue production. Their collection has the benefit of avoiding GHG emissions resulting from their disposal through intentional burning (further details can be found in the next chapter). The harvest of residues would result in lower total water demands than conventional crop production, but might cause a need for the replacement of removed residues, and thus nutrients, with additional fertilizer input, thereby deteriorating water quality. The collection of residues as a biofuel feedstock, however, would considerably minimize other effects such as direct land use changes and impact on biodiversity.

GHG emissions resulting from the biofuel production itself should also be examined. Biorefineries that choose to burn lignin residues produced during biofuel production, instead of fossil fuels would result in lower emissions. Emissions will vary significantly depending on whether or not biochemical or thermochemical processing takes place:

> *"For biochemical conversion, the greatest CO_2 emissions are projected to occur from flue gas due to the burning of byproduct streams and combustion of lignin-rich residue in the boiler system. Relatively small amounts of methane (CH_4) and N_2O are also predicted to be released from this source. (...) For thermochemical conversion, the greatest CO_2 emissions are projected to occur from flue gas due to the combustion of char and the slipstream of syngas to provide heat to power the refinery. Relatively small amounts of CH_4 and N_2O are also predicted to be released from flue gas due to combustion processes." (Williams et al. 2009: 4770)*

The use of sulfuric acid as a pretreatment catalyst during biochemical conversion would result in higher sulfur oxide (SO_x) emissions than those of traditional ethanol biorefineries, but this will probably be the only emission that is higher than for first-generation biofuels. The generation of significant amounts of solid waste during lignocellulosic-biomass conversion poses a problem as to its disposal or use. The use of scrubbing or cleaning agents results in emissions of gypsum or sulfur. At this point in time, it is still difficult to generalize the costs or benefits of biofuels, as various feedstocks are used to produce liquid fuels by a number of different methods.

"When such impacts as soil acidification, fertilizer use, biodiversity loss and toxicity of agricultural pesticides are taken into account, the overall environmental impacts of ethanol and biodiesel can very easily exceed those of petrol and mineral diesel." (Doornbosch/Steenblik 2007: 5) The increasing criticism of the sustainability of first- and second-generation biofuels has led to discussions about the feasibility of biofuel

production from algae and microbacteria, thereby eliminating the need for large areas of land and the need for high water use.

4.2. Economic Aspects

Sustainable production of biofuels is the top concern at the moment, as this issue relates both to social and environmental issues like food conflicts, water depletion, and biodiversity loss. Economically, lignocellulosic biomass has a significant advantage over other biofuel feedstocks such as corn and soybeans, because it can be produced relatively quickly at lower costs than food crops (see NSF 2008: 9). Additionally, energy crops grown specifically for the production of fuel may prove to be beneficial for farmers, because of the potential of gaining subsidies. The famers would have the possibility of growing non-food crops on a specific section of land without losing any existing grants (see Hanegraaf et al. 1998: 345). On a microeconomic level, new lignocellulosic crop possibilities could provide further sources of income especially for local farmers, while biorefineries could help stimulate regional growth. Politicians continue to push for the sustainable production of biofuels, especially in rural areas where the potential exists for local job creation. However, a national strategy based on subsidies could have negative macroeconomic effects as subsidizing energy production usually leads to cheaper energy and an increase in overall energy consumption. The economic benefits must be balanced with the environmental impacts, especially for aspects like soil erosion, ground water pollution from over-fertilization, and increased GHG emissions.

The production of biofuels may also change the geographical distribution of impacts within a country's borders, as well as across borders - even from developed countries to developing countries. *"The extent to which the co-products of biofuel production displace other products and their environmental impacts (...) depends on the elasticity of demand in the relevant markets (the more inelastic the demand, the greater the substitution), the way in which the co-products affect supply curves, and other market and non-market (...) factors." (UNEP 2009: 51)*

For less developed countries, the financing of commercialized second-generation biofuel plants could pose a problem as it demands large investment costs. Furthermore, the complex administrative and bureaucratic processes, as well as corruption, could reduce the willingness of foreign firms to make large investments in such countries. Complicated production processes, large biomass demand (approximately 600,000 t/yr) and good infrastructure are three more prerequisites for the economic production of lignocellulosic biofuels (cf. IEA 2010: 11).

Developing better uses for the by-products of biofuel production could help make the entire process economically more competitive and thus attractive for farmers in developing regions. To increase economic viability, decrease the risks, and maximize security, multiple feedstocks will have to be used. Further research could help develop technologies which address the challenges to sustainability, reduce costs for the production of liquid fuels, and optimize the utilization of by-products.

“Uncertain market prices for energy crops and lack of other market outlets for those crops can make energy-crop profits dependent on uncertain or volatile oil prices and on the location of biorefineries. The uncertainty caused by (…) rapid innovations leading to new, genetically superior varieties of energy crops or improvements in conversion technologies also could influence investment decisions.” (U.S. DOE 2009: 26) In order to attract foreign investment, the Clean Development Mechanism (CDM), one of the flexible mechanisms under the Kyoto Protocol, could prove to be useful. It allows industrialised countries to invest in emissions-reducing projects in developing countries in order to fulfill their own emissions reduction targets. Switching from fossil fuels to biofuels would qualify as a CDM project and should probably be promoted as such.

The trade of lignocellulosic feedstock could help emerging economies profit from biofuel market expansion. *"The lower financial risks and reduced need for highly skilled labour make the production of biomass feedstock considerably more feasible compared to biofuel production." (IEA 2010: 39)* However, before the possibility of feedstock trade is considered, the feasibility of transporting feedstocks, especially those with lower energy density, over long distance should be considered. Expanding such a trade market at an early stage, could help make the transition to the actual production of biofuels in the emerging markets easier, as it would lower investment costs by building upon the existing structures (cf. IEA 2010: 39).

Biofuel sustainability standards and government subsidies should be changed to guarantee that support is only given to those biofuels where there are considerable environmental improvements over fossil fuels. To summarize, poor infrastructure, limited financing possibilities, lack of skilled labor, and technical know-how will likely pose the biggest challenges to the widespread distribution of biofuels in the developing regions of the world.

4.3. Social Aspects

The sustainable production of biofuels raises not only environmental concerns, but also social issues. Aspects such as land occupation, labor force exploitation, and social conflict over limited food resources have been brought up in the context of lignocellulosic biofuels. Job creation and regional growth are sure to be two important changes that come about through the commercialization of second-generation biofuel production sites. Improvement in the job market as a result of the new biofuel market could help improve social conditions and the standard of living. The cultivation of the feedstock and the need for vehicles to transport it from the fields to the biorefineries will expand the local job market. Additionally, through the training of unskilled workers to work in the biorefineries, the social capital will increase.

If arable land starts to become scarce, crop expansion might encroach upon areas dedicated to other activities, thus threatening the local way of life. This could lead to a shift in rural labor force patterns and changes in community densities. Social impacts of lignocellulosic-based biofuel production are closely linked to environmental consequences. The use of marginal lands would entail less negative social impacts than those dedicated to livestock activities.

Biofuel production in development countries should not lead to lower wages and unfair prices for the local farmers or workers. Furthermore, the costs and benefits of biofuels should be distributed equitably and the majority of the negative impact should not fall on developing countries. *“Biofuels policy and future sustainability initiatives should not discourage local, small-scale biofuels production, particularly in developing countries that are fuel poor.” (NCOB 2011: 10)* Under no circumstances should biofuel production come at the expense of people's basic rights, including the right to sufficient food and water, work, and property.

5. Residues and Wastes

Lignocellulosic feedstock includes not only energy crops, oilseed species, and non-food sources, but also agricultural and forest residues. In many countries, the non-food agricultural and forest biomass provides a highly underutilized resource for the development of fossil fuel substitutes. Agricultural and crop wastes are usually defined as those crops that are lost throughout the entire cycle, including during the handling, transportation, processing, and storage of crops. Through the harvest of crop residues, especially those of corn, wheat, and rice, it would be possible to decrease the strain put on an already weakening environment. Crop residues consist mainly of those products that remain after the harvest, such as leaves and stems, and fibers from orchard trimmings. Forest resources include residues like tree bark and scrap wood that remain behind after logging or site clearing. These residues are usually burned or simply left behind on the site. However, these residues do serve an important purpose, namely that of returning essential nutrients for subsequent harvests and maintaining soil stability to prevent erosion. Harvest of these residues has the potential to affect many biological and chemical processes in the soil, thereby affecting soil quality and future food production. Using residual biomass has the potential to reduce the overall environmental impact of biofuel production by increasing energy output and minimizing total greenhouse gas emissions.

5.1. Mass of Wastes

"There are between 140 and 350 million tons of agricultural residues produced annually in the United States. Although some of these residues must be left in the field for soil conservation purposes, the bulk of the residues are [sic!] available for industrial use." (Hayes n.d.: n.p.) More than 75% of this residue comes from corn, wheat, barley, oats, and other popular grains. Worldwide, scientists estimate that about 1500 million tons could be available for biofuel production. For most crops, the amount of residue that is produced is directly proportional to the amount of crop that is grown, i.e. one dry kg of residue is produced per dry kg of grain or grass. The following table gives an overview of the amount of crop wastes and lignocellulosic biomass that could potentially be available for bioethanol production.

Table 4: Quantities of Crop Wastes and Lignocellulosic Biomass Potentially Available for Bioethanol Production (adapted from Kim/Dale 2004: 373)

	Africa	Asia	Europe	North America	Central America	Oceania	South America
Wasted Crop (Tg)							
Corn	3.1	9.8	1.5	0.3	1.7	0.0	4.1
Barley	0.1	1.2	2.0	0.0	0.0	0.1	0.0
Rice	1.0	21.8	0.0	0.9	0.0	0.0	1.4
Wheat	0.8	10.2	4.0	0.0	0.2	0.8	0.9
Sorghum	2.2	0.5	0.0	0.0	0.1	0.0	0.1
Lignocellulosic Biomass (Tg)							
Corn Stover	0.0	33.9	28.6	133.6	0.0	0.2	7.2
Barley Straw	0.0	1.9	44.2	9.8	0.1	1.9	0.2
Rice Straw	20.9	667.5	3.9	10.9	2.7	1.6	23.5
Wheat Straw	5.3	145.2	132.5	50.0	2.7	8.5	9.8
Sorghum Straw	0.0	0.0	0.3	6.9	1.1	0.3	1.5
Bagasse	11.7	74.8	0.0	4.6	19.2	6.4	63.7

The information shown in the table below only gives the approximate ethanol yields that could be produced from theoretical residue amounts. Unfortunately, in practice, the amount of residues that is typically available for biofuel production is only about 10-25% of the total residues. Furthermore, forestry residues are usually harder to collect in comparison to agricultural residues due to their wider geographic distribution and complicated logistics involved in transportation.

Table 5: Example for Theoretical Ethanol Yields of Common Feedstocks (adapted U.S. DOE 2013: n.p.)

Feedstock	Theoretical Ethanol Yield (liter/dry ton of feedstock)
Corn Grain	470
Corn Stover	427
Rice Straw	416
Forest Thinnings	308
Hardwood Sawdust	381
Bagasse	422
Switchgrass	366

5.2. Ecosystem Services Provided by Residues and Sustainability of Using Residues as an Energy Source

"Top four major agricultural crops grown in the world are maize, wheat, rice, and sugarcane, respectively in term [sic!] of total cultivated area and production. Thus, these four crops produces [sic!] majority of lignocellulosic biomass in agriculture sector." (Chandra et al. 2012: 1465)

How much crop biomass is needed to protect the quality of the soil and how much could potentially be harvested to produce biofuels? Determining the amount of residue that can be safely removed from a field depends on factors such as climatic conditions, soil type and erodibility, precipitation rates, frequency of removal, and residue characteristics. *"Crops that generate relatively large amounts of below- and above ground biomass, such as sugar cane and corn would, ceteris paribus, seem to offer more scope for residue removal, than crops that generate relatively low amounts thereof, such as oil seed crops and a variety of cereal crops (e.g. soybean, rapeseed, sunflower, rice, barley, oat, sorghum and wheat." (Reijnders 2008: 655)* Excessive removal of residues would, however, directly affect the nutrient balance, hydrological cycle, soil quality due to a decrease in organic material, and the ability of the soil to withstand erosive forces. Removal of residues would entail a permanent loss of soil system nutrients that have to be mechanically added to maintain soil productivity. Lack of inadequate crop residues can lead to a significant change in physical and chemical properties of soil such as compaction, moisture retention, porosity, aeration, and crusting.

Despite these concerns, one must keep in mind that a plant consists of valuable parts that are harvested for food, residues that are not harvested, but that can be used as a biofuel, and underground biomass such as roots that usually stay in the ground even after harvest. In order to understand how the removal of residues for biofuel production would affect the soil organic content, the nutrient content in both the underground and aboveground biomass must be considered. In the case of some plants, the underground biomass may already contain enough nutrients, so that residues and wastes could be gathered without negative consequences on soil quality. For example, switchgrass can grow to a height of about two meters with roots just as deep, which provide an invaluable source of underground biomass and nutrient retention.

Residues also help reduce abrupt fluctuations in soil temperature and absorb excess agricultural chemicals. The residue layer protects the soil from solar radiation by increasing or decreasing the albedo. *“Residues can intercept 50% to 80% of incoming radiation […], keeping the surface soil temperatures within 20ºC of ambient, whereas bare soil temperatures may rise 30ºC or more above ambient.” (Johnson et al. 2010: 3-4)* Residues also help mitigate global climate change by offsetting CO_2 emissions and other greenhouse gases. Altering the frequency and amount of residue harvest could help reduce the negative effects of biomass removal on the environment. Corn stover has been recognized as an abundant cellulosic feedstock with significant potential. Improved tillage or crop rotation practices could mitigate the losses of crop residue removal. Delayed crop emerging and pathogen buildup have proven to be effects of excess residue cover.

Remaining residues add increased resistance to water vapor fluxes (e.g. soil evaporation) from the soil, leading to decreased soil erosion and drying. Soil loss through erosion removes the fertile topsoil layer needed for high yields and healthy crops. Leftover crop stubble has also been shown to reduce the effect of soil loss caused by wind erosion: *“[…] when soil is at least 50% covered with residue, loss by wind erosion is expected to be 10% or less of losses from flat, bare soil” (Johnson et al. 2010: 25).* Furthermore, the residue cover regulates water infiltration through an added protective layer, reducing soil runoff caused by sudden or excessive precipitation. Increased soil runoff can cause nearby water pollution, algal blooms, and eutrophication due to the fertilizers used. Scientists and environmentalists have not fully understood what effect these water and heat differences can have on overall crop growth as the interconnections are highly complex and convoluted. Leftover organic material in the field plays a big role in maintaining nutrient balance: the decomposition of organic matter has been proven to stimulate nutrient cycling and protect soil structure. *“Most crops concentrate nutrients in their seeds, but significant quantities of nutrients remain in most crop residues and upon decomposition of the residue in soil are slowly released for plant uptake.” (Cruse et al. 2010: 48)*

When biomass is harvested, the quantity of carbon, nitrogen, potassium, calcium, and magnesium inputs change because of the decreased amount of organic matter that is now available for the uptake by plant roots. Soil quality depends primarily on the carbon content and scientists fear that the degradation of the soil through over-harvesting could negate the gains attained from the production of biofuels derived from lignocellulosic residues. Scientists propose that the organic carbon loss could be partially offset by manure or supplemental fertilizer inputs, but whether or not this will be sustainable in the long run is yet to be determined (see Cruse et al. 2010: 48). Soil carbon sequestration is directly related to the soil organic matter and can be altered through harvest techniques and practices such as inversion tillage. Though the exact sequestration ratio is not clear, one estimate suggests that *“20% of the carbon produced by residue remains in the soil after two years and that 25% of soil-sequestered carbon in an agricultural system is derived from crop residue carbon” (Cruse et al. 2010: 52).* Leaving behind a very thick residue layer can also have negative impact as it causes slower soil warming during seed germination, thus leading to lower yields. Determining the appropriate level of crop residue removal for biofuels production will be one of the biggest challenges to its effective utilization.

Forest residues include stumps, branches, sawdust, wood chips, bark, and tree scrap, all of which may have been produced naturally or during logging. Studies have shown that residue retention results in higher potential cash crop yields as a direct result of higher soil carbon content. *"Corn residue can provide as much as 1.7 times more carbon than residue produced by other crops such as barley, oats, sorghum, soybeans, sunflowers, and wheat." (Anand et al. 2011: 198)* Using corn stover (stalk, husk, leaves, and cobs) for lignocellulosic biofuel production may prove to be feasible due to the high cellulose content. Unlike corn stover, however, rice straw does not have to be left on the field to prevent erosion. Thus, rice straw could be fully utilized as a biofuel feedstock.

Energy production from forestry waste and agricultural residues could save a significant amount of GHG emissions without requiring additional land, as both products are already generated in the logging industry and during food production. Residues include those left on the field or in the forest after harvest as well as the leftovers of the processing methods. Some crop and forest residues may not be cost competitive due to the high costs of collection and transportation. Some scientists have raised concerns that the harvest of crop residue would help decrease CO_2 emissions into the atmosphere, but though the decomposition of crop residue releases CO_2, it is reincorporated into the crop tissue itself and serves as a source of carbon for crop growth.

The practice of tillage removes valuable agricultural residues that provide an inexpensive nutrient input, from the field after harvest resulting in additional fertilizer use for the next growing season. Leaving behind residues helps improve the nutrient cycling and maintain soil quality. Countries have started adopting no-till systems which help keep crop residue on the soil surface, but the use for such residues for lignocellulosic biofuel production may mean a sudden return to conventional tillage. Achieving a balance between environmental sustainability and economic viability will prove to be a challenging issue for the future. Biofuel production already faces a big hurdle as many farmers have shown only limited willingness to enter the new market. For farmers, biofuel production means the challenge of growing new crops, learning complex technology, and incorporating it into their production systems, and dealing with possible negative impact of crop residue removal. The harvest of residues could prove to be a lucrative source of income, but its impact on future crop yields has yet to be fully studied. To maintain traditional crop yields farmers would have to replenish lost nutrients through additional applications of nitrogen, potassium, and phosphorus. The collection of crop residue for biofuel production entails shredding, baling, wrapping, storing and transporting - all have to be profitable for lignocellulosic-biofuels to be used widely.

The following table shows the possible costs that farmers would incur in order to replace the nutrients removed due to residue utilization. The following values are calculated by assuming that 1000 kg (1 metric ton) of each residue crop is available, of which 10% (100 kg) can be removed for biofuel production:

Table 6: Costs of Additional Fertilizer Input After Residue Removal (Fertilizer Prices and Nutrient Content Data Obtained from the Following Sources - cf. USDA 2013b: n.p.; OMAFRA 2011: n.p.)

	Amount of Biomass	Nitrogen Content in Biomass	Cost of Nitrogen Fertilizer in $/short ton (€/kg)	Sulfur Content in Biomass	Cost of Sulfur Fertilizer in $/short ton (€/kg)	Total Replacement Costs of Additional Fertilizer Input (€/kg)
Alfalfa	100 kg	2.5% N	266.94 $/t (0.22 €/kg)	0.2% S	103.64 $/t (0.09 €/kg)	0.57 €/kg
Corn Stover	100 kg	0.5% N	266.94 $/t (0.22 €/kg)	0.1% S	103.64 $/t (0.09 €/kg)	0.12 €/kg
Miscanthus	100 kg	0.5% N	266.94 $/t (0.22 €/kg)	0.1% S	103.64 $/t (0.09 €/kg)	0.12 €/kg
Switchgrass	100 kg	0.9% N	266.94 $/t (0.22 €/kg)	0.1% S	103.64 $/t (0.09 €/kg)	0.21 €/kg

An alternative to the use of crop residues for biofuel feedstock is the use of perennial plants such as miscanthus or switchgrass. Crop residue removal is unlikely to be sustainable unless it is coupled with best agricultural practices such as no-till and cover crops, crops grown primarily to maintain soil quality and improve nutrient cycling. To summarize, crop residues are responsible for sustaining soil organic matter, buffering the soil against precipitation and wind, recycling nutrients, improving soil infrastructure, minimizing evaporation, decreasing sedimentation, and conserving soil moisture. With the steadily increasing world population, the need has never been greater to utilize proper agricultural practices, appropriate tillage methods, and water conservation in order to feed the world's citizens. In tandem with the growing world population, the energy demand is also growing, thus fuelling scientific interest in biofuels. In order to sustain the world's population and support energy demand, better resource management is a must.

6. Evaluation Scheme

As stated in chapter 1.2, the goal of the evaluation scheme, found in Table 7 below, is to identify the purpose of some selected studies, to compare their systems' boundaries and their results. The studies were chosen on the basis of a literature search that filtered out second-generation biofuel studies, especially those that conducted a life-cycle analysis of various biomass feedstocks.

Table 7: Evaluation Scheme (Source: author)

Name of Study	System Boundaries	Results
Pleanjai S.; Gheewala S.H. (2009): Full-Chain Energy Analysis of Biodiesel from Palm Oil in Thailand. Applied Energy 86, S209–S214.	Life-cycle stages included palm oil plantation and production, biodiesel production, and transportation in between all stages. Boundaries: 1 year, 1 hectare, palm oil in Thailand.	Calculated the net energy balance for the entire life-cycle (100.84 Gj/ha). The largest energy input was needed for fertilizer production and palm oil production. The production of biodiesel from palm oil showed a positive energy balance.
Prueksakorn K.; Gheewala S.H. (2007): Full-Chain Energy Analysis of Biodiesel from Jatropha curcas L. in Thailand. Environmental Science & Technology 42, 3388–3393.	Life-cycle stages included Jatropha cultivation, oil extraction, biodiesel production, and transportation at all stages. Boundaries: 20 years, 1 hectare, Jatropha in Thailand.	Calculated the net energy ratio and discovered that the agriculture phase had the highest average energy consumption and oil refining the lowest. Jatropha grown on poor land consumed twice the energy as that grown on fertile land for obtaining a similar yield.
Kumar S.; Singh J.; Nanoti S.M.; Garg M.O. (2012): A Comprehensive Life Cycle Assessment (LCA) of Jatropha Biodiesel Production in India. Bioresource Technology	Life-cycle stages included Jatropha farming, oil extraction and transportation, biodiesel production, and transportation to and from sites, and biodiesel consumption in an automobile. Boundaries: 1 ton of biodiesel produced, Jatropha in India.	The primary energy requirements and GHG emissions at each stage and percent GHG emission reduction with respect to petroleum diesel were calculated. It was shown that Jatropha is an eco-friendly biofuel choice.

110, 723-729.		
Borrion A.L.; McManus M.C.; Hammond G.P. (2012): Environmental Life Cycle Assessment of Bioethanol Production from Wheat Straw. Biomass and Bioenergy 47, 9-19.	Life-cycle stages included ethanol use from a well to wheel perspective, namely wheat straw production, ethanol conversion, transport to a blending refinery, and burning of the wheat straw fuel in a small passenger car. It was assumed that two thirds of the wheat straw produced was left behind in the field to maintain soil quality. Boundaries: use in a small passenger car.	Reductions up to 73% (global warming), 50% (ozone depletion), and 40% (fossil depletion) were achieved when a fuel blend consisting of 85% ethanol was used instead of a 100% petrol-fuelled car.
Roy P.; Orikasa T.; Tokuyasu K.; Nakamura N.; Shiina T. (2012): Evaluation of the Life Cycle of Bioethanol Produced from Rice Straws. Bioresource Technology 110, 239-244.	Life-cycle stages included the collection, transportation, pretreatment, saccharification and fermentation, distillation and purification, and waste management. It was assumed that only 60% of residue rice straw could be removed from the field. Boundaries: 1 liter of anhydrous bioethanol produced from rice straw.	It was shown that the CO_2 emission of the life cycle of bioethanol could be reduced by making changes in the feedstock, the source of primary energy, and the alternate use of residues.
Fu G.Z.; Chan A.W.; Minns D.E. (2003): Life Cycle Assessment of Bio-ethanol Derived from Cellulose . The International Journal of Life Cycle Assessment 8/3, 137-141.	Life-cycle stages included feedstock cultivation (fertilizer inputs and diesel for transportation), enzyme production, bioethanol production (enzymatic hydrolysis), conversion into fuel, combustion of fuel in vehicle, and transportation. Boundaries: one-kilometer distance driven by new passenger cars.	It was shown that feedstock cultivation contributed significantly to acidification, eutrophication, and heavy metal pollution. Furthermore, it is possible for ethanol fuel blends to reduce overall life-cycle greenhouse gas emissions, but only if the energy needed to generate process steam is derived from biomass, instead of fossil fuel.
Gonzalez-Garcia S.; Luo L.; Moreira M.T.; Feijoo G.; Huppes G. (2009): Life Cycle Assessment of	Life-cycle stages included crop production, bales formation, ethanol refinery, blending, and fuel combustion in vehicles. Boundaries: distance of 1 kilometer driven by a middle size flexible-fuel vehicle; flax shives in	The study showed a positive effect of the carbon sequestered during crop growth (~ 9.9 ton CO_2/ha), which contributes to offset the GHG emissions. The important discovery was that the

Flax Shives Derived Second Generation Ethanol Fueled Automobiles in Spain. Renewable and Sustainable Energy Reviews 13, 1922-1933.	Spain. The categories of impact that were analyzed: abiotic resources depletion, global warming, ozone layer depletion, human toxicity, fresh water aquatic ecotoxicity, marine aquatic ecotoxicity, terrestrial ecotoxicity, photochemical oxidants formation, acidification, and eutrophication.	choice of allocation factor affected the overall environmental balance of the lignocellulosic ethanol production cycle.
Zhiyuan HuZ.; Pu G.; Fang F.; Wang C. (2004): Economics, Environment, and Energy Life Cycle Assessment of Automobiles Fueled By Bio-Ethanol Blends in China. Renewable Energy 29, 2183-2192.	Life-cycle stages include feedstock production, fuel conversion, fuel distribution, raw material extraction, parts manufacture, vehicle assembly, operation, maintenance, repair, and recycling at the product's end of life. Additionally, the gasoline and bioethanol life-cycles are included: feedstock production and transportation, ethanol conversion and denaturing, distribution, crude oil recovery, gasoline refinery process, and distribution. Boundaries: 200,000 kilometers service life of a vehicle was assumed, cassava-based bioethanol and gasoline fueled flexible fuel vehicle in China.	Objective was to carry out an economic, environment, and energy life cycle study to compare bioethanol fueled automobiles with gasoline fueled automobiles. Results showed that cassava-based vehicle had lower life cycle emissions of CO_2, CO, hydrocarbons, and particulate pollutants than a gasoline fuelled car (20% lower emissions). The combined energy utilization of a bioethanol fueled car was also better than that of a gasoline fueled vehicle.
Cherubini F.; Ulgiati S. (2010): Crop Residues as Raw Materials for Biorefinery Systems- A LCA Case Study. Applied Energy 87, 47-57.	The goal of the study was to perform a life-cycle analysis of two biorefinery systems, which produce bioethanol and various products from corn stover and wheat straw. Life-cycle stages included both fossil fuel and biofuel chains: collecting residues, processing feedstock, transporting, storing, distributing and final use of biofuels, extraction of raw materials, refining, storage, distribution, and combustion of fossil fuel. Boundaries: amount of agricultural residues treated per year, i.e. 477 kilotons.	Both biorefinery systems had lower total GHG emissions than the fossil fuel counterpart, but N_2O emissions were larger for biofuels. Biorefinery systems had lower impacts in categories like human toxicity, global warming, abiotic depletion, but had higher impacts in the eutrophication category.
Hagman J.; Nerentorp M; Arvidsson R.;	Objective was to assess the environmental life-cycle performance of Jatropha,	The largest contribution to fossil energy use was the oil processing phase. The

Molander S. (2013): Do Biofuels Require More Water Than Do Fossil Fuels? Life Cycle-Based Assessment of Jatropha Oil Production in Rural Mozambique. Journal of Cleaner Production xxx, 1-10.	especially in terms of water use, and to compare it to the life-cycle of fossil fuel (diesel). The Jatropha life-cycle included the following stages: nursery, transport, planting, cultivation, oil production, transport, and combustion. The diesel stages included energy inputs for extraction, refining, and combustion processes. Boundaries: Jatropha oil produced in the Northern Province of Niassa, Mozambique.	study showed that the fossil energy use of jatropha oil was significantly lower than fossil fuel, even for the low yield scenario. Jatropha oil had a higher global warming potential when the nitrous oxide emissions were analyzed. The green water footprint for jatropha oil was much higher than the blue water footprint.
Kaltschmitt M.; Reinhardt G.A.; Stelzer T. (1997): Life Cycle Analysis of Biofuels Under Different Environmental Aspects. Biomass and Bioenergy 12/2, 121-134.	A large-scale study was carried out to assess the complete life-cycle of several bioenergy carries that could potentially be produced in Germany and to compare that with fossil fuels. These included solid bioenergy carriers (grasses, cereal plants, short-rotation woods), liquid bioenergy carriers (rapeseed oil and bioethanol from wheat, sugar beet, potatoes), and residues (straw, cut grass, wood). The impacts on the environment and on human health were taken into consideration. Life-cycle stages included raw material cultivation, production, utilization, and disposal. Boundaries: Germany, 1 hectare.	The study showed a net energy gain from the replacement of fossil energy carriers by bioenergy carriers. Wood chips, wheat, and Miscanthus showed the highest energy gains (150 Gj/ha yr), while bioethanol from potatoes and wheat had the least favorable balance. Substantial savings in greenhouse gas emissions could be shown with the substitution of bioenergy carriers. Rapeseed oil was the most favorable bioenergy carrier.
Spatari S.; Zhang Y.; Maclean H.L. (2005): Life Cycle Assessment of Switchgrass- and Corn Stover-Derived Ethanol-Fueled Automobiles. Environmental Science & Technology 39, 9750-9758.	The objective of the study was to examine the environmental implications of the production and use of (switchgrass and corn stover derived) ethanol in automobiles in Canada. The study compared ethanol with low-sulfur reformulated gasoline. Boundaries: Ontario, Canada.	Corn stover ethanol showed slightly lower GHG emissions than switchgrass-derived ethanol. In the near-term, the GHG emissions from switchgrass fueled cars were 57% lower than for gasoline-fueled cars, while for corn stover fueled cars the emissions were 65% lower. It was also shown that future improvements in crop and ethanol yields could further decrease GHG emissions.

Searcy E.; Flynn P.C. (2008): Processing of Straw/Corn Stover. Comparison of Life Cycle Emissions. International Journal of Green Energy 5/6, 423-437.	The life-cycle emissions from four conversion routes (Fischer Tropsch synthesis, electricity output by direct combustion, gasification and combined cycle) were considered relative to a business-as-usual situation. Three major emissions thought to contribute to global warming, CO_2, CH_4, and N_2O, were considered. Boundaries: North America	The net avoided GHG emissions for the conversion techniques was 830 grams CO_2 equivalent/ kilowatthour for direct combustion, 839 grams for combined cycle, 2,060 grams per liter for ethanol production, and 2,440 grams per liter for FT-synthesis.
Yu S.; Tao J. (2009): Simulation-based Life Cycle Assessment of Energy Efficiency of Biomass-Based Ethanol Fuel from Different Feedstocks in China. Energy 34, 476-484.	The objective of the study was to conduct life-cycle assessments of the energy efficiency of various biofuels: wheat-based E10, corn-based E10, and cassava-based E10. Stages included feedstock planting and transportation, ethanol conversion and blending, and combustion as well as vehicle manufacturing, operation, and disposal. Boundaries: wheat-based fuel from central China, corn-based fuel from northeast China, and cassava- based fuel from southwest China.	All three biofuels had positive net energy values. Ethanol conversion was the most energy-intensive process stage. The study suggests that some improvements in the technologies could lead to increased energy efficiency.

Numerous efforts have been made to evaluate the life-cycle of lignocellulosic liquid fuels in order to form conclusions regarding their benefits. Generally, a wide variation of results has been observed, because of the differences in system boundaries, biofuel feedstocks, conversion technologies, biorefinery sizes, allocation methods, and land use considerations. However, it can be said that despite the projected environmental benefits of lignocellulosic-based biofuels, its economic viability remains uncertain at present. Careful consideration of land use changes, conversion techniques, and input demands is necessary to avoid productivity loss and negative environmental impacts. After developing this evaluation scheme, it was clear that conducting an assessment to compare the various emissions over the entire life-cycle of second-generation biofuels and fossil fuels would not be feasible in this thesis. In order to carry out a material flow analysis (MFA) it was necessary to decide on a focus. Therefore, the MFA, found in chapter 7, focuses solely on the CO_2 emissions at the stage-of-use, instead of the entire life-cycle of crude oil and bioethanol.

7. Material Flow Analysis

A material flow analysis (MFA) is a *"systematic assessment of the flows and stocks of material within a system defined in space and time. It connects the sources, the pathways, and the intermediate and final sinks of a material" (Brunner/Rechberger 2004: 3).* The following terms, defined by Brunner and Rechberger (2004: 4), are necessary to understand the function of the MFA:

- A process is defined as a transport, transformation, or storage of materials.
- Stocks are defined as material reservoirs (mass) within the analyzed system. A stock is part of a process comprising the mass that is stored within the process.
- Processes are linked by flows (mass per time) or fluxes (mass per time and cross section) of materials. Flows/fluxes across systems boundaries are called imports or exports. Flows/fluxes of materials entering a process are named inputs, while those exiting are called outputs.
- A system comprises a set of material flows, stocks, and processes within a defined boundary.
- The system boundary is defined in space and time.

The goal of this material flow analysis is to compare the CO_2 emissions at the stage-of-use, namely at the point where the fuel source is burned in the automobile, for gasoline and for bioethanol. Therefore, it will not consider the CO_2 emissions resulting from mining, transportation, energy use, or feedstock cultivation. The MFA system boundary will be the United States in the year 2010 and all values will be calculated in megatons per annum.

7.1. CO_2 Emissions from Fossil Fuels (Crude Oil)

The following figure shows the various flows of crude oil into and out of the U.S in 2010. The U.S. produced 99.99 megatons of crude oil in 2010, imported 215.22 megatons, exported 0.76 megatons, and consumed 350.03 megatons of crude oil (see Index Mundi 2013: n.p.). The total amount of crude oil available for use is 315.21 megatons (import + production). The stock change can be calculated in the following way:

(import + production) – (consumption + export) = stock change

(215.22 + 99.99) – (350.03 + 0.76) = - 35.58 megatons

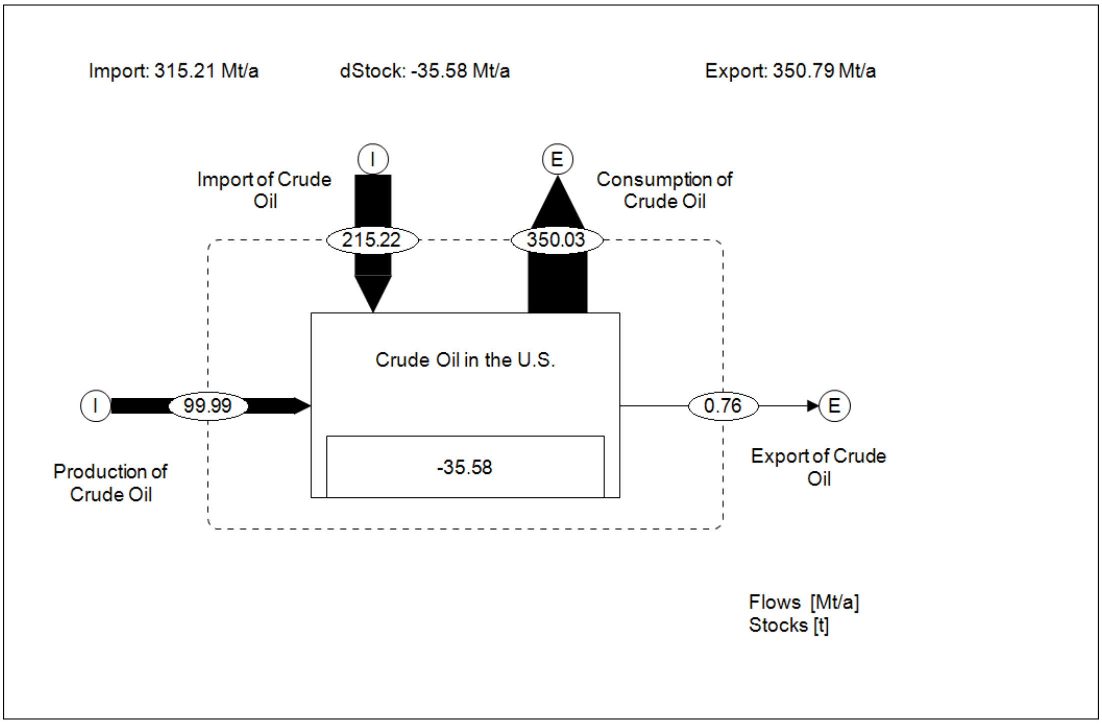

Figure 12: Crude Oil Flows in the U.S., 2010 (Source: author)

Refining is a complex set of processes that converts crude oil into gasoline. During these processes, several by-products are created, namely residual fuel oil, diesel fuel, heating oil, jet fuel, and kerosene. Figure 13 shows the amount of crude oil that is converted into gasoline (50%) and other products during refining. 50% of 350.03 Mt/a yields 175.01 Mt/a of gasoline. The rest of the crude oil is converted into other products: 10% into residual fuel oil and 40% into medium-level products like diesel fuel, etc.

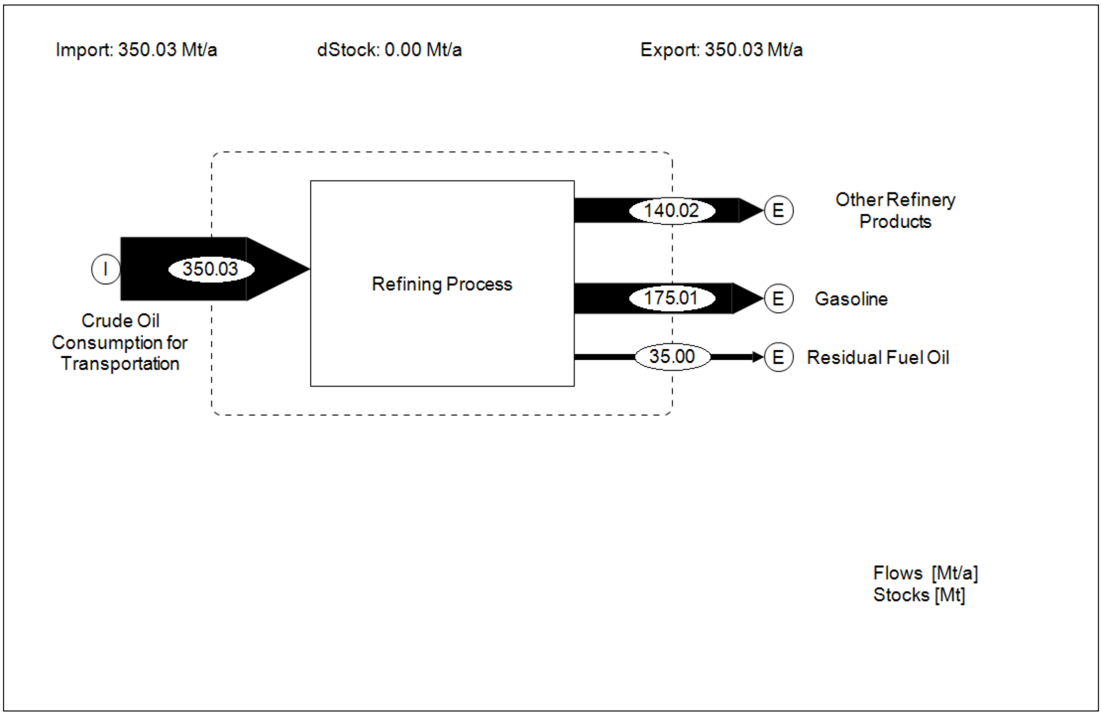

Figure 13: Typical Refining Process in the U.S., 2010 (Source: author)

70% of the converted gasoline is used for passenger cars. 70% of 175.01 Mt is 122.51 Mt of gasoline that are available for use in cars per year. The other 30% of the gasoline is used for different transport vehicles, i.e. trucks and buses. This can be seen in Figure 14.

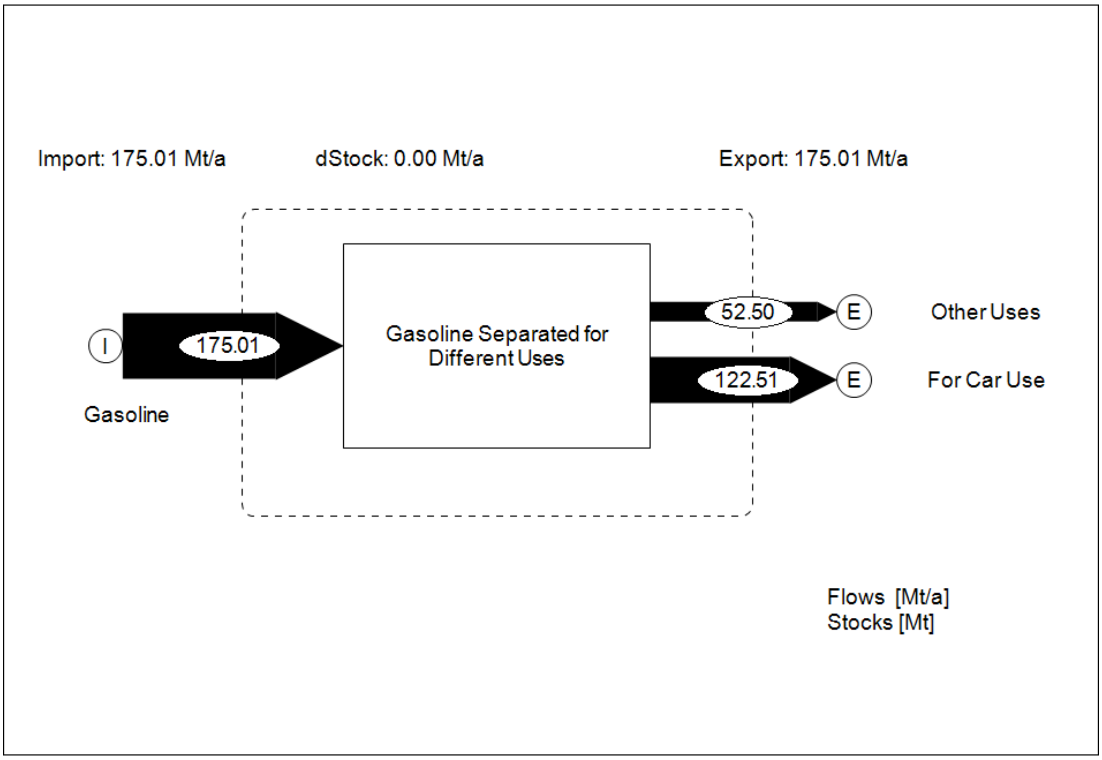

Figure 14: Gasoline Separated for Different Uses in the U.S., 2010 (Source: author)

In order to calculate the amount of CO_2 that is emitted by cars per year, the gasoline combustion reaction is needed: 2 C_8H_{18} + 25 O_2 → 16 CO_2 + 18 H_2O.

First step, convert megatons of gasoline into grams.

1 ton = 1,000,000 grams

122.51 Mt ≡ 12,251,000 t ≡ 12,251,000,000,000 grams

From the chemical reaction, it is clear that for every 2 moles of gasoline that are used, 16 moles of CO_2 are produced.

Second step is to convert grams of gasoline into moles:

12,251,000,000,000 grams of gasoline divided by 114 grams (molecular weight of gasoline) = 1,074,649,123,000 moles of gasoline.

Final step is calculating the CO_2 emissions from the gasoline use:

2 moles of C_8H_{18} produce 16 moles of CO_2

1,074,649,123,000 moles of C_8H_{18} produce 8,597,192,982,000 moles of CO_2

8,597,192,982,000 moles of CO_2 = 378,276,491,200,000 grams of CO_2 ≡ 378.27 Mt/a of CO_2 are produced.

Using the same steps, the values for oxygen and water can be calculated:

Table 8: Inputs and Outputs of the Gasoline Combustion Reaction (Source: author)

		Total Moles Used	**Grams**	**Megatons**
Input	**Gasoline**	85,076,388,890	12,251,000,000,000	122.51
Input	**Oxygen**	13,433,114,040,000	429,859,649,300,000	429.85
Output	**Carbon Dioxide**	8,597,192,982,000	378,276,491,200,000	378.27
Output	**Water**	9,671,842,107,000	174,093,157,900,000	174.09

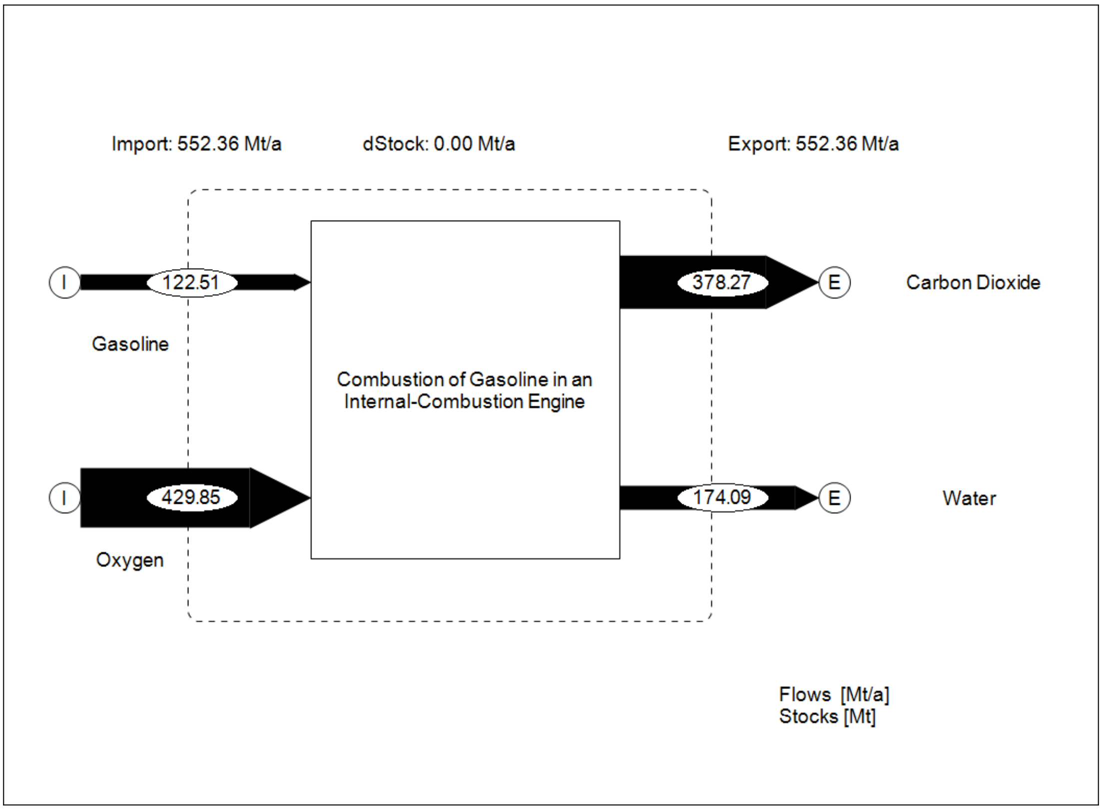

Figure 15: CO_2 Emissions from the Use of Gasoline in Cars in the U.S., 2010 (Source: author)

7.2. CO_2 Emissions from Second-Generation Biofuels (Bioethanol)

On average, an acre of giant miscanthus yields a minimum of 20 tons of biomass, which results in 3250 gallons of ethanol fuel. Another popular second-generation feedstock, switchgrass, yields 3-6 tons of biomass or 400-900 gallons of ethanol fuel. At the moment, 100% ethanol-based fuel is not being used since the energy per unit volume of ethanol is about 30% lower than for gasoline. Most passenger cars now use a blend of gasoline and ethanol in different concentrations ranging from 30-75% ethanol content (E30-E85). Due to the lower energy per unit volume of ethanol, 1.5 gallons of (corn) ethanol (E100) are needed to drive the same distance one could go on 1 gallon of gasoline. The gasoline gallon equivalent for E85 is 1.39 and for E10 it is 1.019 (see Biggs 2013: n.p.).

Let us assume that in the future it will be possible to fuel cars with 100% ethanol. From chapter 7.1., we can see that the U.S. consumes 122.51 Mt/a of gasoline ≡ 43,895,467,570 gallons of gasoline per year. This would mean that the current gasoline consumption in the U.S. would need to be replaced by ethanol (see Figure 16). However, since the gasoline gallon equivalent (GGE) for ethanol is 1.5, the U.S.

would need 43,895,467,570 gallons * 1.5 = 65,843,201,360 gallons of ethanol to satisfy demand.

The gallons of ethanol need to be converted into megatons:

Amount in gallons * 3.7854 L/gallon * 0.7893 kg/L (density of ethanol at 20 °C) * 1 t/1000 kg = ethanol yield in tons

65,843,201,360 gallons * 3.7854 L/gallon * 0.7893 kg/L * 1 t/1000 kg = 196,817,019.5 tons ≡ 196.81 Mt of ethanol fuel.

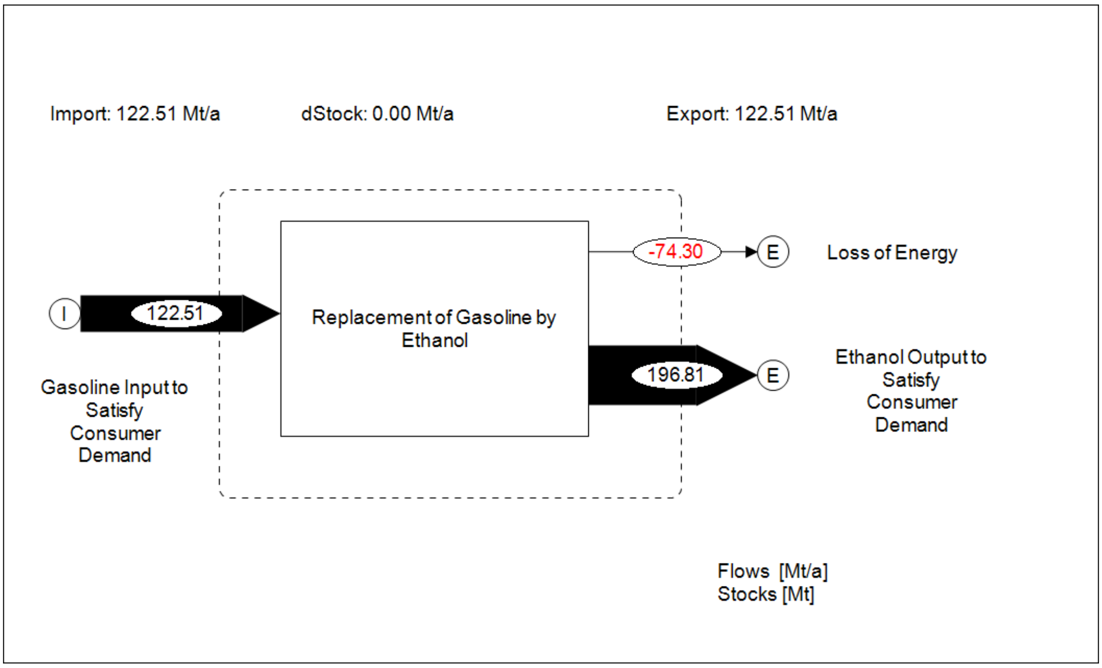

Figure 16: Replacement of Gasoline by Ethanol in the U.S., 2010 (Source: author)

As stated in previous chapters, in order to get an accurate picture of the environmental impact of second-generation biofuels, emissions and inputs at all the stages in the life-cycle should be considered. Though only the emissions at stage-of-use will be considered in the material flow analysis conducted in this thesis, the significance of emissions from other steps in the life-cycle, like the production of biomass, pretreatment, and conversion of biomass to liquid fuel either by biochemical or thermochemical processing, should not be neglected. On average, switchgrass production and harvest results in 116 to 156g CO_2/m^2 (cf. Wang et al. 2013: 5). As an acre of switchgrass yields 6 tons of biomass and 900 gallons of ethanol fuel, the United States would need 73,159,112 acres to satisfy the consumer demand for ethanol. The production of 196.81 Mt of ethanol fuel would result in 34,268,720 to 46,085,520g CO_2/m^2.

What would the CO_2 emissions be from such a replacement of gasoline by ethanol?

The first step is to calculate the grams of ethanol:

1 ton = 1,000,000 grams

196,817,019.5 tons = 196,817,019,500,000 grams of ethanol

The combustion of ethanol has the following chemical reaction: $C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3\ H_2O$

For every 1 mole of ethanol, 2 moles of CO_2 are produced.

Second step is to convert grams of ethanol into moles:

196,817,019,500,000 grams of ethanol divided by 46 grams (molecular weight of ethanol) = 4,278,630,859,000 moles of ethanol.

Final step is calculating the CO_2 emissions from the ethanol use:

1 mole of C_2H_5OH produces 2 moles of CO_2

4,278,630,859,000 moles of C_2H_5OH produce 8,557,261,717,000 moles of CO_2

8,557,261,717,000 moles of CO_2 = 376,519,515,600,000 grams of CO_2 ≡ 376.51 Mt/a of CO_2 are produced.

Using the same steps, the values for oxygen and water can be calculated:

Table 9: Inputs and Outputs of the Ethanol Combustion Reaction (Source: author)

		Total Moles Used	**Grams**	**Megatons**
Input	**Ethanol**	4,278,630,859,000	196,817,019,500,000	196.81
Input	**Oxygen**	12,835,892,580,000	410,748,562,400,000	410.74
Output	**Carbon Dioxide**	8,557,261,717,000	376,519,515,600,000	376.51
Output	**Water**	12,835,892,580,000	231,046,066,400,000	231.04

The CO_2 emissions from the use of ethanol in cars in the U.S can be seen in Figure 17. Here it is assumed that the ethanol will be burned in the internal combustion engines of cars.

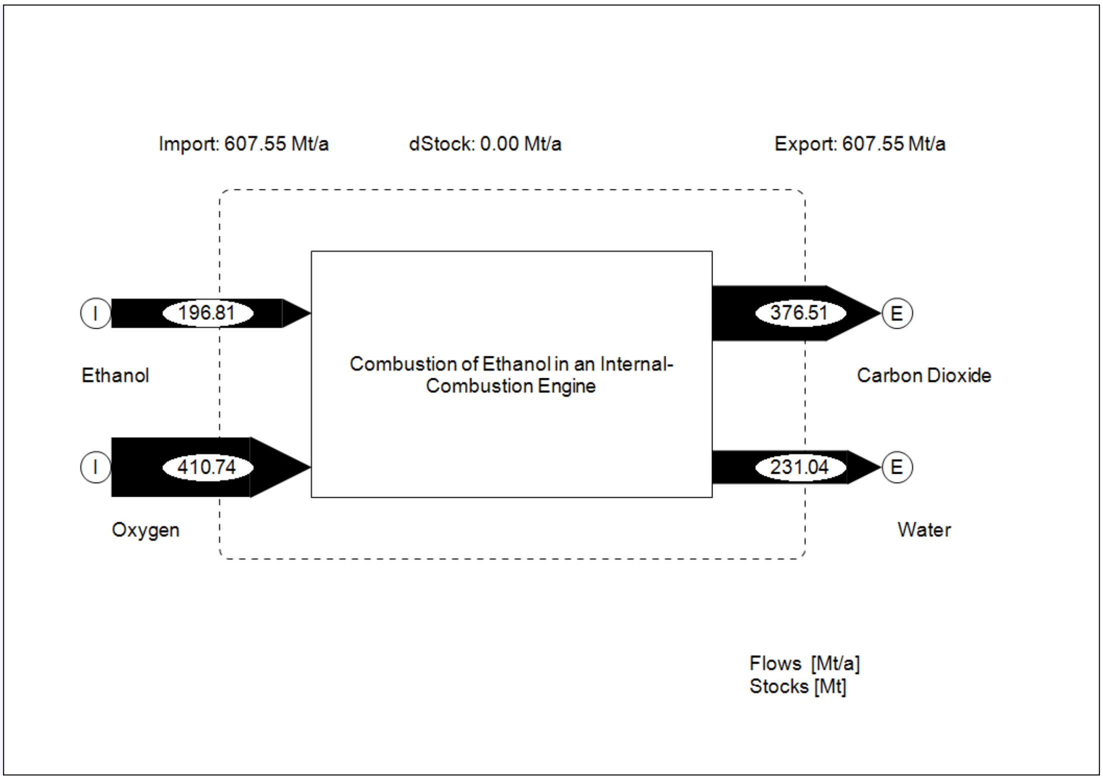

Figure 17: CO_2 Emissions from the Use of Ethanol in Cars in the U.S., 2010 (Source: author)

7.3. Comparison of Results

As we can see from Figure 18, the CO_2 emissions from bioethanol are lower than those from gasoline. 376.51 Mt/a of CO_2 are produced through the use of lignocellulosic-based ethanol, while 378.27 Mt/a of CO_2 are produced through the use of gasoline.

However, as the material flow analysis conducted in this thesis only looks at the emissions at the stage-of-use, it cannot be said if using lignocellulosic-based fuel results in fewer CO_2 over the entire life-cycle. Emissions over the life-cycle of fuel consumption would take into consideration the following processes: feedstock cultivation (farming, seed transportation, fertilizer inputs and fuel for transportation vehicles), enzyme production, bioethanol production (enzymatic hydrolysis), conversion into fuel, combustion of fuel in vehicle, and transportation in between the various stages. Further research is needed to accurately assess the environmental footprint of various biofuel feedstocks before such conclusions can be drawn.

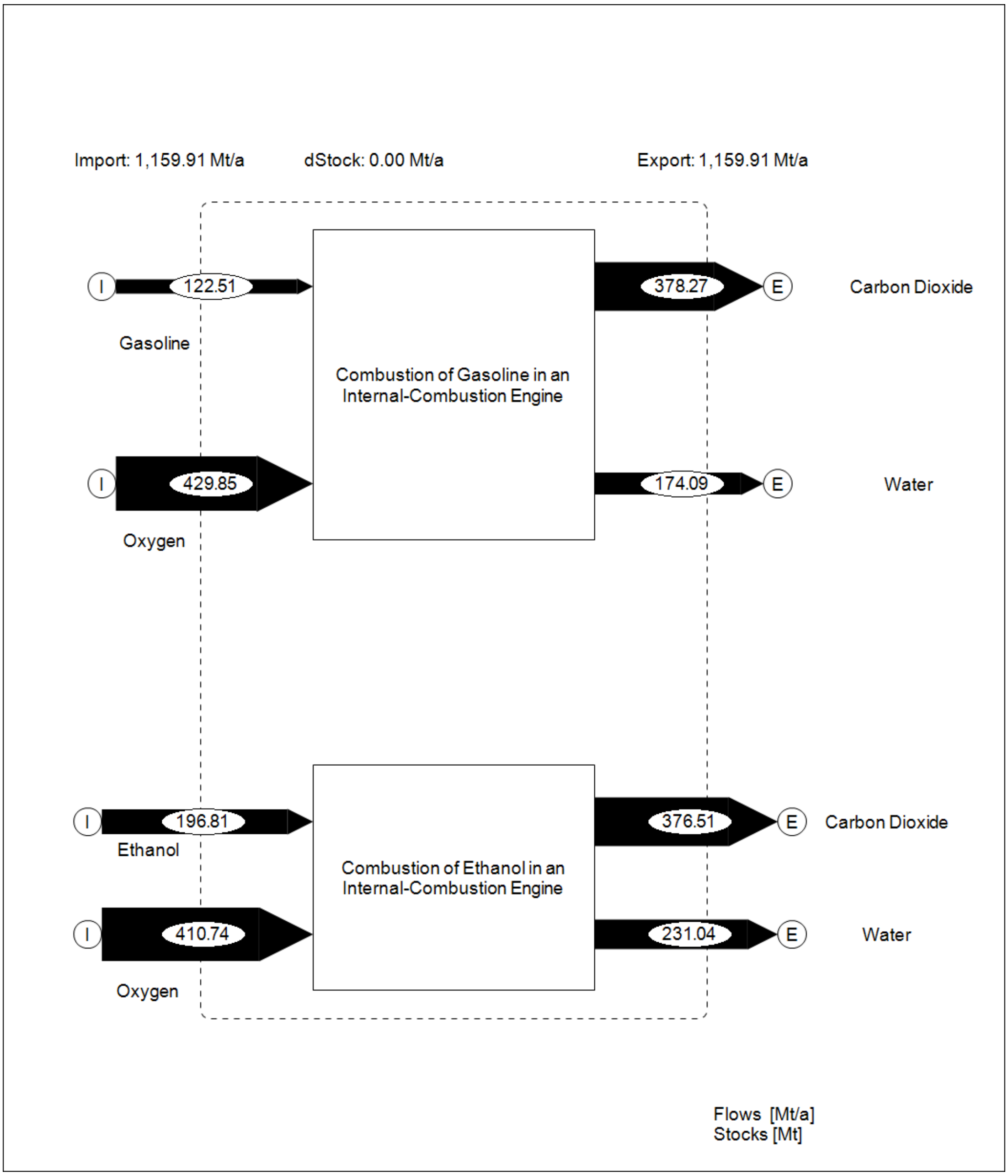

Figure 18: Comparison of the CO_2 Emissions from Gasoline and Ethanol in the U.S., 2010 (Source: author)

8. Outlook

The strong emphasis on lignocellulosic biofuels has been stimulated by four interconnected aspects: the rapidly growing global energy demand, increasing concentration of CO_2 and other greenhouse gases in the atmosphere, climate change dangers, and food scarcity concerns leading to a shift away from the first-generation biofuels. Technological developments and research into best agricultural practices will help lessen the burden on the agricultural industry, which has to feed the world's 7.1 billion citizens while producing large amounts of biomass for fuel purposes. *"The world population continues to increase by about 85 million annually, and within the next decade about 1 billion people will move from rural to urban environments, thus destroying nutritional self-sufficiency and depending on local, regional, and world food markets." (Blum et al. 2010: 64)* The economic potential for lignocellulosic biofuel production depends on the productivity of biomass cultivation, the cost of biomass conversion, and the amount of land that would be used relative to alternate uses. For now however, environmentalists and policy-makers alike are focusing on other renewable energies such as hydro-, wind-, and solar power.

The transition from first- to second-generation biofuels will not gain momentum, until it can be shown that lignocellulosic biofuels are environmentally friendlier than the first-generation biofuels. In countries such as the U.S., Brazil, and Germany, where first-generation biofuels were originally produced, the basic infrastructure already exists, making it easier to shift to another biomass feedstock. However, as long as the costs for first-generation biofuel production remain relatively lower, the prospects for the growth of lignocellulosic biofuels remain dim. Until second-generation biofuels are supported by government policies, grants, and subsidies, more research will go into making first-generation biofuels environmentally beneficial. Continual global research to identify the true GHG emissions of biofuels, regardless of their generation, will help boost capital investments and make the more promising of the biofuels economically viable.

The utilization of agricultural residues for biofuel production currently presents more obstacles than potential economic and environmental benefits, due to the high costs of collection, and importance in maintaining soil quality. Instead of using agricultural residues as a biomass feedstock, the option exists of using the residues for industrial purposes, which may prove to be "greener" than the presently used residue disposal methods (burning or disposal in landfills). Processing residues for use as insulation or as start-up material in the paper industry, instead of the normally used virgin wood pulp, could possibly be a more viable choice. For farmers, agricultural residues can turn into a secondary income source in addition to the income from the standard harvest. It has been estimated that *"a farmer could expect to see a 20 percent increase per acre in net farm income from selling wheat straw" (Hayes n.d.: n.p.).* As burning of residues can cause air pollution and decrease in soil biological activity, farmers would be able to contribute to local environmental improvement by finding alternate uses for these residues. Furthermore, crop residues have been used as animal feed in developing countries, but due to the low digestibility and low protein content, they cannot solely be used as a food source (Owen/Jayasuriya 1989: 131). Improvements in the nutritional value of such residues through treatment or supplement could provide farmers with a cheaper alternative to agricultural residue disposal.

Energy security can only be achieved through capacity building, diversity, and reliability and should not occur at the cost of environmental degradation. Biofuels contribute to increasing diversity and capacity of energy sources, but the reliability of their production is a major drawback to their future success. Uncertainty about the true impact of land use changes and effects of crop residue removal, as well as the high investment costs, are factors that continue to hinder the expansion of biofuels. The diversity of available potential feedstocks and fuel production only adds confusion to the relatively weak understanding of biofuels. Despite large efforts made by scientists in this field, development and commercialization of second-generation biofuels has been very slow. In the long term, investments into research and development of lignocellulosic feedstock, as well as into the conversion process will help lower production costs and make biofuels more affordable. However, this will only be achieved through active government policies and environmentally friendly subsidies.

9. Summary and Conclusion

This thesis addresses various aspects of lignocellulosic-based biofuel production, from the cultivation of the feedstock to its combustion. It also provides a detailed overview of the environmental, social, and economic impacts of the use of these biofuels. Additionally, this thesis presents a straightforward way to compare the effects of gasoline consumption with those of bioethanol consumption.

Summary

The following research questions, posed in chapter 1.1., are answered by this thesis:

- Taking into consideration the demands made on water, nutrients, and land usage, are second-generation biofuels truly more sustainable than first-generation biofuels?

✓ One of the main benefits of the second-generation biofuels is that they are not produced from food crops such as wheat and maize. Furthermore, most second-generation biofuel feedstocks can be grown on marginal lands, thereby reducing competition for arable land that is typically needed for food production. They also have the potential to have higher yields per hectare than conventional crops, thus reducing water and land demand. These biofuels are also expected to result in fewer greenhouse gas emissions due to fewer land use changes and reduced fertilizer inputs. Until further research on the entire life-cycle of second-generation biofuels, from feedstock cultivation to liquid fuel conversion, is taken into consideration, the complete environmental impact remains in doubt.

- What are the limiting factors preventing the expansion of the biofuel market?

✓ The high costs of enzyme and catalyst production, the energy-intensive technologies needed to convert lignocellulose to liquid fuel, low separation efficiency in the pretreatment steps, and the logistics of biomass transportation are some examples of factors that are limiting the commercialization of biofuels.

- Would using agricultural residues and wastes improve the sustainability of biofuels?
- ✓ As residues and wastes are not separately produced, but are just diverted from other streams of use, they may prove to be more sustainable than other biomass feedstocks. The harvest of residues would also lower disposal costs and minimize land use changes.

- What role do agricultural residues play in the maintenance of soil quality and balance?
- ✓ Residues help reduce fluctuations in soil temperature, absorb excess agricultural chemicals, protect the soil from solar radiation and floods, prevent soil erosion, and maintain soil organic content and quality.

- How much waste is produced from a single field?
- ✓ On average about one dry kilogram of residue is produced per dry kilogram of grain or grass.

- What agricultural residues are particularly suitable for the production of biofuels?
- ✓ The use of residues from the cultivation of maize, rice, wheat, and sugarcane would be especially cost-effective, due to their widespread distribution and status as the four major agricultural crops in the world.

- How much energy can be obtained from agricultural residues?
- ✓ The biofuel yields of common feedstocks depend highly on the maturity of the plant and the method and timing of harvest. The ethanol yield can vary between 308 liters per dry ton of forest thinnings to 470 liters per dry ton of corn grain.

- Does the use of bioethanol in a passenger vehicle result in lower CO_2 emissions than from the use of gasoline?
- ✓ With the help of the material flow analysis, it is shown that the use of bioethanol in a passenger vehicle at the stage-of-use results in lower CO_2 emissions than the use of gasoline. However, more research is required to study the entire life-cycles of bioethanol and gasoline in order to accurately state if biofuels are truly the better option.

Conclusion

"Championed as a panacea to climate change, an agent for rural economic regeneration, [and] a means to (…) [secure] energy independence, biofuels have not turned out to be the perfect solution to these policy concerns." (Lin 2010: 6)

As countries turn towards "greener", renewable energy sources, the cost-benefit ratio of biofuels has been increasingly questioned. Despite the ability of some second-generation biofuel feedstocks to reduce greenhouse gas emissions, their widespread distribution could lead to habitat destruction, displacement of agricultural production onto uncultivated, possibly protected lands, harmful air, water and soil emissions, and the possibility of labor exploitation in developing countries. The widespread commercialization of lignocellulosic biofuels still faces a number of technical challenges, such as the costly pretreatment steps, the effective disposal or utilization of process by-products, and the high energy inputs.

Scientists wonder if the use of agricultural and forestry residues could decrease the overall environmental footprint of lignocellulosic biofuel production. Energy production from these residues could save a significant amount of greenhouse gas emissions without requiring additional land or water, because the residues are already generated during food production or logging. However, these residues serve an important role in maintaining soil stability and organic content and in preventing erosion. It remains to be seen whether sufficient amounts of residual biomass could be removed after harvest and/or logging without disrupting the delicate environmental balance.

Second-generation biofuels will only prove to be better than fossil fuels, if the emissions from land use changes, biofuel production costs, fertilizer and water inputs, and energy use can be minimized. However, further research is needed to accurately assess the environmental footprint of various biofuel feedstocks before such conclusions can be made and before biofuels can be declared the best option for a sustainable future.

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List of Figures and Tables

Annex

ANNEX 1

The following table gives an overview of the CO_2 emissions/per capita of selected countries.

	CO_2 emissions/per capita in 2010 (tons/year)	**CO_2 emissions/per capita in 2011 (tons/year)**
Afghanistan	0.02	0.02
Austria	9.00	8.58
Brazil	2.20	2.30
China	6.60	7.20
EU-27	8.57	8.57
France	6.10	5.70
Germany	10.20	9.90
India	1.50	1.60
Indonesia	2.00	2.00
Mexico	3.90	3.90
Nigeria	0.59	0.59
South Africa	7.10	7.20
Switzerland	5.70	5.88
United States	17.80	17.30

(EC EDGAR 2013: n.p.)

ANNEX 2

(adapted from OMAFRA 2011: n.d.)

The following table lists the energy content and chemical composition of some common biomass feedstocks.

Biomass Type	Ash %	Carbon %	Hydrogen %	Nitrogen %	Sulfur %	Oxygen %[1]	Total Chlorine (µg/g)
Grass/Forages							
Big blue stem	6.1	44.4	6.1	0.8	0.1	42.6	1,880
Miscanthus	2.7	47.9	5.8	0.5	0.1	43.0	1,048
Sorghum	6.6	45.8	5.3	1.0	0.1	42.3	760
Switchgrass	5.7	45.5	6.1	0.9	0.1	41.7	1,980
Straw/Residue							
Alfalfa	9.1	45.9	5.2	2.5	0.2	39.5	3,129
Barley Straw	5.9	46.9	5.3	0.7	0.1	41.0	1,040
Corn Cobs	1.5	48.1	6.0	0.4	0.1	44.0	2,907
Corn Stover	5.1	43.7	6.1	0.5	0.1	44.6	1,380
Flax Straw	3.7	48.2	5.6	0.9	0.1	41.6	2,594
Wheat Straw	7.7	43.4	6.0	0.8	0.1	44.5	525
Processing By-Products							
Oat Hulls	5.1	46.7	6.1	0.9	0.1	41.1	1,065
Soybean Hulls	4.3	43.2	6.2	1.8	0.2	44.3	266
Sunflower Hulls	4.0	47.5	6.2	1.0	0.2	41.2	3,034
Wood							
Bark	1.5	47.8	5.9	0.4	0.1	45.4	257
Willow	2.1	50.1	5.8	0.5	0.1	41.4	134
Hardwood	0.4	48.3	6.0	0.2	0.0	45.1	472

Ultimate analysis for a variety of biomass fuels in Ontario (all values reported on a dry matter basis)

The content level of ash, chlorine and other elements can be lowered through crop selectivity, growing conditions, plant fractionation, harvest time and harvest method.

[1]Calculated by difference. Percent by difference refers to the difference between two numbers as a percent of one of them. For example, the percentage difference from 5 to 3 is: 2/5 = 0.4 = 40%.