

A review of biomass utilization in a Northern European context

An overview of biomass innovations

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List of abbreviations:

Aromatic compounds: Cyclic compounds in which all ring atoms participate in a network of pi bonds, resulting in an unusual stability. Typical aromatic compounds are benzene and toluene

Bio-based: A material made from substances derived from living (or once-living) organisms.

Bio-refining: A process of refining products from biomass similar to a petroleum refinery process.

C3 plants: C3 plants flourish in cool, wet, and cloudy climates, where light levels may be low, because the metabolic pathway is more energy efficient, and if water is plentiful, the stomata can stay open and let in more carbon dioxide. However, carbon losses through photorespiration are high.

C4 plants: C4 plants, which inhabit hot, dry environments, have very high water-use efficiency, so that there can be up to twice as much photosynthesis per gram of water as in C3 plants, but C4 metabolism is inefficient in shady or cool environments.

Catalytic processes: A process using a catalyst to increase the rate of a chemical reaction, the catalyst is not consumed and can often be reused.

Cellulose: an organic compound with the formula $(C_6H_{10}O_5)_n$, a polysaccharide consisting of a linear chain of several hundred to over ten thousand $\beta(1\rightarrow4)$ linked D-glucose units.

De-carboxylation: a chemical reaction that removes a carboxyl group from a molecule and releases carbon dioxide (CO_2).

De-hydrogenation: A chemical reaction that involves the removal of hydrogen from a molecule.

De-oxygenation: a chemical reaction involving the removal of molecular oxygen (O_2) from a reaction mixture or solvent, or the removal of oxygen atoms from a molecule.

Enzymes: Large biological molecules which act as catalysts for accelerating both the rate and specificity of metabolic reactions, from the digestion of food to the synthesis of DNA.

Esters: A functional group produced from the condensation of an alcohol with a carboxylic acid. They are characterized by a carbon bound to three other atoms: a single bond to a carbon, a double bond to an oxygen, and a single bond to an oxygen.

Etherification: The process of making an ether by the removal of alcohols from products by reacting it with sulfuric acid.

Fermentation: The conversion of sugar to acids, gases and/or alcohol using yeast or bacteria.

First generation sources: Sugars derived from food crops e.g. sugar cane, corn, wheat, and sugar beet which are used for the production of biofuels.

Fischer-Tropsch synthesis: A collection of chemical reactions that converts a mixture of carbon monoxide and hydrogen into liquid hydrocarbons.

Glucose: An organic compound of simple monosaccharide found in plants which has the following molecular formula $C_6H_{12}O_6$. Glucose is a C6 sugar mainly used as a raw material for ethanol production.

Hemi-cellulose: An organic compound of several heteropolymers containing many different sugar monomers including xylan, glucuronoxylan, arabinoxylan, glucomannan, and xyloglucan.

Hydrolysis: The cleavage of chemical bonds with the use of water as a reaction medium.

Ionic liquid: A salt in liquid state largely made of ions and short-lived ion pairs.

Lignin: A complex organic compound forming an integral part of the secondary cell walls of plants.

Lignocellulosic biomass: plant matter composed of cellulose, hemicellulose, and lignin

Lipids: A group of naturally occurring molecules that include fats, waxes, sterols, fat-soluble vitamins, monoglycerides, diglycerides, triglycerides, phospholipids, and others. The main biological functions of lipids include energy storage, signaling, and acting as structural components of cell membranes.

Methane: A chemical compound with the chemical formula CH_4 which is the simplest alkane and the main component of natural gas.

Monomers: A molecule that may bind chemically to other molecules to form a polymer e.g. a natural monomer is glucose which can bind into polymers such as cellulose

Niche market: A small but profitable segment of a market suitable for focused attention. Market niches do not exist by themselves, but are created by identifying needs or wants that are not being addressed by competitors, and by offering products that satisfy them.

NO_x emissions: A generic term for mono-nitrogen oxides NO and NO₂ (nitric oxide and nitrogen dioxide) emissions.

Oleo chemicals: chemicals derived from plant oils or animal fats

Pectic substances: Structural heteropolysaccharide contained in the primary cell walls of terrestrial plants.

PJ: Peta-joules which is equal to 10^{15} joules.

Second generation sources: Biomass derived from lignocellulosic plant matter e.g. residues or dedicated energy crops such as grasses and short rotation coppice.

Short rotation coppice: Woody biomass cultivated for energy using coppice land management wherein the biomass is harvested above the stems and roots so the plants regenerate from the stems in the following years.

SNM: Strategic Niche Management

Super-critical fluids: Any substance at a temperature and pressure above its critical point, where distinct liquid and gas phases do not exist.

Syngas: Also called synthesis gas, is a fuel gas mixture consisting primarily of hydrogen, carbon monoxide, and very often some carbon dioxide. It has a lower energy density than natural gas.

Third generation sources: Biomass used for biofuel production derived from advanced sources such as algae, bacteria, duckweed or seaweeds.

Transesterification: A reaction between an ester of one alcohol and a second alcohol to form an ester of the second alcohol and an alcohol from the original ester.

Triglyceride: An ester derived from glycerol and three fatty acids. Saturated compounds are saturated with hydrogen. Unsaturated compounds have double bonds ($\text{C}=\text{C}$) between carbon atoms, reducing the number of places where hydrogen atoms can bond to carbon atoms.

US-DOE: United States Department of Energy

Xylose: An organic compound with the molecular formula $\text{C}_5\text{H}_{10}\text{O}_5$, a monosaccharide of the aldopentose type containing five carbon atoms and formyl functional group.

Management summary

The demand for resources and energy has been continuously increasing over the past centuries. Fossil fuels are the main source of energy driving the growth but this dependence is leading to urgent problems e.g. climate change. There is now a general consensus that the economy should move to a more sustainable direction. Biomass is seen as an important alternative energy source and has received much attention over the past decade. The intensified research into the utilization of biomass has led to a large array of technological solutions. This research is conducted for the Arbor project which aims to accelerate the sustainable use of biomass in North Western (NW-) Europe. The project is in need of an inventory of the innovations able to develop the biomass potential of Europe ([chapter one](#)). The theoretical background for the study is the concept of Strategic Niche Management (SNM) which has been proposed as instrument for accelerating the adaptation of sustainable technologies. It is suggested as a method to escape from a so called 'lock-in' within a certain technological system by stimulating the development of alternative technologies ([chapter two](#)). The perspective of SNM is used to analyze the utility of biomass technologies. There are two main research tools used to identify the most promising niches in the field of biomass utilization. A systematic review will be performed to identify 1) the bioenergy crops suited for NW-Europe 2) promising biomass conversion technologies and 3) possible target chemicals for bio-refining. Additionally, the methodology of a PESTEL (Political, Economic, Social, Technological, Environmental and Legal) analysis is used to identify the trends in the macro environment which affect the implementation of biomass technologies ([chapter three](#)). The two streams of research will be used to draw conclusions about the most favorable technological pathways for NW-Europe.

Biomass is often categorized in first, second and third generation biomass sources. First generation sources refer to food-crops such as maize, sugar cane and rapeseed, these crops are currently the main source of bio-fuels. Yet, the crops are generally grown via intensive agriculture and the greenhouse gas emission savings achieved by these fuels appears to be limited in most cases. Second and third generation sources are considered to be more sustainable sources of biomass. Second generation sources refers to lignocellulose biomass which is plant matter composed out of three main components cellulose, hemicellulose and lignin. The biomass can be collected from residue streams e.g. forest and agricultural residues or can be derived from dedicated energy crops such as Willow, Switchgrass and Miscanthus. Residue streams are currently an important source of energy for Europe e.g. via the co-firing of biomass in coal power plants. However, the available amounts of residues are not expected to increase significantly in the future. Dedicated energy crops are needed to considerably increase the sustainability of the energy supply in Europe via the utilization of biomass. Willow, Switchgrass and Miscanthus are second generation biomass sources suited for Northern Europe. The crops are able to achieve relative high yield with low levels of input. However, the processing techniques to derive liquid fuels and chemicals from these sources are currently not commercially available. Third generation sources such as algae and bacteria are able to achieve the highest yields of all sources of biomass. They are a potent biomass source for large scale bioenergy production but many improvements are still needed to make their production commercially viable. Waste streams are currently the most cost-effective source of biomass and can be used to increase the level of biomass utilization in Northern Europe ([chapter four](#)).

Second generation sources are seen as an important future source of renewable energy by the European Union. Yet, lignocellulose biomass is much more difficult to process than first generation sources. Pre-treatment is required to make the biomass suited for conversion. Thermal conversion techniques require only limited pre-treatment. Chopped biomass can directly be used in gasification and pyrolysis techniques (moister content below 20%) or combusted to generate electricity (moister content below 50%). Additional pretreatment processes such as pelletisation or torrefaction can be applied to increase the efficiency of the thermal conversion process as well as to improve the storage properties of the biomass.

More extensive pretreatment processes are needed to allow lignocellulose biomass to be processed via biological transformation. The (hemi)cellulose contained in the biomass needs to undergo a hydrolysis process to transform the molecules into fermentable sugars. An additional pretreatment step is needed to make the (hemi)cellulose molecules accessible for the chemical (acid) or biological (enzymes) hydrolysis process. There are three main categories of pretreatment technologies available to make biomass suited for a hydrolysis process i.e. physico-chemical, chemical and biological treatment (Menon and Rao, 2012). An important aspect in the pretreatment process is the separation of lignin from the biomass because it increases the efficiency of the fermentation process. The diluted acid and steam-explosion processes are well-developed concepts and good candidates for biomass pretreatment. Advanced processes such as the use of ionic liquids, biological or pulsed-electricfield (PEF) pretreatment are also being developed. However, none of the pre-treatment processes is currently commercially available; this is a major barrier for the implementation of second generation biomass sources ([chapter five](#)).

The conversion of biomass into higher value products such as liquid fuels and chemicals can be achieved via three main mechanisms i.e. chemical, thermal and biological conversion. An important aspect in choice of conversion technology is the chemical composition of the original feedstock and the intended product application. Biological conversion methods are mainly used for the production of ethanol whereas thermal conversion methods are able to produce a wider range of products. The economic viability of the biological transformation of second generation sources is currently hindered by a lack of microbes able to ferment non-glucose sugars into ethanol as well as the lack of effective pretreatment methods. Thermal conversion i.e. pyrolysis and gasification are presently the main conversion methods for second generation biomass sources e.g. agricultural residues or Switchgrass. However, the products produced via the thermal conversion methods are of low quality and needs to be upgraded to allow wider use. This is a major challenge for the large scale implementation of thermal conversion technologies since bio-oil and syngas upgrading technologies are currently not commercially available. The greatest potential to reduce the processing cost of second generation biomass sources can be found in biological transformation technologies. Yet, due to the different end products produced by the conversion technologies it is likely that a range of technologies will be commercialized targeting different segments of the current petrochemical market ([chapter six](#)).

Biomass can serve as a raw material for energy but can also be used to derive bio-chemicals. There are more than 300 chemical compounds which potentially could be produced from biomass. The bio-chemical industry is still in its infancy and has not yet been able to identify the most cost-effective bio-chemicals to produce. The technologies to make bio-chemicals are still developing which makes it difficult to predict which compounds will become the most popular. Some bio-chemicals can be directly separated out of biomass but most compounds are produced via the biological, chemical or thermal-catalytic modification of seed oils, animal fats, sugars, glycerol or ethanol. The production of ethylene from ethanol is a well advanced process and is commercially developed in regions with a large ethanol industry e.g. Brazil. Glycerol is the main byproduct of biodiesel production from seed oils and a relative low cost raw material for a range of bio-chemical products. The potential of the bio-chemical compounds: lactic acid, succinic acid, levulinic acid, 5-HMF, furfural, sorbitol and xylitol are also discussed. The development of bio-chemical industry can be an important step for the biofuel sector. The sale of higher value chemical compounds can increase the economic viability of biomass refineries. The lack of feedstock and cost effective conversion technologies currently limits the development of a large scale bio-chemical industry. The most viable short term strategy is to convert biomass into higher value functional products such as food additives, cosmetics, lubricants etc. for which there are no petrochemical alternatives ([chapter seven](#)).

The PESTEL analysis framework serves as a basis for identifying the macro environmental factors which influence the patterns of innovation within the biomass sector. The biofuel sector in Europe would not have existed without the financial support of governments. Bio-fuels offer a politically stable alternative

energy sources for the transportation sector. Yet, the effects of stimulating biofuels on energy security, economic development and greenhouse gas emissions reductions appear to be limited. The opportunity costs of biofuels policies are increasingly scrutinized under pressure from organizations and individuals as well as the current economic downturn. Furthermore, international competition is making it more difficult for farmers in Northern Europe to be competitive in the biofuel market. The greatest potential for biofuel production can be found in tropical regions. The favorable climatic combined with cheap lands and low cost labor makes them very suitable for biofuel production. Wind and solar power are vastly becoming more cost competitive but sunk cost make a quick replacement of the currently infrastructure difficult. The co-firing of biomass for electricity production is likely to remain a cost competitive source of renewable energy for some time. The Renewable Energy Directive 2009/28/EC of the European Union obligates member states to increase the use of sustainable energy to 20% by 2020 with at least 10% renewable energy in the transportation sector. Liquid fuels are important market for clean energy since they have the advantage of being compatible with the current infrastructure. Hydrogen fuel cell or electric cars provide a more radical departure from the current transportation system but are much harder to implement widely. Biofuels are a proven technology and an alternative source of liquid fuels which can be implemented on a relative short time scale ([chapter eight](#)).

Strategic Niche Management (SNM) provided the theoretical background for the study. From the perspective of SNM second generation sources are mostly an incremental innovation compared to first generation sources. The technological opportunities are moderate, the sector is heavily dependent on the support of governments and the environmental benefits are relatively small ([paragraph 8.7](#)). Numerous innovations and support policies are still needed to make large scale energy production from dedicated energy crops economically viable. From the perspective of SNM, the development of agricultural based biofuels cannot be considered an effective policy for steering the economy into a more sustainable direction. Projects based on the use of waste streams or agricultural residues do meet the criteria of SNM. Using waste streams as a feedstock does not compete with food production, has low feedstock costs, can deliver clear environmental benefits and can be used as a means to deal with waste. The production of bio-chemical e.g. from residues streams or dedicated crops is also a niche market able to meet the criteria of SNM. The bio-chemical production is still in its infancy and there are major technological opportunities for improving production methods. Focusing on bio-chemical production in NW-Europe is a sensible strategy since the lower biomass yields in Northern Europe will make it difficult for large scale bioenergy production to become competitive. The multiple technological pathways which can be explored to derive bio-chemicals make it possible to create a diverse portfolio of solutions. This help to create the variation and selection pressures needed for effective SNM. Novel third generation sources e.g. algae or duckweed are also eligible for support from the perspective of SNM. They hold great promise for increasing the sustainability of liquid fuels, have great learning opportunities and are well aligned with needs and values present in society. It can be concluded that support policies should not be aimed at the agricultural based bioenergy but at developing more radical alternative energy technologies. The bio-chemical sector and the use of waste streams do have good potential in a NW-European context and are well suited for SNM policies ([Chapter nine](#)).

Chapter 1 – Research context

1.1 Introduction

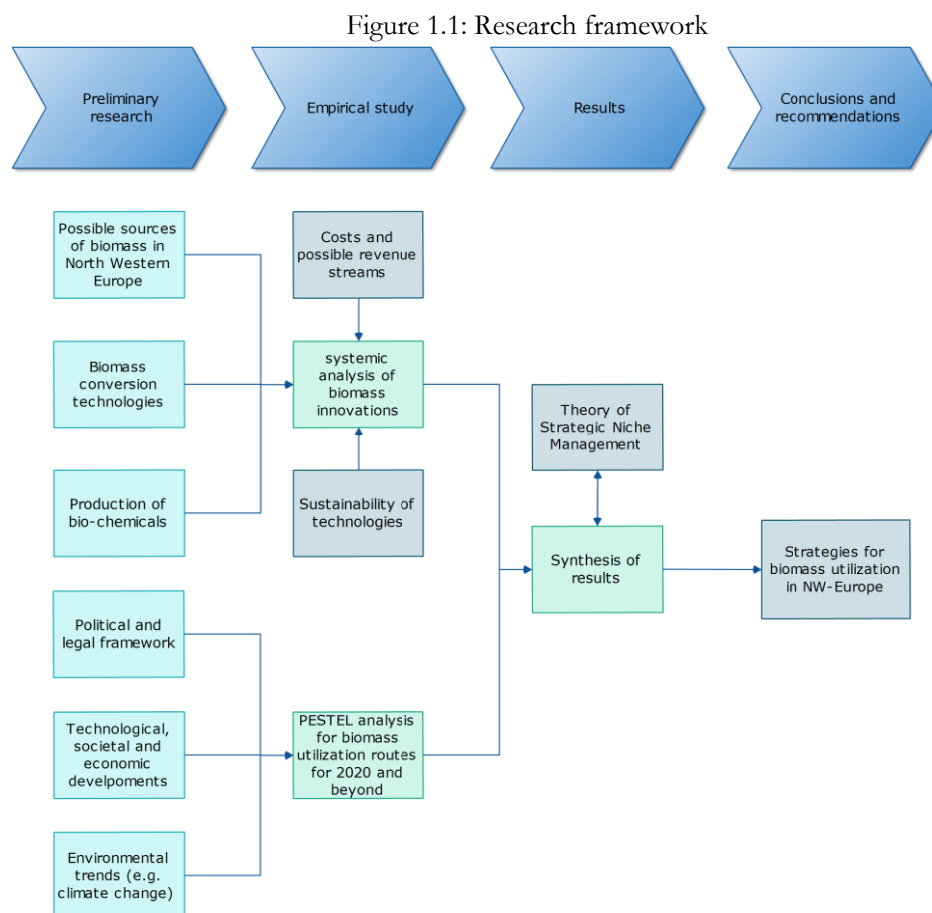
The demand for resources and energy has been continuously increasing over the past centuries. The two main drivers of the increased demand for natural resources have been the industrialization of the world economy and the rise of the human population during the last century (Demirbas, 2009). Plants and animals were the most important sources of energy before the industrial revolution. Fossil fuels are currently the main source of energy but this dependence is leading to urgent problems. The burning of fast amounts of fossil fuels is increasing the concentration of CO₂ in the atmosphere causing a shift in the global climate (IPCC, 2007). Furthermore, the major reserves of fossil fuels are concentrated in politically unstable areas and the depletion of the resources is posing a threat to economic stability. If the current oil consumption rates are maintained then supply will become severely limited during the coming decades (Zhang, 2008). There is now a general consensus that the economy should move to a more sustainable direction (UN, 2012). This will require significant changes in the way in which industrial society use natural resources. However, many of the more environmentally friendly methods of production, such as renewable energy, have difficulty competing with conventional production processes. The additional costs of more sustainable production cycles makes large scale implementation of these technologies difficult (IPCC, 2011).page n

This research will analyze the possibilities for the utilization of biomass to provide industrial resources. The utilization of biomass has received much attention over the past decade. Researchers, companies and governments e.g. EU 2005 and SER 2010 have intensified the research into the use of biomass. This has led to a large array of technological solutions and potential uses of biomass. Numerous papers, articles, books and policy documents have been written concerning the use of biomass (e.g. Tabak 2009, Octave and Thomas 2009, Taheripour *et al.* 2009, IEA 2011). However, many of these documents focus on a single aspect like biofuels and do not provide an in-depth account on alternative uses or neglect the environmental effectiveness of the technologies. Furthermore, the bias towards certain solutions can have an effect on the outcome of the study or policy decision (Briner and Denyer, 2010). It is therefore difficult to decide which of the solutions are the most favourable. This research aims to make a systematic analysis of the relevant literature to assist decision makers with the developing policies for this highly complex field.

The research is specifically conducted for the Arbor project which aims to accelerate the development of the sustainable use of biomass in North Western Europe (NW-Europe). It involves organizations from the UK, Ireland, Germany, Luxembourg, the Netherlands and Belgium. The project intends to foster knowledge transfer between NW-European regions and reduce the barriers for the implementation of technologies transforming biomass into useful products (Arbor, 2012). The University of Wageningen is asked to work on a 'innovation watch' to be able to track the system, process and product innovations that are known, expected and desired. The project is in need of an inventory of the innovations able to develop the biomass potential of Europe in a sustainable manner. The Arbor project is intends to provide useful intelligence to policy makers to help them develop plans for the sustainable utilization of biomass in NW-Europe. The objective of the research is summarized in the following statement: *"To contribute to the development of effective policies for biomass utilization in NW-Europe by providing an inventory of the current and future innovation for biomass utilization based on a systemic review of the literature."*

The theoretical background for the study is the concept of Strategic Niche Management (SNM) which has been proposed as instrument for accelerating the adaptation of sustainable technologies. The main premise is that novel technologies tend to be developed first on a small scale in so called niches. SNM proposes that these niches need to be shielded from market pressures in order to give the technology time to mature. The utility of the biomass technologies will be analyzed from the perspective of SNM. The research will use two tools to identify the most promising niches in the field of biomass utilization. First a systematic review will be made of the possible biomass conversion technologies and

sources of biomass in NW-Europe. Secondly, the PESTEL analysis will identify the trends in the macro environment which can have an effect on the implementation of biomass utilization technologies. The two streams of research will be used to draw conclusions about the most favorable technological pathways for biomass utilization in NW-Europe. Figure 1.1 depicts the research framework used for the study. A research framework is a schematic representation of the steps needed to achieve the objective of the research (Verschuren and Doorewaard, 2010). The first part of the research framework represents the steps needed to perform a systematic review of the literature. The second part of the research framework depicted the PESTEL analysis conducted for the research.



The review will start with an analysis of the possible sources of biomass in NW-Europe. This will be followed by an analysis of the major industrial applications of biomass i.e. bio-energy and the production of chemicals. The technological progress and economic competitiveness of the methods used to produce these products will be assessed. The second part of the research will be a PESTEL (Political, Economic, Social, Technological, Environmental and Legal) analysis of the external macro environment of biomass innovations. The results will be combined to identify those biomass innovations which have the potential to make the energy and chemical production in NW-Europe significantly more sustainable. The central research question for this study is: *“What is the most effective strategy to increase the sustainability of energy and chemical production in North-Western Europe via the utilization of biomass?”* The question will be answered via the following sub-research questions (1) *Based on a systemic review of the literature what are the most favourable technologies for biomass utilization in terms of sustainability, costs and possible sources of revenue?* (2) *Based on a PESTEL analysis for biomass utilization in NW-Europe, which external macro developments are likely to affect the implementation of biomass utilization technologies?* (3) *Based on the results of sub research question 1 and 2, what are the most favourable socio-technical trajectories for the utilization of the biomass potential in NW-Europe?*

1.2 **Biomass as a sustainable resource**

Multiple alternative forms of alternative energy production methods are currently being developed e.g. solar and wind energy. Biomass however is the only sustainable source of energy which is able to produce electricity, liquid fuels as well as the raw materials for the chemical industry. Biomass is a renewable resource and seen as carbon neutral because during the growth of plant matter organisms absorb CO₂. The combustion of the organic matter leads to the same CO₂ emissions as when the material is degraded by natural processes¹. This means no additional CO₂ is released into the atmosphere. Furthermore, the feedstock is distributed relatively evenly throughout the world and the development of biomass production chains can provide a boost to rural economies (Dapsens *et al.*, 2012). For these reasons the utilization of biomass has received much attention from national and international governmental organizations (e.g. LNV 2007, EU 2012, US-DOE 2012). The term bio-based economy is often used to describe a future based on the manipulation of natural process to provide industrial resources (e.g. Octave and Thomas 2009, Dapsens, 2012). The carbon molecules extracted from plants have the potential to substitute many of the products now derived from fossil fuel resources. The concept of bio-refineries, analogous to petrochemical refineries, is used to describe the production facilities for fuels and chemicals derived from a biomass feedstock (e.g. Kamm and Kamm 2004).

In Europe the bio-refining sector is still in its infancy and there is much uncertainty about the best strategy to follow. A large array of potential biomass feed stocks and processing technologies are currently being researched. In the Americas, the processing of biomass, most notably sugarcane in Brazil and corn in the USA, into ethanol is already taking place on a large scale. In 2011 the total production of ethanol for north- and south-America was around 75 billion liters². However, the use of dedicated energy crops which have traditionally been used to produce food is cause for concern. The social sustainability of the ethanol production methods is called into question; is it ethical to fill up our cars with a fuel derived from food while still many people die of hunger every day? There is little enthusiasm for these so called 'first generation' bio-fuels in Asia and Europe where the population densities are much higher (Ghatak, 2011). Furthermore, since fossil fuel energy is needed to cultivate, harvest and process the crops the net environmental benefits of the fuels are not easily determined (Gnansounou *et al.*, 2009). Moreover, cultivating e.g. palm oil in Malaysia on converted rainforest might actually increase the amount of CO₂ in atmosphere (Ghatak, 2011).

The global demand for biofuels has more than tripled since 2000 largely due to governmental support programs (Sims *et al.* 2008, Urbanchuk 2012). In Europe the most notable biofuel is the biodiesel produced from rapeseed oil in Germany. The governmental support program is large driven by concerns over the security of the energy supply, a reduction of energy imports, support for rural economies and potential environmental benefits of the fuels. However, the first generation biofuels have been an expensive method of increasing energy security, provide only limited CO₂ emissions savings, can increase global food prices and can have negative environmental consequence such as deforestation or water depletion. These concerns place limits on the implementation of these technological options in a European context (Sims *et al.*, 2008).

The cumulative concerns over 'first generation' biofuels have increased the interest in the development of biofuels from other sources. Research is now focusing on 'second generation' i.e. agricultural residues and woody biomass and 'third generation' i.e. aquatic biomass resources for the production of fuels and chemicals (Ghatak, 2011). The most ideal source of biomass is currently to utilize the existing waste streams so that the production of fuel and chemicals does not compete with agricultural lands. However, in many regions these supplies will not be sufficient to meet the demand for large scale production (Bentsen and Felby, 2012). The use of non-food crops, i.e. not containing easily accessible sugars or oil and with much higher yields per acre, will be needed in order to make a significant difference. These still compete with arable land for food production but it can greatly reduce the concerns over food

¹ <http://www.agentschapnl.nl/onderwerp/bio-energie>

² <http://ethanolrfa.org/pages/World-Fuel-Ethanol-Production>

security depending on the productivity of the crops. However, lignocellulosic biomass i.e. plant matter composed of cellulose, hemicellulose, and lignin, is much more difficult to process than the sugar and oils derived from food crops. Usually there are more intermediated steps required to produce a useful product from the lignocellulosic biomass making it more costly and technologically challenging (Sims *et al.*, 2008). A multitude of different conversion methods are currently being researched. The biomass can be processed via the use of physical/thermal methods like pyrolysis, with the use of microorganisms, with chemical treatment or by a combination of these methods (Demirbas, 2009).

Currently the second generation biofuels are not competitive and there is no clear technological or commercially preferred route to process second generation biomass into useful products (Sims *et al.*, 2008). There is still a large technological gap between refining oil based hydrocarbon and the refining of hydrocarbons derived from biomass due to the focus on oil based hydrocarbons during the past century. One important aspect of the future economic viability of bio-refineries will be their ability to coproduce multiple products. Biofuels are a high volume but low value product making refineries focused exclusively on fuels less cost effective. Refineries focused on the production of chemicals could be more profitable but these will not be able to deliver large energy savings and CO₂ reductions. Since bio-refinery projects are largely dependent on governmental support, who are also interested in energy security and CO₂ reductions, a combination of biofuel and chemical production seem to be the most favorable route to follow in Europe (Bozell, 2008). The major implementation of these technologies will take at least another decade (Sims *et al.*, 2008).

The implementation of third generation bio-fuels will also take at least another decade. Although there is currently much interest in this field, a lot of research still needs to be done to be able to produce fuels and chemical from micro-organisms like algae on a commercially viable scale (Venter 2012, Daroch *et al.*, 2013). Biomass holds a great potential as a sustainable source of fuel and chemicals but major investments are needed in order to lay the ground work for a future bio-based economy (Sims *et al.*, 2008). However, due to the high uncertainty within the field and the large array of possible technological solutions under development it is difficult for decision makers to develop effective policies in regard to biomass utilization. It is therefore important for policy makers to continuously track the developments in the field to be able to make decisions based on the latest insights and technological developments.

1.3 Concluding remarks

Alternative energy sources are required in order to provide future generations with the energy needed to live a prosperous life. Biomass is seen as an important natural resource for the future energy supply because it can be used to produce electricity, heat, liquid fuels as well as provide the raw materials for the chemical industry. Potential sources of biomass are usually classified as ‘first generation’, ‘second generation’ or ‘third generation’ sources. First generation biomass is biomass obtained from dedicated food crops such as sugar cane or corn. There has been a lot of criticism on these sources of biomass due to their impact on food prices and relative low environmental benefits. Within the European Union the focus has therefore shifted to ‘second generation’ i.e. woody biomass and waste streams and ‘third generation’ i.e. marine sources of biomass resources. Furthermore, the EU developed sustainability criteria in order to guarantee that biofuel are produced in a socially and environmentally responsible way. There are a number of technologies currently under development able to provide a renewable source of biofuels and chemicals. However, many of the second and third generation biofuel refining technologies are still in the development phase and not yet able to compete within the market. There is no clear front runner yet in biomass processing. The sustainable biomass technologies can be implemented faster if the R & D developments are closely aligned with governmental support policies. The Arbor project attributes to bridging this gap by providing decision makers with up to date knowledge about the current state of affairs in the field of biomass utilization. This research intends to contribute to the Arbor project by providing an overview of biomass sources and processing techniques and by identifying the chemical products which could be derived from biomass.

In the following chapter theoretical background of the research context will be discussed in further detail. Theoretical perspectives on innovation are discussed as well as the intervention strategy of proposed by SNM. Chapter three will discuss the methodological approaches of a systematic review and a PESTEL analysis. The research protocol will also be presented. In chapter five a systematic review of the possible sources biomass in NW-Europe is presented. The available pretreatment technologies for biomass are discussed in chapter six. Chapter seven provides an overview of possible conversion technologies for biomass. Possible bio-chemical products are presented in chapter eight. The chapter will all conclude with a discussion on the most favourable technologies for each stage in the product chain. The PESTEL analysis is presented in chapter nine and will form the basis for answering the second sub-research question. The chapter will conclude with a synthesis of the results of the literature review and the PESTEL analysis to answer the third research question. The results will also be related to the theoretical background of the study to determine if SNM can be applied to the biofuel sector. In the final chapter of the research the main research question will be addressed and a conclusion will be drawn on possible biomass utilization strategies for NW-Europe.

Chapter 2 – Theoretical background

Innovation is one of the main drivers of economic progress and an important factor for the successful implementation of more sustainable production methods (Schot and Geels, 2008). The drivers of innovation have been researched by scholars of management studies for several decades. Multiple frameworks, e.g. competitive forces and dynamic capabilities or resources approaches, have been proposed to conceptualize the ability of firms to gain a competitive advantage based on their technological capabilities (Teece *et al.*, 1997). Innovation has now also become an essential element in public policy making due to the broadly supported recognition that the economy should move to a more sustainable direction (UN, 2012). However, the frameworks used to analyze the innovative capacity of single firms are less relevant for those who aim to accelerate the large scale introduction of alternative production methods. To develop effective innovation policies the dynamics of innovation have to be analyzed from a broader societal perspective. This chapter will first discuss the patterns of innovation identified by scholars which can explain why the large scale introduction of sustainable production methods is so difficult. In the following section Strategic Niche Management (SNM) will be introduced. It has been proposed as a policy instrument to accelerate the introduction of sustainable production methods. The chapter will end with some concluding remarks about innovation and the need to implement SNM policies.

2.1 Patterns of technological innovation

The study into innovation, i.e. why some technologies succeed and others fail to catch on, can be divided in two broad schools of thought, the economist and sociologist perspectives. The approaches differ in the sense that economists tend to concentrate on economic factors while sociologists emphasize the social forces that shape technological change. The focus of this research will be on the theories which explain innovations patterns on the basis of social interactions rather than economic logic or pure engineering. The economic perspective on technological change is mainly based on neo-classical thinking. The most important assumption is that technological innovation is steered by the demand and supply of the market. The core assumptions are that a) agents are rational and aimed at profit maximization b) markets attain or move to equilibrium states and c) information needed to make decisions is always available (Bruun and Hukkinen, 2003). However, it is argued that this model is too simplistic as studies have shown that people often make decisions which are not rational from a purely economic perspective (Kahneman, 2011). Furthermore, it is suggested that agents do not have perfect knowledge about the market and tend to rely on existing heuristics and routines.

Evolutionary Economics (EE) was developed in response to the criticism and recognizes that decision makers do not possess perfect knowledge (Bruun and Hukkinen, 2003). As with Darwinian evolution it is argued that technology develops in a cumulative matter, wherein unsuccessful designs are abandoned, in response to certain variation and selection pressures (Bruun and Hukkinen 2003, Raven 2005). Technological change is not considered to be completely random because innovation tends to cluster around certain problems and solutions i.e. technological paradigms. This restricts the imagination possibilities or creative processes of organizations and can lead to the development of standardized technological trajectories (Dosi, 1982). Nelson and Winter introduced the closely related concept of ‘technological regimes’ to conceptualize the cognitions of technicians, engineers, scientists and decision-makers which determine what kind of innovations are developed (Kemp *et al.*, 1998). The alignment of cognitions around certain technologies can limit the ability of actors to consider the development of alternative solutions.

Two of the patterns of innovation distinguished by Schumpeter are instructive for understanding how such a technological paradigm or regime can emerge. The first is the pattern of ‘creative destruction’ whereby new firms introduce new ideas and innovations which are able to attract a significant market share, a process referred to as widening. The second and most common pattern of innovation is referred

to as deepening in which incumbent firms are mostly oriented to process innovations (Breschi *et al.*, 2000). During the process of deepening organizations become increasing static because the production processes are standardized and technological progress slows over time. Production costs are reduced whereby larger firms gain a significant competitive advantage i.e. economies of scale (Utterback and Suhez, 1991). The accumulation of resources in large firms and their ability to continuously innovate production processes makes it increasingly difficult for new firms to enter the market. The routines of the dominant actors act as a powerful barrier for new players to enter the market (Breschi *et al.*, 2000). Societies can become 'locked-in' in sub-optimal technological trajectories because incumbent firm have huge advantages e.g. political strength, knowledge networks, financing and institutional alignment over new technologies (Elzen and Wieczorek, 2005). Large scale technological systems e.g. the energy sector tend to change slowly because the main focus is on incremental innovation and furthermore there are entry barriers which shield the market from radical innovations (Weber and Rohracher, 2012).

Radical innovations incorporate a substantial different technology that can provide a higher consumer benefits than previous products. Usually these technologies diffuse slowly at first or fail to catch on entirely due to problems with implementation and institutional alignment (Raven and Verbong, 2007). Incumbent firms are thought to be reluctant to introduce radical innovations for three main reasons 1) the perceived incentive is lower for incumbent firms because a radical innovation could jeopardize the profits made on the existing product base 2) organizational filters are in place that focus the attention on maximizing the utility of existing technologies 3) the organizational routines are geared towards incremental innovations since radical innovations are difficult, costly and risky (Chandy and Tellis, 2000). It is suggested that large firms are more prone to inertia due to their greater level of bureaucracy which makes them slow to react to radically new products.

On the other hand, incumbent firms also have better opportunities to develop radical innovations. They have greater knowledge about consumers and people are more willing to accepted radical innovations from established firms. The firms have a greater market power, better distributions channels and are less vulnerable to the failure of a single R&D project. Since the Second World War the number of radical innovations from major incumbent firms has increased and they are now more likely to introduce radical innovations than small firms. The main reason for this is that products are becoming more complex and their development requires large R&D expenditures (Chandy and Tellis, 2000). To develop the technologies needed to build a more sustainable economy both large and smaller firms will need to pursue the development of radical innovations.

From a sociologist perspective innovation is not the result of an economic rational but emerges from societal preferences. The *Social Construction of Technology* (SCOT) argues that technological change is the result of a social processes rather than a technological or economic logic (Bruun and Hukkinen, 2003). Initially people view the utility of artifacts, e.g. a product or service, in many different ways which leads to multiple interpretations of its use. However, when one or a combination of interpretations becomes dominant, controversies about the design fade away. Stabilization occurs and a 'technological frame' develops in which meaning is attributed to a certain technology. The nature of technological change depends on the technological frames which surround the technology. If no single frame is dominant than problems are addressed in an unbiased way and there is more room for radical innovation. However, in the presence of a dominant technological frame innovation tend to follow existing patterns of thinking (Bruun and Hukkinen, 2003). The notions of technological paradigm, technological frame and the concept of technological regimes can explain why social-technical systems tend to change slowly (Breschi *et al.*, 2000, Lovell 2007, Nill and Kemp 2009).

Specific technological pathways emerge because firms engage in a cumulative process of innovation and social preferences are aligned to their technologies. Engineers determine what is feasible so they are more likely to innovate on technologies that are related to their own activities (Raven 2005, Leten *et al.* 2010.) Firms in top positions have means to continuously improve their production processes and develop their competitive advantage, especially when the intellectual property is well protected

(Breschi *et al.*, 2000). Incumbent firms also have an incentive to raise entry barriers for new competitors. For instance, patent strategies are commonly used by large firms to reduce the chances for new entrants into the market (Czarnitzki *et al.* 2010). These theories on technological development emphasize that technological change is not random but has a structured nature i.e. it tends to follow recognizable patterns. Dominant actors can create a stable ‘technological regime’ because the societal rules, dominant cognitions and innovation activities are aligned to their activities (Bruun and Hukkinen, 2003). The result can be a ‘lock-in’ in a sub-optimal technological system even though other technologies exist which provide a higher net social benefit (Nill and Kemp, 2009). Patterns of innovations cannot be simply deduced from demand and supply forces within the market but are the result of social interactions on multiple levels.

2.2 Strategic Niche Management

Strategic niche management (SNM) has been proposed as a policy instrument to escape from a ‘lock-in’ by stimulating the development of alternative technologies. This research will use SNM to analyze the utility of the biomass innovations discussed. Furthermore, it can be used as a basis for the development of future Arbor projects. SNM can be defined as (Kemp *et al.*, 1998): *“the creation, development and controlled phase-out of protected spaces for the development and use of promising technologies by means of experimentation, with the aim of 1) learning about the desirability of the new technology and 2) enhancing the further development and the rate of application of the new technology”*. SNM is based on insights from the SCOT, EE and constructive technology assessment (CTA) (Raven 2005, Verbong *et al.* 2008). It is intended for technologies which are socially desirable on a long-term and constitute a radical novelty faced by market barriers (Schot and Geels, 2008). The main premise is that radical new technologies tend to be developed on a small scale before they are disseminated further (Nill and Kemp, 2009). Radical innovations are usually first developed for the local market and constitute a specific application i.e. a market niche. These technological niches are seen as breeding grounds for new innovations (Raven, 2005). Places to test a technology, to create networks, stimulate learning and the development of proto-markets to jump-start innovation.

SNM focuses on developing and supporting niches of promising technologies to stimulate experimentation and learning around social desirable technologies (Schot and Geels, 2008). Technological niches can be temporarily shielded from market pressures by subsidies or private support because of potentially high economic or social returns. Experiments can bridge the gap between variation and selection pressures leading to a more rapid diffusion of alternative technologies (Raven, 2005). SNM recognizes that policies might have to be adjusted in the face of changing circumstances. It therefore focusses on organizing the variation and selection pressures and not on specific technologies (Nill and Kemp, 2009). It is not intended as a top-down technological push strategy with a set of pre-defined policy goals. Rather, it is meant as a dynamic tool focused on the policy process, interactive learning, networking and institutional adaptation (Raven, 2005). SNM can be used by governments but can also be implemented by NGOs or other societal groups (Schot and Geels, 2008).

SNM strategies can be developed with the following intervention cycle: the choice of technology, the selection of experiments, the set-up of experiments, scaling up of experiments and the subsequent breaking down off the protection measures. A technology must have certain attributes in order to make SNM effective. First, it needs to have major technological opportunities. Second, it must exhibit increasing rates of return or great learning opportunities. Third, it must be compatible with important user’s needs and values that are already present in society. Finally, it needs to be an attractive option for various applications in the current market. The experiment should preferably be set up in an environment where the user benefits are more important than the additional cost of investment e.g. large emissions savings. Furthermore, to stimulate the co-evolution of technology it is important to explore a variety of options simultaneously (Kemp *et al.*, 1998). The selection of projects must be based on a vision for sustainability and the interest of the local stakeholders. Three internal interactions are identified as important factors in

successful niche development (1) The articulation of realistic expectations and visions which are relatively specific and shared by a number of actors. (2) The building of social networks which are broad and characterized by a high level of commitment. (3) The level of the first and second-order learning e.g. on technical aspects, design specifications, market and user preferences, cultural and symbolic meaning, infrastructure networks and environmental effects (Schot and Geels, 2008).

In order to generate selection pressures SNM measures should be implemented temporarily. The policies must be based on the specific barriers that are faced by the technology which is supported (Kemp *et al.*, 1998). The example of the Dutch wind energy sector showed that too generous subsidies can lead to technological stagnation. A balance needs to be sought between creating stability for investors and the objective of evolutionary technological development (Nill and Kemp, 2009). Niches can become successful if there is a pattern of continuous and parallel developments leading to more stability around the technology (Raven, 2005). SNM has shown to be useful for stimulating learning processes, the facilitation of networking and preparing technologies for market introduction (Raven 2005, Nill and Kemp 2009).

Empirical experiences with SNM are scarce and some well-prepared niche strategies e.g. Swiss electric cars, have not led to a wider implementation of the technology. SNM has been criticized for being too simplistic, too much focused on a bottoms-up approach and neglecting wider societal trends (Raven 2005, Nill and Kemp, 2009). The positive feedback generated by experiments was weaker than expected (Raven, 2005). Without wider acceptance within society, governmental support alone will not lead to successful implementation of niche innovations. It is even argued that the role of government in SNM is unwanted and ineffective. Governments tend to be deeply imbedded into the dominant social-technical system making them biased towards certain solutions. Niches could be the target of policy not to change the status quo but to act as a showcase for policies supporting sustainable innovation. Political points can be scored without the need to implement structural changes. The inclusion of non-governmental actors is therefore important to maintain the integrity of the process and make sure it is indeed focused on structural changes (Lovell, 2007).

The measures implemented during the last decades to support the introduction of renewable energy technologies in the Netherlands were analyzed by Verbong *et al.* (2008). The support for niche innovations is initially characterized by high expectations. Innovators make high promises to attract funding but these expectations generally proved to be too optimistic. Technical problems emerged leading to slower implementation than expected. Support was usually based on a technological push approach while aspects such as the commercial prospects, societal acceptance or the legal framework were neglected. In many cases the process was dominated by regime actors, subsidies were divided among incumbents and outsiders were hardly involved. Industrial and economic arguments were prominent, not the need to radically transform production methods. Furthermore, the instability of policy measures and lack of long term commitment lead to a limited learning curve for niche innovations. The Dutch government has tried to stimulate the introduction of renewable energy technologies for over 30 years. Yet, the Netherlands still ranks low on the implementation of renewable energy compared to other Europe countries (Verbong *et al.*, 2008). Experiments have usually been too isolated events not connected to a broader strategy. The power of experiments to induce structural change is limited since they have mostly an indirect effect. No single niche innovation alone can transform a regime which is why external factors also need to be addressed (Schot and Geels, 2008). As a standalone policy instrument SNM appears to be insufficient to significantly alter a stable regime (Weber and Rohrer, 2012). It should be part of a wider and integrated evolutionary approach providing long term support for sustainable innovation (Nill and Kemp, 2009). The success of niches does not only depend on the quality of the experiment but also on the support and acceptance of the technology by society and industry. The perceptive will be used in this research to analyze the potential of the biomass utilization technologies to steer technological development into a sustainable direction.

2.3 Concluding remarks

The theories on innovation presented in this chapter all point to ways in which technology can become 'locked-in' in certain innovation patterns. Technological change is not simply the result of a supply and demand model which moves markets to equilibrium but results from the complex interaction between economics, technological developments and societal preference. The linkages and interaction between actors at the level of niches, i.e. the dominant technological regime and the macro environmental forces, over which individual actors have little control, influence the speed and direction of change. It is therefore important to look beyond simple input-output relations in order to effectively steer technological development into a more sustainable direction (Nill and Kemp, 2009). Strategic Niche Management (SNM) has been proposed as a strategy to stimulate radical new innovations. It is argued that emerging innovations need to be temporarily shielded from market pressures in order to give them time to develop. SNM has shown to be able to stimulate learning and the formation of networks around technologies. However, the approach has been criticized for being simplistic, too much focused on a bottoms-up approach and neglecting wider social trends. Examples from the Netherlands show that people are usually too optimistic about the prospects of novel innovations. The failure to meet these expectations decreases support and eventually prevents wider implementation of the technology. No single experiment can shift a technological regime; broad and long-term support from industry and society is needed in order to induce change. Consumers, politicians, large companies and small firms will all need to be engaged in an evolutionary cycle of innovation in order to develop the technologies capable of moving the economy into a more sustainable direction. The success of biomass as an alternative energy source will heavily depend on the support from society, businesses and governments for the technological solutions it can provide.

Chapter 3 – Methodology

The concept of Strategic Niche Management has been proposed as an instrument to accelerate the introduction of sustainable production methods. The aim is to lower the entry barriers into a market by providing protected spaces in which technologies can develop. SNM requires the identification of promising technologies which are able to provide a viable alternative to current production methods. This research will use the methodology of a systematic review to analyze which technologies for biomass utilization provide high net social benefits and are thus eligible for support. A systematic review is a method of assessing the available literature in a transparent and systemic way; this will be explained in the first paragraph of this chapter. SNM has been criticized for being too much focused on individual experiments and neglecting wider social trends. The research will therefore also make use of a PESTEL analysis to identify the macro environmental developments which are likely to affect the introduction of biomass utilization technologies, see paragraph 4.2. The two methodological approaches will form the basis for identifying the most favourable technological pathways for the sustainable utilization of biomass in NW-Europe.

3.1 Systematic reviews

This section will address why systematic reviews are an important tool for researchers as well as explain how they can be conducted. Policy makers are increasingly expected to make decisions based on scientific evidence. However, in the last 20 years the amount and availability of research information has exploded making it impossible to keep up-to-date on all scientific research. Information is often scattered making it difficult to make sense of the knowledge base. Furthermore, placing faith in a single study to draw general conclusion is often misleading (Mulrow, 1994). A larger sample of the literature is needed to be able to provide a reliable answer to a question e.g. via a systematic review. Standard method of synthesizing the available knowledge base is by conduction a literature review. Yet, literature reviews are vulnerable to the bias of the researcher because people can be influenced by their own favorite theories, their research funders or the need to get a publication (Petticrew and Roberts, 2006). Reviews are usually intended to build an argument about the importance of a field of study or to identify existing knowledge gaps. There is a possibility that researchers have cherry picked literature sources since the methods used to select papers are usually not communicated (Briner and Denyer, 2010).

Systematic reviews are a method of organizing the available literature in a more scientific manner. It is aimed at limiting the systematic error (bias) by attempting to identify all the relevant studies needed to answer a question (Petticrew and Roberts, 2006). Systematic implies that the reviewer uses an appropriate research design and explicitly communicates how the review is conducted. It is widely used in fields such as medicine and education but not so much in management and organization studies (Briner and Denyer, 2010). The main difference with a traditional literature review is that the protocol for searching studies that to be included in the review are determined in advance of the review. The key features of systematic review can be summarized as following (Briner and Denyer, 2010 p.11):

“Systematic/organized: Systematic reviews are conducted according to a system or method which is designed in relation to and specifically to address the question the review is setting out to answer.

Transparent/explicit: The method used in the review is explicitly stated.

Replicable/updatable: The method and the way it is reported should be sufficiently detailed and clear such that other researchers can repeat the review, repeat it with modifications or update it.

Synthesize/summarize: Systematic reviews pull together knowledge in a structured and organized way in order to summarize the evidence relating to the review question.”

An essential element in systematic reviews is the research protocol which details the process and research methods used in the review. This is not intended as a rigid action plan and can be adapted if needed once the study has begun (Petticrew and Roberts, 2006). The protocol is intended to ensure that

the key features of a systematic review i.e. systematic, transparent and replicable are respected. Four broad steps are required to conduct a literature review; the steps need to be made explicit in the review protocol (Briner and Denyer, 2010). First, a relevant review question needs to be developed. This can best be done in collaboration with the commissioners of the research or researchers assisting the reviewer. The literature should also be evaluated to see if other systematic reviews have already been done in the field. Once a question has been determined, a comprehensive literature review needs to be carried out to locate and select relevant studies for the review (Petticrew and Roberts, 2006). Grey literature can also be included depending on the scope and nature of the research. Papers found via e.g. electronic databases need to be screened in more detail and the references can be examined to find additional publications of interest. Furthermore, citation searches or asking experts for advice may also be a useful method of finding relevant papers (Briner and Denyer, 2010). A systematic review is guided by a set of principles, not a standard protocol which can be applied to all reviews. For instance, the importance of grey literature depends on the availability of information in the academic literature. If there are few relevant published articles then it becomes more important to include additional sources (NBS, 2011).

The decision to include or exclude certain studies must be based on the inclusion/exclusion criteria developed in the research protocol. The criteria describe the types of studies which are eligible for in-depth review and those that can be excluded. In the field of medicine the 'Hierarchy of Evidence' is often used to rank the designs of studies according to their ability to answer questions about effectiveness. The highest form of evidence to prove the effectiveness of an intervention is systematic reviews/meta-analyses and the lowest are case-control studies. This could be used as a guide to develop the criteria for a review about the effectiveness of a certain intervention. Other criteria may be the use of qualitative or quantitative data and the types of outcome of the studies. The choice of the criteria is not standardized but is based on the decisions made by the researcher. A range of studies may be included in a systematic review as long as the choices are motivated and documented in the research protocol (Petticrew and Roberts, 2006).

Once the sources which are to be included in the study have been identified, the quality of the data found in the studies needs to be assessed i.e. critical appraisal of the studies. It is important to determine if the studies are adequate for answering the research question. For instance, some may have systematic errors or contain too little information on the methods used in the study. There are multiple check-lists available for assessing different kinds of research e.g. randomized controlled trials or case control studies. The goal is to find errors that are large enough to possibly affect the outcome of the study. Studies can be ranked as high, medium or low quality based on e.g. brand of the journal, number of citations or internal validity of the study. The review protocol should contain a checklist with questions for the critical appraisal of the studies in order to make sure that it is transparent and repeatable.

The assessment of the quality of the studies is often an integral part of the data extraction process. During the data extraction processes the relevant information from the studies is collected and stored in a database. There is a danger of creating a data-extraction bias based on e.g. the disciplinary background of the researcher. To ensure that an unbiased data extraction process was done the process can be validated by another researcher (Petticrew and Roberts, 2006). The next stage in making a systematic review is to synthesize the results and write a report. The goal is to break down the individual studies into components and see how they relate to each other. By combining the studies new knowledge is created which is not apparent from the individual studies. The synthesis should lead to a greater understanding of the subject under study than can be learned from a single study (NBS, 2011). The findings of the study can be organized in tables based on e.g. methods, results or quality. This is especially important for narrative synthesis and a meta-analysis but can increase the transparency of all systematic reviews (Petticrew and Roberts, 2006).

It will depend on the research topic and the methods used which form of synthesis is most appropriate. Overall, there are four things which the synthesis should aim to do. It should 'tell the story' to paint the bigger picture of the research field. It should categorize constructs to make it easier to

interpret the data. Furthermore, the relationships between the data should be made explicit and it should infer what the study means for those who want to make use the results (NBS, 2011). In management studies the focus is usually on the narrative of the synthesis i.e. address different aspects of a subject and uses the information to map out the bigger picture. The final stage of a systematic review is to disseminate the review findings to a wider audience e.g. by publication or by making it available online (Briner and Denyer, 2010). The methodology of a systematic review will be used in this research mainly to make the selection of the papers to include into the study more transparent.

3.2 PESTEL analysis

A PESTEL analysis is a strategic planning technique which can be used to analyze the external environmental pressures on an organization. It will be used in this research to analyse the macro environmental developments which effect the utilization of biomass. It is an easily understandable tool used to summarize large scale developments which can influence an organization. PESTEL stands for Political, Economic, Social, Technological, Environmental and Legal macro development. The PESTEL analysis is similar to a PEST analysis but has two additional categories namely, environmental and legal. The two categories are included due to their relevance to biomass utilization techniques. The legal aspects are of interest due to governmental support policies for biomass technologies and EU regulation on sustainability criteria for bio-fuels. Other similar techniques such as the DEEPLIST analysis or the InSPECT analysis are less suited for the purpose of this research. The InSPECT analysis does not include any environmental or ecological factors. The DEEPLIST analysis is similar to the PESTEL framework but includes the category informational intended to analyze the knowledge position of a single firm. This category is not relevant for this research.

The factors included in a PESTEL analysis cover the most important aspects related to the utilization of biomass. The political factors should indicate to what extent a government may influence a certain industry e.g. tax policies or trade tariffs. Economic factors refer to the influences that stem from macro-economic developments such as economic growth, inflation rates, foreign investments etc. Social factors include those cultural trends, demographic developments etc. which can have an influence on an organization. Technological factors refer to the how innovations are developed and how they may affect the operations of an industry. Legal factors include the effects of regulation, old and new, on an industry. Environmental factors are the influences of the surrounding environment such as climate change or the attitude of governments and industry to environmental issues³. A summary of the range of different factors which can be considered in a PESTEL analysis can be found in appendix 2. The outcomes of the analysis can be ranked according to the significance of their impact (Trodd, 2007). The advantages of using a PESTEL analysis are that it is easy to understand and that it can incorporate a wide range of external factors. However, the macro environment is very complex, dynamic and constantly changing which makes predicting relevant trends difficult. The listed factors are arbitrary and the interpretation of their relevance is subjective. A PESTEL analysis can help identify key factors that influence an organization but the macro environment should be continuously monitored to incorporate changing circumstances. The PESTEL included in this research will be able to give an indication of the most important trends affecting biomass utilization but should not be seen as a definitive list of factors.

3.3 Research Protocol

This section will present the research protocol used in the study wherein the methods of data collection are made transparent. The research will focus on the utilization of biomass in NW-Europe. A macro-economic analysis will be made of the potential sources of biomass in a North-Western European context. The review will analyze the potential of biomass utilization for energy and chemical production. It is intended as an international overview of technological innovations for biomass utilization. The main source of knowledge will be review studies published in the academic literature. The review studies

³ <http://pestleanalysis.com/>

provide insight into the general trends in biomass research and are less prone to be too optimistic over single technological solution. The topic of biomass has been extensively studied over the past decades. Similar review studies have published (e.g. Limayem and Ricke, 2011 and Robbins et al., 2011) which provide good overviews of the current innovations in biomass utilization. However, since the field of biomass utilization is complex the studies are usually not able to address all aspects of the issue. For instance, reviews on the production of chemicals usually do not discuss the potential source of biomass in detail. Yet, the chemical composition of the biomass and chosen conversion method are important to consider when determining which chemicals to produce. The aim of this review is to identify multiple review studies to provide a comprehensive overview of the total supply and value chain of biomass utilization, table 3.1 shows the research planning for the research.

The inclusion criteria for the study will be:

- Relevance to the research questions
- Date of publishing 2000 and later
- Reviews published in scientific journals
- Biomass sources must be suited for a North-western European context.
- Papers must review biomass innovations

The Exclusion criteria will be:

- Sources focused on case studies
- Publications not available via WUR search engines.
- Papers focused on waste treatment
- Reviews not dealing with technological innovation
- Reviews focused on genetic engineering
- Reviews dedicated to economic or environmental analysis

Two main databases namely Scopus and Web of science will be used for the research. English reviews discussing innovations for biomass utilization published after 2000 are included. The quality of the data i.e. critical appraisal of the reviews was assessed based on the following check list. Is the review relevant for the study? Is the study published as peer reviewed paper in a scientific journal? Does the study focus on biomass sources or conversion technologies? Is the study providing an overview of technological innovation? Does the study meet all inclusion and exclusion criteria? Studies which are able to meet all these criteria were included in the review.

The search strings for information gathering were developed by screening the key words listed in the publications found via basic search strings. The search string 'biomass and chemicals and products' was used for an initial search on the topic of bio-chemicals. The first two hundred most cited hits were screened; the key words from 34 papers were extracted. The most cited key words were used to develop the following key strings for the topic of bio-chemicals 'Renewable AND Chemicals OR Chemical AND Biorefinery OR Bio- refineries OR Biorefining' and 'Biobased economy'. The string was used in Scopus and Web of science in February 2013. The results were refined on review papers only and further screened on their relevance for the research. Forty-five review papers were found to be of interest for this study. Sixteen additional papers were found by looking at frequently cited references. The papers were read in further detail and used as a basis for the section on bio-chemicals.

The keywords 'biomass and crops and Europe' were used as an initial search string in Scopus to find publications on the subject of biomass sources in Europe. The first 200 papers were screened to find relevant key words on the subject. Forty-two papers were found to be of relevance and their key words collected. The string was 'Biomass and Europe or Energy crops or Bioenergy or Residues or Waste' was used in Scopus and Web of science in March 2013. Fifty-five papers were found to be of interest for the study. Nineteen additional papers were extracted from the references. The papers were read in further detail and used as a basis for the section on the sources of biomass suited for NW-Europe.

The keywords 'biomass and energy' were used as an initial search string in Scopus to find relevant publications on the subject of biomass conversion. The first 200 hits were screened on their relevance for the research. Key words were extracted from 82 studies. Based on these key words the search string 'Biofuel or bioenergy and renewable and conversion and hydrolysis or pyrolysis or fermentation' was developed to search for publications on biomass conversion technologies. The search string was used in Scopus and Web of science in March/April 2013. Seventy-six studies were found to be of interest and read in more detail, these serve as the basis for the section on biomass conversion technologies. No additional papers were extracted from references. Table 3.2 summarizes the search string used for the study.

The study will synthesize the data in a narrative synthesis to attempt to build the bigger picture of the field of biomass utilization and help identify the best way forward. The data will be presented in written form as well as via schematic representations. The possible conversion pathways for biomass will be presented in a flow diagram and an overview will be given of the highest quality studies. The review will present the trends in biomass research and can be used as a basis for the collection of data on biomass utilization.

Table 3.1: Research planning

Date:	Week	Activity
1 – 10 February	1	Research context
11-17 February	2	Theoretical background
18-24 February	3	Presentation and finalize research protocol Select relevant papers and begin synthesis of pre-treatment methods
25 February - 3 March	4	Finalize synthesis on Pre-treatment technologies
4 - 10 March	5	Search for articles on sources of biomass sources and start synthesis
11 - 17 March	6	Finalize synthesis on sources of biomass.
18 - 24 March	7	Search for articles on biomass conversion technologies
25 - 31 March	8	Synthesis of bio-conversion technologies
1 - 7 April	9	Search for articles on bio-chemicals
8 - 14 April	10	Finalize systematic review
15 - 21 April	11	PESTEL analysis
22 - 28 April	12	Finalize PESTEL analysis and synthesize results
29 April – 8 May	13	Conclusions and recommendations
9 May – 17 May	14	Finalized report
22 May	15	Submit report

Table 3.2: Summary of search strings used for the study

Subject :	Search string:	Number of papers:	Additional papers from references:
Sources of biomass	Biomass and Europe or Energy crops or Bioenergy or Residues or Waste	55	19
Biomass conversion	Biofuel or bioenergy and renewable and conversion and hydrolysis or pyrolysis or fermentation	76	0
Bio-chemicals	Renewable AND Chemicals OR Chemical AND Biorefinery OR Bio- refineries OR Biorefining / Biobased economy	45	16

Chapter 4 - Sources of biomass in NW-Europe

An important aspect for the economic viability of biomass energy is the availability and price of the feedstock. The building blocks of biomass are synthesized by plants via photosynthesis, a reaction between water, carbon dioxide, and sunlight. The energy is stored in the structural bounds within the biomass which can be harvested for energy and/or chemical production. The three main components of biomass are cellulose, hemicellulose and lignin. Cellulose is made up out of long chains of glucose polymers and forms the primary cell wall of green plants (McKendry, 2002). Hemicellulose is made up out of shorter molecular chains consisting of a mixture of heterogeneous branched sugar monomers such as cellulose, xylose and mannose. Lignin is a complex molecular compound which fills the spaces between the cellulose and hemicellulose facilitating water uptake and thereby giving structural strength to plants (Agbor *et al.*, 2011). Biomass usually also contains smaller amounts of other compounds such as ash and minerals. The levels depend on the type of biomass, the soil, growing conditions and time of harvest. The molecular buildup of plant matter is an important determinant for the efficiency of biomass processing. Woody biomass is composed of firmly bound fibers with high lignin content and is well suited for thermal conversion. Plants which can be harvested yearly, e.g. grasses, have more loosely bound fibers and a lower lignin content. The lower lignin content is beneficial for biological conversion processes. The moisture content of biomass is also important to consider. The moisture content can be affected by external factors i.e. weather conditions but biomass also has an intrinsic moisture content which is related to the type of biomass. A low moisture content is required to gain good process efficiencies in the thermal conversion of biomass. The biochemical conversion of biomass favors plants which have a higher moisture content (McKendry, 2002). This section will describe some of the most studied biomass sources available to Northern European regions i.e. poplar, willow, miscanthus, hemp, reed canary grass, switchgrass and 3rd generation biomass.

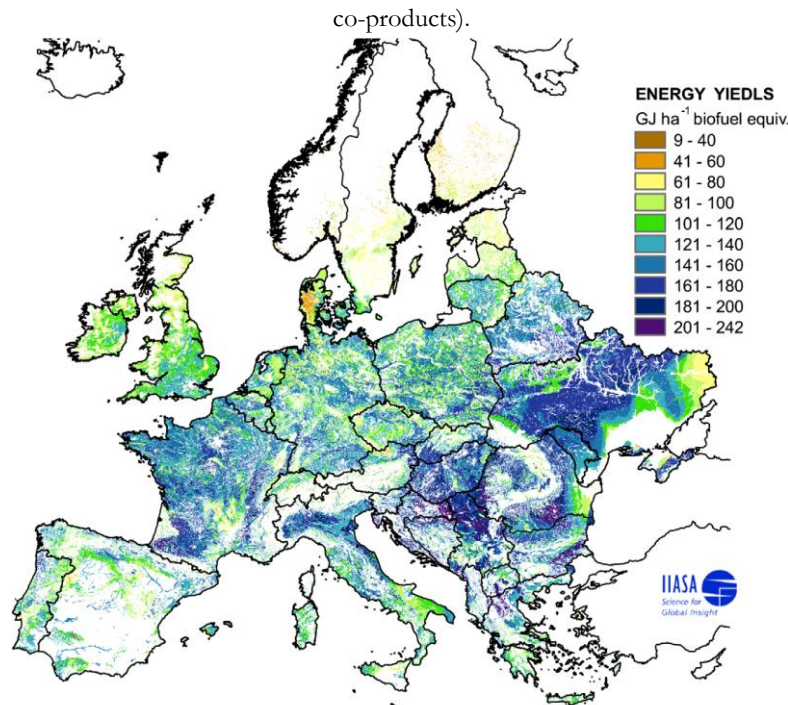
4.1 Biomass in Europe

This section will discuss general aspects related to the biomass potential of NW-Europe. The availability and potential yields of biomass is heavily depended on local climatic conditions. Northern European regions have a short growing season, high levels of precipitation and mild temperatures. In countries like the UK and the Netherlands agriculture is dominated by the livestock industry due to the favorable climatic conditions. Scandinavian countries have low fertile soils and thus limited potential for agricultural production (Fischer *et al.*, 2009a). However, the forests in these areas can supply large amounts of forest residues (Scarlat *et al.*, 2011). Southern regions have a longer growing cycle and receive more sunlight but can also be hot and dry (Fischer *et al.*, 2009a). The most productive regions in Europe in terms of climate are located in the Ukraine, Germany, France and Southeastern Europe, see figure 4.1. These regions produce a large proportion of the food in the EU and are potentially major players in the biomass industry (Ericsson and Nilsson, 2006). Climate change is expected to have an effect on the production capabilities of agricultural lands in Europe. Northern Europe is modeled to become more accommodative for plant species now restricted to Mediterranean areas. Southern European regions are more vulnerable to the effects of climate change. The agricultural productivity of countries like Spain could be affected by water shortages and more extreme weather (Tuck *et al.*, 2005, Cosentino *et al.* 2012). These effects can potentially be mitigated by increasing technology capabilities e.g. more draught resistant crops (Cosentino *et al.*, 2012). North-Western European countries are more expensive due to high wages and high costs of agricultural lands making the production of biofuels in Eastern Europe attractive (de Wit and Faaij, 2009). Especially the Ukraine could become an important source of biofuels (Fischer *et al.*, 2009b).

The most energy efficient source of raw materials for bio-refining is biomass waste e.g. forest and agricultural residues. Significant amounts of residue are created during agricultural production. France and Germany are major agricultural producers of cereals and produce the majority of agricultural residues in

Europe (Bentsen and Felby, 2012). Estimates on the available agricultural residues range from 86 to 133 million tons of dry matter a year. However, not all of the available residues can be used for bio-refining. A certain proportion of the residue needs to be left on the field to protect the soil from erosion and maintain fertility. Biofuels also have to compete with other uses of agricultural residues e.g. animal feed, mushroom cultivation, and industrial uses (Scarlat et al., 2009). A number of studies have estimated the potential supply of biomass waste in Europe for energy generation. The scope and methodologies used in the studies differ leading to a range of estimates. Somewhere between 800 PJ to 3300 PJ a year could be available from residue streams (1900 PJ/year would generate four percent of the total energy demand of EU27) (Scarlat et al. 2009, Fischer *et al.*, 2009_a, Bentsen and Felby, 2012). Residues are the least expensive sources of biomass and a good starting point for the biomass industry (Fischer *et al.*, 2009_a). However, the agriculture and forestry residues are not expected to increase significantly in the future (Scarlat et al., 2009). The use of waste streams alone will not be enough to provide a major alternative source of fuel. Dedicated energy crops will be needed to increase the availability of biomass in Europe (Bentsen and Felby, 2012).

Figure 4.1: Potential energy yield of second generation biomass sources in Europe (figure does not include the use of co-products).



Source: Fischer et al., 2009a

Most of the bio-fuels produced today are derived from first generation biomass sources such as corn, rapeseed and sugarcane. These crops are generally grown via intensive agriculture which is known to cause negative environmental externalities (Petersen *et al.*, 2007). Furthermore, the greenhouse gas emission savings of first generation sources are limited. The environmental and social sustainability of these sources of biomass is therefore contested (Jaeger and Egelkraut, 2011). Especially rapeseed oil performs poor in life cycle assessment studies due to the extensive use of fertilizer and pesticides (Fischer *et al.*, 2009_a). The energy yields of rapeseed is among the lowest (between 30 and 50 GJ ha a year) of all biomass crops. Other first generation sources e.g. corn can yield between 80 and 120 GJ ha a year. Second generation sources have a smaller environmental impact and lower production costs compared to first generation sources (Rowe. *et al.*, 2007). The average yields are projected to be higher (100 and 150 GJ ha) and less agro-chemicals are required to grow the crops (Petersen *et al.*, 2007).

An advantage of first generation sources is however that they require minor adoptions/adaptations in the supply chain leading to a favorable adoption climate for these technologies among farmers (Fischer *et al.* 2009a). The use of lignocellulosic biomass is more complicated. Second generation sources usually have a lower energy density and a higher moisture content than first generation biomass. The logistics of the process heavily influence the profitability of the technology (Richard 2010, Zhang 2011, Awudu and Zhang 2011). For instance, traveling a distance of 100 kilometres by truck can account for 10% of the inherent energy content of the biomass. It usually also needs to be dried, naturally or forced, to prevent degradation during transport and storage. Densification is also important but increasing the bulk density of grasses can account for 20 to 40% of the total cost of biofuel production (Zegada-Lizarazu *et al.* 2010, Tumuluru *et al.* 2011). Experience with commercial energy crops in Europe is limited. New farm management practices, additional infrastructure and novel equipment are needed to facilitate second generation biomass utilization (Fischer *et al.* 2009a, Zegada-Lizarazu *et al.* 2010, Miao *et al.* 2011).

The available second generation biomass sources can be divided into two broad categories, annual crops and crops that grow for multiple years (perennial plants). Miscanthus, reed canary grass, willow and poplar are multiyear crops. In the first years productivity is low but after 1-5 years the maximum productivity is reached where after the plots can be harvested for 10-25 years (Jing *et al.*, 2012). Woody biomass has a higher flexibility than grasses because they can be harvested any time of the year reducing the need for storage. An advantage of annual crops is that they can be integrated into a crop rotation cycle where they can be beneficial for the fertility and pests control (Zegada-Lizarazu and Monti, 2011). The agricultural production of second generation sources is less developed than well-established food crops. The grasses and woody crops have just recently been domesticated for energy production and are in the early stages of development. The crops Miscanthus Willow, and Poplar are the most advanced second generation sources and already used commercially in some parts of Europe (Zegada-Lizarazu *et al.*, 2010). This section made clear that the biomass potential is heavily dependent on local conditions and that dedicated energy crops will be needed to reach the European energy targets via the utilization of biomass. In the next paragraphs the most studied second generation biomass sources suited for Northern European climates will be discussed in more detail.

4.2 Industrial hemp

Hemp is one of the oldest nonfood crops in the world and there is a wide variety of species available (Struik *et al.*, 2000). Hemp is annual seeded C3 plant which can be grown from the equator up to the northern regions, see figure 4.2 . In countries like Canada, Sweden and Germany the crop is grown on an industrial scale for their fibers and seeds. The use of hemp as an energy crop has not been widely investigated so there is limited knowledge about the potential of hemp as an energy crop (Prade *et al.*, 2011). Studies indicate that the energy yield is similar to other energy crops used in Northern Europe. In northern Europe, annual yields vary from 5-15 t ha, seed yields range from 250-1200 kg ha (Venendaal *et al.*, 1997, Deleuran and Flengmark, 2005, Zegada-Lizarazu *et al.* 2010). The stem of the hemp plant can be separated into bast fibers (35%) and woody material (65%) from the inner core. The fibers are made out of 57–77% cellulose, 16% hemicelluloses, 5–9% lignin and 18% pectic substances. The woody inner core has a higher lignin content of 21–24% and a lower (hemi)cellulose content. The low lignin content of the fibers is an advantage for a bio-conversion process (Rehman *et al.*, 2012). Additional advantages of hemp are that little or no pesticides and herbicides are needed, it is easy to grow and it can improve soil health if integrated into a crop rotation cycle (Venendaal *et al.*, 1997, Struik *et al.*, 2000, Sipos *et al.*, 2010). Furthermore, the establishment costs are low and the risk to farmers is much smaller compared to multi-year crops. A disadvantage of hemp is its association with illegal narcotics, hemp species with a THC content of >0.03 are banned in Europe. This limits the amount of species which can be grown (Struik *et al.*, 2000). The moisture content of hemp at an autumn harvest (around 50%) is also problematic and the crop can be vulnerable to fungi in wet years (Venendaal *et al.*, 1997). Furthermore, the fertilizer

requirements for hemp are high compared to other second generation crops (Balezientiene *et al.*, 2012). Hemp has potential as an energy crop. It can easily be integrated into crop rotation cycles giving higher flexibility for farmers than most other second generation biomass sources. More research is needed to determine if the crop is able to compete with energy production from maize (first generation) as an annual energy crop.

Figure 4.2: Industrial hemp production in Belgium (2010)



Source: inagro.be

4.3 Switchgrass

Switchgrass is native to North America where it naturally grows from the Southern region of the US up to Canada. It was one of the dominant grasses on the American plains before they were mostly converted to agricultural lands (Shastri *et al.*, 2012). The plant has been able to evolutionary adapt to multiple environments leading to a large variety of sub species. The large genetic diversity makes it possible to cultivate switchgrass in diverse climatic conditions, see figure 4.3 (Jessup, 2009, Zegada-Lizarazu *et al.* 2010). The crop received much attention because of the relative high amounts of biomass which can be generated with low levels of input (Lewandowski *et al.* 2002, Deepak *et al.* 2008, Jessup 2009). Switchgrass can be grown on marginal lands and can provide ecological benefits such as increased soil quality and nesting places for migrating birds (Sanderson *et al.* 2006, Monti *et al.* 2008). It is well suited for sandy soils which occasional experience droughts (Lewandowski *et al.*, 2002). Switchgrass has a cellulose content of around 46%, a hemicellulose content of 32% and a lignin content of around 12.3% (Robbins *et al.*, 2012). The Department Of Energy of the United States identified Switchgrass as one of the most potent energy crops available for the US (Wright and Turhollow, 2010). In Southern parts of the US the grass can grow up to 3 meters high with roots going as deep as 3,5 meters (Lewandowski *et al.*, 2002). The investments made by the US significantly increased the scientific understanding of the crop (Sanderson *et al.*, 2006).

There are two main types of switchgrass, lowland plants and plants adapted for upland ecosystems. The lowland plants grow taller and are more suited for wetter conditions whereas the upland species are shorter, thinner and more adapted to dry conditions (Shastri *et al.*, 2012). The crop has a C4 photosynthetic pathway and is well suited for central and southern regions of Europe (Lewandowski *et al.*, 2002). It is planted via seeding which is a relatively cheap and easy method of crop establishment compared to the other grasses which need to be propagated first (Zegada-Lizarazu *et al.*, 2010). A problem for the establishment of switchgrass plantations is however the high levels of seed dormancy and poor seed quality (Sanderson *et al.*, 2006). This issue will need to be addressed in order to increase the viability of switchgrass as an energy source (Shastri *et al.*, 2012). The availability of water and nitrogen are important determinants in the productivity of the crop. The crop response positively to additional fertilizers in case nitrogen is not present in ample supplies in the soil (Monti *et al.* 2008). Economically viable plots will require the addition of 50–100 kg Nitrogen (N) ha fertilizer a year (Lewandowski *et al.*, 2002). Yields of up to 23 tons per ha/yr haven been reported under optimal conditions but average yields

are between 7 – 14 tons ha/yr for Northern European regions (McLaughlin *et al.* 1999, Christian *et al.* 2001, Lewandowski *et al.* 2002, McLaughlin *et al.* 2006, Fike *et al.* 2006, Sanderson and Adler 2008 Monti *et al.* 2008, Wang *et al.* 2010)

Figure 4.3: Switchgrass field in Groningen, the Netherlands (2003)



Source: switchgrass.nl

In the first year the crop cannot be harvested, it reaches two-thirds of the capacity in the second year and full capacity from the third year after plantation (McLaughlin *et al.*, 1999). During the first years weed treatment is needed to ensure the viability of the plantation (Shastri *et al.*, 2012). There is a lack of knowledge about the long term productivity of switchgrass plots but it is possible to annually harvest a plot for at least 10 years (Sanderson *et al.*, 2006, Shastri *et al.* 2012). Yields have not shown to decline significantly over the years but switchgrass is vulnerable to some fungi and viruses (Lewandowski *et al.* 2002, Fike *et al.* 2006, Jessup, 2009). The crop is usually harvested in the fall due to the lower ash and moisture content of the biomass at that time. The total yields are than however lower compared to an end of summer harvest. Harvesting after a freeze is recommended because the nutrients then move to the roots minimizing nutrients loss during harvesting (Shastri *et al.*, 2012). Different annual harvesting methods have been studied, a one-time harvest, a two time harvest or even multiple harvest a year. A two-cut systems has shown to increase yields during a year. However, the productivity in the following year can be affected and the additional investments needed for an extra harvest offset the potential gains of the additional biomass. A onetime harvest is the most favorable harvesting method (Monti *et al.*, 2008).

Switchgrass has a low bulk density which is problematic for the economics of the production chain. Size reduction (densification) is therefore an important aspect to increase the efficiency of the process. Since grasses are harvested only one time a year, storage is needed in order to guarantee a continued supply for a bio refinery. Storage can however result in a loss of biomass of between 2 and 35% depending on the type of storage used. Open air storage is the cheapest form but results in high losses of up to 35%. Covered storage is more expensive but can reduce the loss to 3% or almost nothing. The production costs are mainly determined by the transportation costs, costs of harvesting and storage cost (Shastri *et al.*, 2012). Switchgrass has some positive attributes as a bioenergy crop. The yields are lower compared to the other grasses but it is cheaper to plant and the farming equipment needed is similar to that already used by farmers (Monti *et al.*, 2008). However, it is currently not competitive with coal for electricity production (Smeets *et al.* 2009). Higher rates of seed emergence are needed as well as increased tolerance for cold, improved yields, better harvesting techniques and more efficient fertilizers strategies (Sanderson *et al.* 2006, Shastri *et al.* 2012). The systematic breeding of switchgrass for energy production is still in its infancy stage. The yields and climatic adaptability of switchgrass could be increased during the coming decades due to the large gene pool available for crop improvements (Sanderson *et al.* 2006, Jessup 2009).

4.4 Reed canary grass

Reed canary grass is native to the temperate regions of Europe, North America and Asia. It is one of the few grasses which able to grow well in the higher Northern regions of Europe. It is a C3 type grass

which is commonly used for hay and grazing. The crop is adapted to many stresses and thrives on wet, humus-rich soils where it can reach heights of 1.5 to 3 meters, see figure 4.4 (Venendaal *et al.* 1997, Casler *et al.* 2009). It is a persistent plant which can tolerate flooding and very wet conditions or very dry conditions. The large variation between the plants adapted to different ecosystems is beneficial for breeding programs (Lewandowski *et al.*, 2003). It is adapted to cool weather conditions and it is winter hard. It has been investigated in Sweden as bioenergy crop for over a decade. The highest yields can be obtained when harvested in the autumn on humus-rich soils (9 t ha/y). However, if the plant is harvested in the autumn the grass has poor fuel quality and needs to be extensively dried (Lewandowski *et al.*, 2002). The mineral elements present in the grass cause corrosion of power plants limiting the amount of grass which can be co-fired for energy production (Casler *et al.*, 2009, Hiensoo *et al.*, 2010). The (hemi)cellulose content can be as low as 48% with a 14% content of lignin and high amounts of ash and minerals. This makes the harvest for direct energy generation in the summer or autumn in the higher Northern regions not possible. The mineral content is reduced if the plant are left on the field during the winter and harvested in the early spring (Robbins *et al.*, 2012).

The plantations are established via seeding but the seeds are slow to germinate and can have high rates of dormancy. Weed treatment is only needed in the first year. After plantation the fields can be harvested over a period of 10–12 years with minimum input (Venendaal *et al.* 1997, Lankoski and Ollikainen 2006). Low levels of fertilizers are required, 100 N, 15 phosphorus (P) and 80 potassium (K) kg ha is recommended after the first year of sowing. After that lower levels of 50 N, 5 P, and 20 K kg ha/yr are required (Lewandowski *et al.*, 2002). The yields of the crop under favorable condition are within the range of 8–10 tons ha/yr (Venendaal *et al.* 1997, Casler and Undersander 2006, Jasinskas *et al.* 2008, Casler *et al.* 2009, Hiensoo *et al.* 2010, Stražil, 2012). However, in most Northern regions the crop needs to be harvested in the spring which results in a loss of yields of around 20%. Yields of 6–8 t/ha can be expected for most Northern regions (Venendaal *et al.* 1997, Lankoski and Ollikainen, 2006).

Figure 4.4: Reed canary grass winter harvest in Finland (2006)



Source: Turku University Finland (2008)

The advantages of the grass are that the establishment costs are low, no special harvesting equipment is needed and the land can easily be converted back to other purposes such as food crops (Venendaal *et al.* 1997, Stražil 2012). It is also the only grass which is able to grow well in the higher Northern regions of Europe. However, the yields are low compared to the other grasses and the species is still largely undomesticated, cultivated species are only one or two cycles removed from natural occurring strains (Casler and Undersander, 2006). Issues with ineffective seeding and low yields need to be addressed to increase the attractiveness of the crop to farmers in the higher Northern regions of Europe.

4.5 Miscanthus

Miscanthus is a C4 type grass with high solar radiation, fertilizer and water use efficiency (Lewandowski *et al.*, 2002). The grass is native from Asia where it can be found from tropical and subtropical conditions to warm temperate climates (Zub and Brancourt-Hulmel, 2010). Although the crop is adapted to warmer climates it can also grow in northern regions such as the Southern parts of Sweden and the U.K., Denmark, and Ireland, see figure 4.5 (Venendaal *et al.*, 1997). It is among the very few grasses with a C4 type photosynthetic pathway which is able to grow in these colder regions (Lewandowski *et al.* 1999, Anderson *et al.*, 2011). The plant can grow up to 4 meters high and produces large quantities of biomass with low levels of input (Zub and Brancourt-Hulmel, 2010). It is one of the highest yielding energy crops available (Boehmel *et al.* 2008, Jessup, 2009). The Miscanthus (M) genus contains around 11 to 25 species of which the M. Giganteus is the most commonly researched species. Extensive field trials have been conducted in Europe with the M. Giganteus strain. Denmark, Netherlands, Germany, Austria and Switzerland have invested public funds into research projects (Zub and Brancourt-Hulmel 2010, Anderson *et al.* 2011).

The crop can grow on a wide range of soils but the highest yields can be obtained on soils with a good water holding capacity (Lewandowski *et al.*, 2002). The (hemi)cellulose (Cellulose 40/60 % and Hemicellulose 20/40 %) content of the crop ranges typically from 76.20 to 82.76 % and lignin content ranges from 9.23 to 12.58 %. The rates depend on the harvest times and the condition under which the crop is grown (Brosse *et al.*, 2012). M. giganteus is a sterile hybrid of the species M. Sinensis and M. Sacchariflorus which means that the crop cannot produce fertile seeds. This prevents the crop from spreading to unwanted areas but it also makes the establishment of the crop more difficult and expensive (Atkinson, 2009). The crop is established by planting small plants in the spring which are cloned from a mother plant via vegetative propagation. There are two methods of obtaining plant clones, macro and micro propagation. Macro propagation is the mechanical harvesting of small plants from a field by cutting new plants from the stems. Micro propagation is the propagation of plants via tissue cultures (Lewandowski *et al.* 1999, Lewandowski *et al.* 2002). The genetic diversity of the crops used is therefore low (Zub and Brancourt-Hulmel, 2010).

Figure 4.5: Miscanthus harvest in the UK. (2010)



Source: energycrops.com

During the first 2-5 years, depending on the climate, the crop is building up yield and cannot be harvested (Lewandowski *et al.*, 2002). Weed control is vital in first years of growth to obtain high yielding plantation (Venendaal *et al.*, 1997, McKendry 2002). After the first years the yields reaches a maximum and can be annually harvested for up to 25 years (Anderson *et al.*, 2011). The crop can only be harvested once a year due to damage caused to the plants during harvest (Lewandowski *et al.*, 2002). Miscanthus requires low levels of inputs and leads to a low loss of minerals during harvest (Venendaal *et al.*, 1997). Fertilizers are only needed in large quantities on soils with a low Nitrogen (N) content. At places with good condition

the N can be limited to 50–70 kg ha/y (Lewandowski *et al.*, 2002). The highest yields can be obtained in the autumn when the plants are flowering but the moisture and mineral content is higher around that time. It is therefore often harvested in the spring so that the crop is dry and mineral content lower and it can be stored without further drying (Venendaal *et al.*, 1997).

The harvest delay improves the quality of the biomass but results in 25%–35% lower biomass yields (Lewandowski *et al.* 2002, Brancourt-Hulmel 2011, Anderson *et al.* 2011). The average total biomass loss is estimated to be around 35% (this includes the loss of biomass during the harvest itself) (Lewandowski *et al.*, 1999). In the southern regions of Europe with high temperature and high levels of solar radiation stable yields of up to 28 tons ha/yr over a ten year period were obtained. The maximum yield obtained in Europe (France) under well irrigate and fertilized conditions was around 49 tons ha/yr (Zub and Brancourt-Hulmel, 2010). The highest recorded yield in cooler climates (U.K) is around 20 tons ha/yr (Zegada-Lizarazu *et al.* 2010). The average yields in Northern regions range from 10 to 16 tons ha/yr depending on soil type and climate (Venendaal *et al.*, 1997, McKendry 2002, Lewandowski *et al.* 2002, Atkinson 2009 Somerville *et al.* 2010 Zegada-Lizarazu *et al.* 2010 Zub and Brancourt-Hulmel, 2010., Anderson *et al.* 2011, Brosse *et al.* 2012). In the higher Northern regions the *M. Sinensis* genotypes (which is more winter hard) can produce similar yields as the *M. Giganteus* (Lewandowski *et al.* 2002).

An advantage of the crop is that no yield decreasing pest or diseases are known although infections of insects, fungi and viruses have been reported in some plantations (Atkinson 2009, Zub and Brancourt-Hulmel 2010, Anderson *et al.*, 2011). Furthermore, the biomass yields are high and similar harvesting equipment as for hay can be used. Yet, standard machines must operate slower due to the higher density of the biomass so more specialized equipment is needed to increase harvesting efficiency (Venendaal *et al.* 1997, Lewandowski *et al.* 1999, Anderson *et al.* 2011). A major problem for the crop in northern regions is the low survival rate of the plants in the first winter after plantation. The roots of the young plants start to die off at temperatures below –3,5 °C (Lewandowski *et al.*, 2002). In subsequent winters the plant is able to survive (Lewandowski *et al.*, 1999). The establishment costs of *Miscanthus* plantations are high (Lewandowski *et al.* 2003, Zegada-Lizarazu *et al.* 2010, Zub and Brancourt-Hulmel, 2010). The low winter hardness in the first year is therefore a major obstacle for the crop in Northern region (Atkinson, 2009). Increasing the frost tolerance and techniques which can reduce the cost of propagation are essential for the increasing of the cultivation of *Miscanthus* in Northern regions (Atkinson 2009, Brancourt-Hulmel 2010, Glowacka, 2011).

4.6 Short rotation coppice

Short rotation coppice refers to the growing of woody biomass using a coppicing woodland management system. Coppicing is the cutting of trees at their base which results in the generation of new stems from the stump or roots in the following year. Willow and poplar are the two most commonly investigated short rotation coppice species which are well suited for the Northern European climate. Willow has been cultivated by human civilization for a long time. The crop has been used as a raw material for baskets, fences and shields since Roman times. Poplar has also been cultivated by humans mainly for timber and pulp. Recently these crops have received interest as a source of energy because of their high yields and fast growing rates (Afas *et al.* 2008). Poplar is among the fastest growing trees in temperate climates (Afas *et al.* 2008, Hinchey *et al.* 2009). The family of poplar comprises of 25 to 35 different species of which hybrid species are the fastest growing (Sannigrahi *et al.*, 2009). The willow family has a larger genetic diversity of around 350-500 species. Poplar is more suited for warmer climates whereas willow is also able to grow in the higher Northern regions of Europe (Venendaal *et al.*, 1997).

The trees are cultivated in multi-year cycles, see figure 4.6. During the first 3-5 years the trees need to take root and be allowed to grow into mature plants. After the first years of growing the biomass can be harvested in rotation cycles of 3 till 5 years for up to 30 years (Deckmyn *et al.* 2004, Karp and Shield 2008, Zegada-Lizarazu *et al.* 2010). Both species are relatively easy to propagate but require an ample supply of water to be able to achieve high yields (Venendaal *et al.* 1997, Pellis *et al.* 2004 karp and

Shield 2008). Poplar has a cellulose content of around 40%, hemicellulose content of around 23% and a lignin content of around 20%. Willow has a higher cellulose content of 56%, a hemicellulose of around 14%, and lignin of around 19% (the remaining weight is moisture, ash and minerals) (Karp and Shield, 2008).

Figure 4.6: On the left willow harvesting in Sweden, on the right poplar harvesting in the USA.



Source: fao.org (left), eere.energy.gov (right)

Weed treatment is essential in the first years of willow cultivation because the young sprouts are vulnerable to weed overgrowth. After the first years little to no insecticides or fungicides and few herbicide are needed. Furthermore, the fertilizer requirements for the willow are low (Venendaal *et al.* 1997, Labrecque and Teodorescu, 2005). Willow can be planted in high density, is able to uptake heavy metals from soils and can facilitate the breakdown of non-toxic organic compounds (Volk *et al.*, 2006). Short rotation coppice can have a positive effect on biodiversity if the use of herbicides is low and the crop is cultivated on relative small plots. In a landscape which is dominated by conventional large scale agriculture the crops provides a nesting place for birds (Hoffmann and Weih 2004, Londo *et al.* 2004, Labrecque and Teodorescu, 2005).

The reported yields of willow range from as low as 6 tons ha/yr to as high as 30 tons per ha/yr under well fertilized and irrigated conditions. In a review study on willow cultivation multiple sources where examined describing the yields of willow cultivation. A mean harvestable yield of 11.5 ton per hectare a year was found (Djomo *et al.*, 2010). Based on this study and the results published elsewhere an average yield of 10 till 15 tons biomass per hectare year can be expected in Northern European climates (Venendaal *et al.* 1997, Hoffmann and Weih 2004, Labrecque and Teodorescu 2005, Djomo *et al.* 2010, Miao *et al.* 2011, Kasmioui and Ceulemans 2012). Poplar is able to achieve relative high yields with no irrigation and limited use of fertilizers but yields are considerably higher on well irrigated and fertilized plots (Deckmyn *et al.* 2004). Under optimal conditions yields of up to 20–25 tons ha/yr can be achieved (Pellis *et al.* 2004). However, annual yields between 6 till 13 t ha/y are more realistic for most Northern European areas (Venendaal *et al.*, 1997, Pellis *et al.* 2004, Laureysens *et al.* 2005, Aylott *et al.* 2007, Fischer *et al.*, 2009a, Djomo *et al.* 2010, Somerville *et al.*, 2010). The crops are usually harvested in the winter as the leaves have fallen off making the harvesting easier. However, this does lead to a high moisture content of around 50% at harvest (Gasol *et al.*, 2009). This can be problematic for further processing depending on the intended application (Miao *et al.*, 2011). After harvest the trees are cut and usually made into chips by mobile chipper (Zegada-Lizarazu *et al.* 2010). Harvesting and transportation cost can account for 39–60% of the total production costs (Labrecque and Teodorescu, 2005).

The breeding of willow and poplar for energy purposes has not taken place widely so there is room to increase the yields of the crops by genetic manipulation or natural breeding programs (Labrecque and Teodorescu, 2005). The POPFULL project is an example of efforts to increase the knowledge about popular plantations in a NW-European context⁴. The genome of poplar has recently been sequenced which increases the possibility to develop new varieties (Sannigrahi *et al.*, 2009). The main barrier for

⁴ <http://webh01.ua.ac.be/popfull/index.php?lang=nl>

implementation is currently the questionable economic viability of short rotation coppice cultivation for energy production (Aylott *et al.* 2007, Kasmoui and Ceulemans 2012, Kasmoui and Ceulemans 2012). The short rotation coppices have long rotation cycles which increase the investments risks (Venendaal *et al.*, 1997). Improvements in harvesting techniques and higher biomass yields are needed to make growing short rotation coppice more attractive for farmers.

4.7 3rd generation biomass

This section will describe more advanced sources of biomass often referred to as 3rd generation sources. Algae are among the oldest living organisms on the planet and hold great potential for the development of biofuels. There are an estimated one to ten million species of algae which can be categorized into two broad categories, macro algae and micro algae. Traditionally algae have been grown for human consumption (proteins) but in recent decades interest has shifted to the development of biofuels and chemicals (Aitke and Antizar-Ladislao, 2012). The benefits of algae are that they can have higher solar conversion efficiency and carbon fixation rates than any terrestrial plant (Ratha and Prasanna, 2011). The growth rates of algae can be very high; some are able to double their biomass in 3.5 hours (Brennan and Owende, 2009). Microorganism such as algae and bacteria can produce biomass year round and have a very short harvesting cycle which allows the continuous production of biomass (Singh and Dhar, 2010). They can therefore generate far greater yields than any other biomass source. No herbicides or pesticides are needed and limited amounts of water are required. They can be cultivated on non-arable lands and also be designed to produce valuable co-products (Brennan and Owende 2009, Singh and Dhar 2010, Ratha and Prasanna 2011). These attributes make microorganisms an attractive source of biomass for fuel and chemicals.

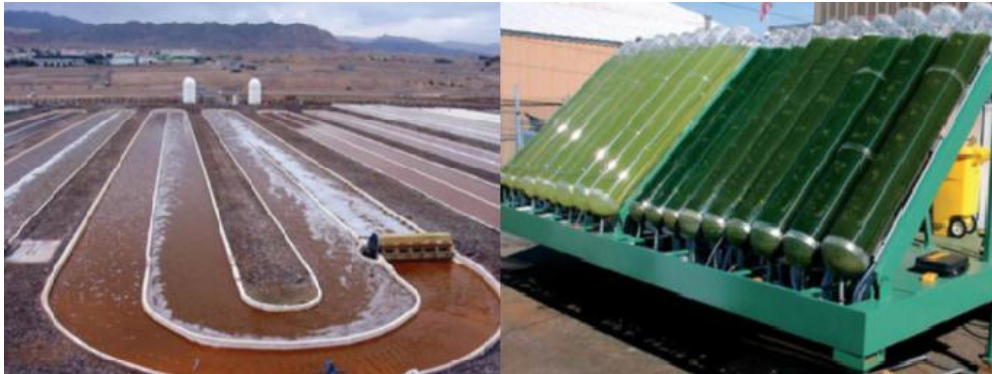
One possibility would be to use macro algae such as brown seaweed or duckweed for biomass production (Williams and Laurens, 2009). Seaweeds can be cultivated in open sea, for instance in combination with off shore wind farms (Carlsson *et al.* 2007, Kraan 2010). However, limited research has been done on the use of seaweeds as a source of biomass in Northern regions. It is currently expensive and advancements are needed in plantation establishment and harvesting techniques to make this option economically viable (Hughes *et al.*, 2012, Wei *et al.* 2012). Research for biomass production has focused on the use of micro algae which are small primitive plants which have no roots, stems or leaves. The most important species of microorganisms under investigation are algae and cyanobacteria. The algae are classified as autotrophic, heterotrophic or mixed algae species. Autotrophic algae only require CO₂, salts and light to grow, heterotrophic algae are non-photosynthetic which means they require an external energy source and nutrition e.g. glucose to grow. Mixed algae species are able to use light as well as an external source of energy to grow. Cyanobacteria are autotrophic requiring only sunlight and CO₂ to grow (Brennan and Owende 2009, Singh and Dhar 2010).

Multiple production methods can be employed to grow microorganisms depending on the characteristics of the species used (Williams and Laurens, 2009). They can be grown using natural sunlight or via fluorescent lamps. The use of lamps makes continuous production possible but also increases the energy demand of production. Algae can use the CO₂ available in the atmosphere for growth but can also tolerate and use much higher levels of CO₂. Additional CO₂ can be introduced into the growth media to increase production rates. Nutrients such as nitrogen and small amounts of phosphorus and silicon are also commonly added to increase algae yields (Brennan and Owende, 2009). These nutrients can potentially be obtained from waste streams providing a low cost source of nutrients as well as a method of waste water treatment (Koller *et al.*, 2012). Photoautotrophic algae are the most economically feasible species for large scale production.

Two production systems can be employed to grow algae, an open pond system or a closed photo-bioreactor, see figure 4.7. Open pond systems are the cheapest form of algae production but the system is vulnerable to biological contamination and less efficient than closed photo-bioreactor (Brennan and Owende, 2009). To reduce the risk of biological contamination extreme culture condition e.g. high salinity

can be used to limit the number of natural occurring organisms in the media (Ratha and Prasanna, 2011). Closed systems permit the cultivation of more sensitive single-species for longer periods of time. Hybrid systems have also been developed. Heterotrophic algae can grow on organic materials e.g. glucose in tanks independent of light. They have good conversion efficiency and can be grown using simpler equipment but require more energy input due to feed requirements. This also significantly increases the cost of production. Mixotrophic algae are able to use photosynthesis as well as ingest organic compounds. These algae show improved growth rates and could become an important part of algae production in the future (Brennan and Owende, 2009).

Figure 4.7: An open ponds system for micro algae production (left) and a closed photo-bioreactor (right).



Source: Williams and Laurens, 2009

Once the algae have been produced they need to be separated from the growth media. The downstream processing of algae is costly and complicated (Parmar et al. 2011). The main components of algae biomass are carbohydrates, proteins, nucleic acids and lipids (Williams and Laurens, 2009). The primary products of interest for biofuel production are lipids (Brennan and Owende, 2009). Lipids serve as an energy reserve for algae and are similar to seed-oil, they can be easily converted to biofuels via transesterification (Williams and Laurens 2009, Day *et al.* 2011). The separation of the useful materials from the aquatic media is however challenging and can account for 20-30% of the total production costs (Brennan and Owende 2009, Lam and Lee 2011). Centrifugation is the most commonly used method in research projects but other methods such as flocculation and ultrasonic aggregation, filtration or flotation are also possible (Brennan and Owende 2009, Williams and Laurens 2009). Immobilization technology could also provide a cheap and energy efficient method of algae harvesting but more research is needed to develop the technology (Lam and Lee, 2011). After separating the algae from the growth media the lipids need to be extracted. The cell wall of algae is relatively thick which completes the extraction process. Different methods can be used such as solvent extraction or supercritical fluid extraction e.g. with CO₂ suited for wet biomass streams. Chemical solvent extraction is the most common method although highly toxic substances are usually needed. Super critical fluids are more environmentally friendly but the process is more expensive (Lam and Lee, 2011, Lee *et al.* 2012). The byproducts of production (non-lipid biomass) can be used as a source for human nutrition, animal feed or bio-fertilizer or further processed via e.g. pyrolysis or gasification into bio-oil or fermented e.g. into ethanol (Brennan and Owende, 2009, Lam and Lee, 2011).

The large scale production of microorganisms for biofuels is currently not economically feasible. There are multiple issues such as high costs, low yields and production rates, costly harvesting and processing steps which impeded the scale up of algae production (Brennan and Owende 2009, Williams and Laurens 2009, Amaro et al 2012). The energy demand for algae production is mainly determined by the nutrient source, reactor design, dewatering and drying processes and lipid extraction. Substantial amounts of nitrogen are usually needed to grow the algae leading to higher energy demand of the total production process. Cheap and environmentally friendly sources of nitrogen will be needed for the large

scale production of these algae (Kam and Lee, 2011). The efficiency can be improved by finding more efficient strains or use genetic engineering to increase growth rates and lipids production (Singh and Dhar, 2010, Lam and Lee, 2011). Improving reactor designs and integrating processing steps can also increase the economics of production (Amaro *et al.* 2012, Kirrolia *et al.* 2012). Genetically engineered strains can increase yields but potentially also pose a major treat to the environment in case they escape. These concerns need to be taken into account when design new strains and production processes (Flynn *et al.*, 2012). The production of co-products can also increase the economic benefit of algae production (Williams and Laurens, 2009). The production of hydrogen via algae is an interesting short term option since the selling price of hydrogen is considerably higher than diesel fuel (Kirrolia *et al.*, 2012). Algae hold great potential as a source of biofuels and chemicals but much more R&D efforts are required. Major technological breakthroughs are needed to make algae biofuels competitive and able to significantly reduce CO₂ emissions of energy consumption (Williams and Laurens 2009, Malcata 2011, Lam and Lee, 2011, Day *et al.* 2011, Flynn *et al.* 2012, Amaro *et al.* 2012).

4.8 Concluding remarks

Forest and agricultural residues are a good starting point for the biomass industry in places where they are readily available (Fischer *et al.*, 2009_a). However, the supply of residues is limited and will not be enough to meet the energy targets set by the European Union (Scarlat *et al.*, 2009). The biomass supply will need to be increased via dedicated energy crops to allow large scale biofuel production (Bentsen and Felby, 2012). An important determinant of the energy balance of crops is the use of nitrogen fertilizer. It can account for 41–64% of the energy consumption of annual crops and between 17–45% for multi-year crops. The low input requirements for second generation crops are an important aspect of their increased sustainability compared to first generation sources biofuels (Boehmel *et al.*, 2007) Table 4.1 summarizes the most important findings of the literature review on dedicated second generation energy crops.

Table 4.1: Summery of the finding of the literature review on second generation biomass sources suited for northern European regions (Yields are adapted to a North European Climate)

Crop	Photo-synthetic pathway	Productivity (T/ha/year)	Water requirments (cm/year)	Fertilizer input	Feedstock quality	Genetic variation
Miscanthus	C4	10-16	75-120	modest	moderate	low
Switchgrass	C4	7-14	45-75	modest	moderate	high
Reed canary grass	C3	6-10	No data	modest	low	high
Poplar	C3	6-13	70-105	low	high	low
Willow	C3	10-15	100	low	high	medium
Hemp	C3	5-15	40-60	moderate	moderate	high

Choosing the right crop for a specific location is important for the economic viability of bioenergy. The viability is dependent on the local climatic conditions, the quality of the soil, cost of production and the preferences of the farmers (Lewandowski *et al.*, 2002). Under optimal condition the highest yields via second generation crops can be obtained with Miscanthus crop. However, crop establishment is expensive and the crop is vulnerable to the cold which makes it more difficult for the crop to be economical viable in Northern regions (Lewandowski *et al.* 2002, Zegada-Lizarazu *et al.* 2010). Switchgrass generally has lower yields compared to Miscanthus but is less valuable to the cold, less expensive to establish and able to grow well on marginal lands (Sanderson *et al.* 2006, Monti *et al.* 2008). The short rotation coppice willow and poplar produce relative high yields with low inputs. The crops are easy to establish and the quality of the feedstock is high compared to the other sources (Balezientiene *et al.*, 2012). These crops are among the most interesting energy crops for Northern European regions since they combine low inputs with high yields (Boehmel *et al.*, 2007). However, the long rotation cycles are a

barrier for farmers to cultivate the crops for energy production. Plantations of Willow, Switchgrass or Miscanthus take 2-5 years to mature and can be harvested for 10-25 years. Uncertainty about the price of energy, governmental support policies and possible technological advancements makes investing in these sources risky (Sims *et al.* 2009, Gnansounou and Dauriat 2010, Awudu and Zhang 2011).

The conversion technologies for second generation sources are expected to become commercially available between 2015 and 2020. Yet, investments are now needed to establish the plantations, gain practical experience with the crops and increase yields to make the feedstock readily available for future the refineries (Sticklen 2006, Taylor *et al.* 2008, Feltus and Van den brink, 2012). Without increased efficiency in feedstock production the desirability of second generation sources in Northern European regions is questionable. The potential yields are modest compared to more warm and humid regions of the world (Ridley *et al.* 2011, Bonin and Lal 2012). The development of additional annual energy crop such as hemp which can be easily integrated into rotation cycles can help decrease the risk to farmers. The annual crops can be produced as capacity becomes available and can be more easily abandoned in cases of overcapacity and low margins.

Third generation sources are a potent source for large scale biofuel production. They can potentially provide a greater return on investment, in terms of yields and environmental benefits, than second generation sources. Yet, it is difficult to determine when these sources will become commercially available (Williams and Laurens 2009, Flynn *et al.* 2012, Amaro *et al.* 2012). Conventional sources and biomass residues are the best short term alternative for liquid fuels. These source are needed to be able to meet the energy targets set by the EU for 2020. Second and third generation sources are long term alternatives and will require large investment into bio-refining capacity and energy crop plantations (Gnansounou, 2010). The desirability and viability of the production of biofuels from second generation sources in NW-Europe is still questionable. More research is needed to assess their production capacity under different geographical conditions and determine the energy balance of the crops in NW-European climatic conditions.

Chapter 5 – Pretreatment technologies

Lignocellulose biomass e.g. wood residues or switch grass is seen as a promising source of biomass since the feedstock is cheap and has a limited impact on food security (Zhang, 2008, Menon and Rao, 2012). The biomass is however much more difficult to process than first generation sources (Cukalovic and Stevens, 2008). The first step is usually the densification of the biomass by chopping it into a finer particle size. Chopped biomass can directly be used in gasification and pyrolysis conversion techniques. However, additional pretreatment processes such as pelletisation or torrefaction can also be applied to increase the efficiency of thermal conversion. More extensive pretreatment processes are needed to allow lignocellulose biomass to be processed via biological transformation (Kamm and Kamm 2004, Agbor *et al.* 2011). Lignocellulose biomass usually is build up out of 40-50% cellulose, 25-30% hemicellulose, 10-20% lignin and a small proportion of other components (Menon and Rao, 2012). The separation of lignin early in the process can increase the efficiency of biological conversion. The lignin can also serve as a raw material for a range of high value chemicals. The (hemi)cellulose contained in the biomass is converted via chemical (acid) or biological (enzymes) hydrolysis to fermentable sugars. Pretreatment is required because in untreated lignocellulose the molecules are packed so tightly together that the enzymes or acid cannot penetrate the structure (Zhang, 2008, Menon and Rao, 2012). Untreated biomass is only affected by the enzymes or acid at the surface leading to low yields (e.g. 20%) (Balat *et al.* 2007, Lestari *et al.* 2009). There are three main categories of pretreatment technologies which can be used to allow biological conversion, physico-chemical, chemical and biological treatment (Menon and Rao, 2012). This chapter will first present the pretreatment techniques of pelletisation and torrefaction used before thermal conversion. This will be followed by a discussion of techniques used in biological conversion i.e. lignin separation, physico-chemical, chemical and biological pretreatment methods and the hydrolysis process.

5.1 Pelletisation

This section will discuss the advantages of using the pelletisation process to increase the density of biomass. Second generation biomass require size reduction to increase the efficiency of transportation and allow further processing. For instance, a particle size of 1–2mm is recommended for effective hydrolysis. The moisture content may also need to be reduced i.e. drying to allow conversion or long term storage. These processes can be energy intensive especially if the biomass has a high moisture content (Kratky and Jirout, 2010). Biomass can be stored largely untreated but this leads to high mass losses. An advanced process of making biomass more suited for conversion, transport and storage is pelletisation. It is used on a commercial scale in Europe to produce pellets, cubes or briquettes from sawdust residues. Heat and pressure is applied to compress the material into a more dense and easy to handle product. Chopped biomass is forced through round holes at a pressure of 35 MPa. The biomass reaches a temperature of 90-150 °C making the lignin act as glue to bind the fibers. The temperature is the main determinant for the density, strength and durability of the pellets. Small amounts of additional materials e.g. pyrolysis tar can be added to increase the quality of the pellets. The pellets are cooled to stabilize and harden the material. Woody biomass with high lignin content is favorable for the pelletisation process. It allows for milder process conditions and lignin increases the biological resistance of the product. However, the bark of wood can contain undesirable compounds for combustion. Short rotation coppice and forest residues are only suited for large scale production where the biomass can be cleaned before treatment. The moisture content of the biomass has a large influence on the heating value of the pellets (-2.3 MJ/kg per 10% increase). A moisture content below 10% is required to make products of high quality. The advantages of pelletisation are that the heating value of the biomass improves and it that it is easier to handle, transport and store. Pelletisation converts biomass into a higher value intermediate product which can be used for co-firing, thermal conversion or small scale boilers (Robbins *et al.* 2012).

5.2 Torrefaction

The pretreatment technique of torrefaction will be discussed in the following paragraph. Torrefaction is a process in which biomass is heated without oxygen to 200 till 300 °C for 15-30 min. It can be done close to or at atmospheric pressure. Wet biomass is processed under higher pressure to allow processing without the need for drying. The process was first proposed in the 1930s. The Energy research Centre Netherlands (ECN) has been working on torrefaction since 2002 (Stelt *et al.* 2011). The process yields around solids 80-95% solid products, 2-10% liquids and 2-15% gas (Ciolkosz and Wallace 2010). Woody biomass can maintain 70%-96% of its mass and maintains around 90% of the initial energy (Van der Stelt *et al.*, 2011). The process mostly affects the hemicellulose structures in the biomass (Ciolkosz and Wallace 2010). The hemicellulose becomes less fibrous and less able to store water. The cellulose and lignin are only slightly effected (van der Stelt *et al.*, 2011). The mass loss is therefore mostly determined by the hemicellulose concentration. The process leads to an increased heating value, lower moisture content and less volatile substances. The increased energy density is mostly due to the loss of oxygen (Ciolkosz and Wallace 2010, van der Stelt *et al.* 2011). The end-product is comparable to low-grade charcoal. It is more resistant to biological degradation, has a higher energy density and is easier to grind to powder (van der Stelt *et al.* 2011, Robbins *et al.* 2012). A lump sized feedstock can be used in the process (e.g. 2 cm²) (Ciolkosz and Wallace 2010). Yet, the energy requirements for pelletization are reduced by 50% and grinding requires only between 10% and 20% of the energy of untreated biomass processing (Ciolkosz and Wallace 2010). Microwave radiation has been proposed as an additional heating method to further increase the energy efficiency of the process (van der Stelt *et al.*, 2011).

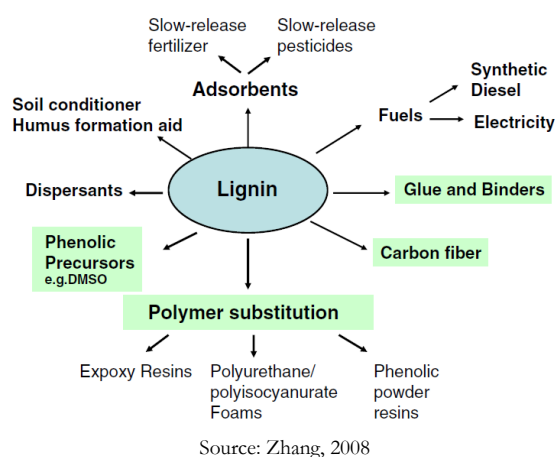
The increased ability to grind is an important advantage for use in coal fired power stations or in a gasification processes. The product can also be formed into pallets for improved handling however the pallets are more brittle making transportation difficult. Safety precautions are needed because the material becomes more prone to aerial dispersion (Ciolkosz and Wallace 2010). Torrefaction is not used on a large scale and much is still unknown about the fuel properties of different biomass sources. Combustion trials have shown successful results and it is also possible to ferment torrefaction products. The process does not inhibit the enzymic or fermentation process however the loss of hemicellulose reduces the yields (Robbins *et al.* 2012, Verma *et al.* 2011). Main potential applications are entrained flow gasification, small scale combustion and co-firing in coal fired power plants. It can also provide a method of densification to increase transport efficiency. However, the techno-economic feasibility of torrefaction is not well studied due to the lack of commercial-scale performance data (Ciolkosz and Wallace 2010, van der Stelt *et al.* 2011). Additional research on the kinetics of the process is needed to design reactors for large scale facilities (van der Stelt *et al.* 2011). Torrefaction can become an important method to make intermediate products well suited for biomass gasification but more information is needed on the economics of large scale facilities.

5.3 Lignin separation

Lignin is one of the main components of hemicellulose biomass and acts as a process inhibitor during the biological conversion of biomass into fuel and chemicals. The separation of lignin from the other components is difficult but can increase the efficiency of biological conversion. Technologies are needed which can separate lignin early in a biomass utilization process under mild conditions to increase the efficiency of biological conversion and to conserve the molecular structure of the derivatives (Bozell *et al.*, 2007). The paper industry is a major source of lignin but it is mostly used for energy generation. Relative small amounts of R&D funding have been spent on the use of lignin as a chemical feedstock. The DOE published a report in 2007 which specifically addressed the potential of lignin utilization. The production of chemicals from lignin was identified as a medium and long term option due to the current technological limitations (Bozell *et al.* 2007). Lignin is a heterogeneous compound which makes it difficult to control and standardize the properties of lignin products (Zhang *et al.*, 2011). Yet, lignin is an interesting raw material because it is a potential source for a wide range of high-value aromatic

compounds and fine chemicals (Cherubini and Strømman 2011, Zakzeski *et al.* 2010, Saito *et al.* 2012). It is in fact the only renewable source for a number of aromatic compounds. The properties of the lignin depend on the biomass source and the isolation technique used. Once the lignin is separated it can be converted to chemicals via multiple methods e.g. hydrolysis, catalytic reduction or catalytic oxidation. The reduction reactions are best suited for the production bulk chemicals whereas oxidation can produce fine chemicals (Zhang, 2008). Lignin can also be converted to chemicals via a pyrolysis process. However, this yields a complicated mixture of chemical compounds which makes downstream processing difficult (de Wild, 2011). Microbiological processes could potentially also be employed to selectively convert lignin into chemicals but this is not well developed (Zhang *et al.* 2011). A high value derivative from lignin is vanillin which is used in perfumes and as a food additive. Other interesting commodities which could potentially be derived from lignin are xylene, toluene and benzene. Figure 5.1 shows what kinds of products can be produced from lignin derivatives (Zhang, 2008). Key enabling technologies for lignin utilization are efficient separation technologies and cost effective lignin depolymerization technologies (Bozell *et al.* 2007, Zhang 2008, Zhang *et al.* 2011). Furthermore, improved catalysts are needed to effectively convert lignin to bio-chemicals (Bozell *et al.* 2007, Zakzeski *et al.* 2010). A significant amount of additional research will be needed to make efficiently separate lignin from biomass as well as to make the production of chemicals from lignin technological and economically viable.

Figure 5.1: Possibilities for the utilization of lignin, the green boxes represent high value products.



5.4 Physico-chemical pretreatment

This section will explain the physico-chemical pretreatment methods which are available to make lignocellulose biomass suitable for biological conversion into fuel or chemicals. There are a number of pretreatment methods available which use hot water or steam to cleave the molecular bounds within biomass. Steam explosion is one of the most widely studied pretreatment technologies (Carvalho *et al.*, 2008). During this processes the biomass is subjected to saturated steam under high pressure. A temperature of 160-260 °C is usually used at pressures ranging from 0.7 to 5 Mpa. The pressure is suddenly released which causes an explosive decompression of the material (Kumar *et al.* 2009, Menon and Rao 2012). The lignocellulosic matrix of the biomass disintegrates making the (hemi)cellulose accessible for enzyme or acid hydrolysis. The reaction times are very short ranging from several seconds to minutes. The efficiency of the process depends on the reaction conditions and type of biomass used. It is one of the most cost effective methods for hardwoods and agricultural residues but less suited for softwoods (Kumar *et al.*, 2009). The advantages of steam explosion are that the equipment is commercially available, it requires low capital investments, it causes limited corrosion on the equipment and has a low environmental impact (Carvalho *et al.*, 2008, Menon and Rao 2012, Liu 2010). However, separation of the individual components (cellulose, lignin, etc.) is difficult and some degradation of the materials can take place due to the high temperatures and pressure (Carvalho *et al.* 2008, Kumar *et al.* 2009).

Furthermore, the biomass needs to be washed after processing to remove fermentation inhibitors and the process has a relative low hemicellulose sugar yield (Zheng *et al.*, 2009). It is currently one of the most cost effective pretreatment methods but product separation is difficult and other methods are able to produce higher yields.

Water at high temperatures has acidic properties which can dissolve some of the molecular linkages within biomass (Zheng *et al.*, 2009). The liquid hot water processes is similar to the steam explosion method but does not suddenly release the pressure. It maintains the pressure and high temperatures for several minutes to an hour so that the water remains in a liquid state (Menon and Rao, 2012). The acidic properties of water under these conditions dissolve the molecular bounds within the biomass without the need for chemicals or solvents (Zetzel *et al.* 2011, Menon and Rao 2012). The limitations of the method are that a number of fermentation inhibitors are formed and that the separation of co-products is problematic (Menon and Rao, 2012). Another pretreatment method using hot water is supercritical fluids pretreatment. In this method water is subjected to even higher temperatures of around 300-400 °C in combination with a high pressure of around 25-40MPa, this forces the water into a supercritical state. Effective biomass decomposition can be achieved and less process inhibitors are created than during other hydro-thermal methods. However, the high temperatures cause some degradation of the material leading to lower hemicellulose sugar yields. An alternative is to use of CO₂ as a supercritical fluid because of the lower temperature required transforming CO₂ into a supercritical fluid. The process can be used in combination with an explosive decompression step (Kumar *et al.*, 2009). The main limitations of supercritical fluid pretreatment are the high costs of the equipment, the high energy requirements and safety issues (Rose and Palkovits 2012, Arai *et al.* 2009). Hydro-thermal technologies are green (no chemicals needed) and well developed pretreatment methods but the energy intensity can be high, other methods can produce higher yields and a limited number of by-products can be separated (Gullón *et al.*, 2012)

The Ammonia fiber explosion (AFEX) process is similar to steam explosion but liquid ammonia (1-2 kg per kg dry mass) is added to facilitate the processing. A lower temperature of 40-140 °C can be used but a high pressure (250-300 psi) is needed (Carvalho *et al.*, 2008). The residue times vary from a few minutes to an half hour (Carvalho *et al.* 2008, Menon and Rao 2012). The process can increase the fermentation rate of herbaceous crops and agricultural waste but is not well suited for biomass with high lignin content (Carvalho *et al.* 2008, Kumar *et al.* 2009). Important advantages are that a limited number of inhibitors are created and there is no need to reduce particle size which simplifies the processing (Zheng *et al.* 2009, Busch *et al.* 2006). The ammonia can be recovered but at a high cost and the toxicity of the substance is a problem. Another type of ammonia based pretreatment method is ammonia recycle percolation (ARP). During this process aqueous ammonia is used under a temperature of 150-170 °C in a flow-through reactor which makes the recycling of the ammonia easier (Carvalho *et al.*, 2008). High theoretical glucose yield can be obtained with ammonia pretreatment but the efficiency and optimum reaction condition depend heavily on the type of biomass processes (Kumar *et al.*, 2009). Little process inhibitors are created with ammonia pretreatment but the cost of recycling the ammonia are high. The chemical is also highly toxic and can cause corrosion of the equipment making it a less attractive option (Carvalho *et al.*, 2008, Kumar *et al.*, 2009). Physico-chemical pretreatment can offer an effective method of biomass pretreatment although the energy consumption and toxicity of the chemicals used can reduce the sustainability of production process.

5.5 Chemical pretreatments

Chemical methods are the most studied pretreatment technology for making lignocellulose biomass suitable for biological conversion because they have been used in the paper industry for decades. One possibility is to use a combination of steam explosion with a catalyst e.g. sulphuric acid (H₂SO₄) or CO₂ to increase the efficiency of the reaction (Kumar *et al.* 2009, Talebnia *et al.* 2010). This has been recognized as one of the most cost effective methods of pretreatment (Menon and Rao, 2012). It leads to

higher enzymatic digestibility of biomass and limited creation of inhibitor compared to un-catalyzed steam explosion. SO_2 is one of the most effective catalysts for this process but this is a highly toxic substance. It leads to some degradation of the product and causes incomplete removal of lignin (Zheng *et al.*, 2009). One of the most used catalysts for chemical pretreatment are acids. Acid pretreatment is especially effective for the removal of hemicellulose (Menon and Rao, 2012). There are two types of acid pretreatment based on the dosage of acid used, concentrated- and diluted-acid hydrolysis. In the concentrated acid process a high concentration e.g. H_2SO_4 is used at ambient temperatures. The process can lead to high sugar yields but has a high acid consumption. The main drawbacks are that concentrated acids are toxic, corrosive and hazardous and the acid needs to be recovered leading to high processing costs (Kumar *et al.* 2009, Talebnia *et al.*, 2010).

The diluted acid approach is a more widely used pretreatment method. It is used commercially to manufacture furfural from cellulosic materials (Kumar *et al.*, 2009). Diluted acid pretreatment requires a lower concentration of acid but higher temperatures than concentrated acid methods (Carvalho *et al.*, 2008). Different types of acid and reaction condition can be used depending on the type of biomass processed. Usually high sugar yields and biomass separation rates can be obtained in a short time (Menon and Rao, 2012). A drawback of the method is that it leads to a relative high rate of hemicellulose loss although a two stage processes can be employed to decrease the decomposing rate (Talebnia *et al.* 2010). The acid is corrosive on the equipment but this problem is less severe than with concentrated acid. The process does create many process inhibitors and Ph. neutralization is required before further processing (Talebnia *et al.*, 2010). Research is continuing to find more mild acid catalyst which are able to produce high yields. A recent study looked at the possibilities to use a solid acid catalyst instead of liquid acids. The advantages are they are more easy to recycle and more environmentally friendly. However, more research is needed to further develop this technology (Guo *et al.*, 2011). Overall acid pretreatment methods are effective but expensive and can cause many operational problems due to the toxicity of the acids (Zheng *et al.* 2009, Carvalho *et al.* 2008, Kumar *et al.* 2009).

Alkaline pretreatment methods employ sodium, potassium, or calcium hydroxide as a catalyst to induce a molecular breakup of the biomass. Sodium and calcium hydroxide (lime) are the most commonly used catalyst. The biomass is soaked in an alkaline solution for several hours to days. The residue time depends on the process temperature. The process can be done at room temperature but this requires very long residues times of around a week (Menon and Rao, 2012). The alkaline induces a swelling of the biomass which decreases the structural bounds in the material making it more susceptible to hydrolysis. The process is well suited for agricultural residue and hard woods with a low lignin content but less effective on soft woods with a high lignin content (Kumar *et al.* 2009, Talebnia *et al.* 2010). The alkaline can bind as a salt to the biomass acting as a fermentation inhibitor (Carvalho *et al.*, 2008). The salts need to be removed before further processing, increasing the cost of the process. The efficiency of the reaction can be increased by the addition of an oxidant agent (air/oxygen or Hydrogen peroxide). A steam explosion process can then be used to decrease the residue times (Carvalho *et al.* 2008, Talebnia *et al.* 2010). The processes of acid and alkaline pretreatment can also be done in a sequence to produce a very pure end product although this significantly drives up the cost of processing (Carvalho *et al.*, 2008). The advantages of the alkaline pretreatment method are that the lignin structures are separated from the (hemi)cellulose and that lime is a cheap material. The main drawbacks are the long residue times, high concentration of alkaline needed and the production of process inhibitors (Zheng *et al.* 2009, Menon and Rao 2012).

Ionic liquid (IL) are a new class of chemical solvent which can be used for pretreatment. They are also referred to as green solvents due to their possible low environmental impact. The solvents are liquid at room temperature and come in two main categories; simple salts and binary ionic liquids. They are non-volatile, thermally stable, bio-degradable and produce high reaction rates giving them an advantage over other solvents (Zheng *et al.* 2009, Guo *et al.* 2011). The properties of the solvent can be adjusted to suit the requirements of a process. The advantages are that high sugar yields can be obtained, the energy

demand is low and the process is easy to operate. IL's have great commercial potential but the field is still under development and many issues remain. IL's are expensive and need to be regenerated before they can be reused. The separation of the IL and other extractives e.g. lignin is important but increases the cost and complexity of the process. There is also little known about the toxicology of the liquids and there is a lack of knowledge about their physico-chemical characteristics. IL are a promising technology but currently only used experimentally, more research is needed to address the challenges (Menon and Rao, 2012).

The organosolvation process involves the use of an organic solvent mixed with an inorganic acid catalyst (HCl or H₂SO₄). The use of ethanol and methanol is favorable as organic solvent because of their low price. The solvents do need to be removed after treatment because they can inhibit further processing. The process increases the hydrolysis yield and can separate relative pure lignin from biomass (Kumar *et al.*, 2009). Currently the process is of limited industrial interest because large pressure vessels are needed making the process complex and expensive (Zheng *et al.* 2009). Ozonolysis is studied as a means to greatly reduce the lignin content within biomass making the biomass more susceptible to hydrolysis. By subjecting biomass to ozone the lignin and hemicellulose are degraded without the formation of many inhibitors. However, large amounts of ozone are required making this not a commercially attractive option (Kumar *et al.*, 2009). Pulsed-Electric Field (PEF) pretreatment has also been studied. This uses a short burst of high voltage between two electrodes to decompose biomass. It can be done under ambient temperatures, has a low energy use and requires simple equipment. However, the ash production can be high and more research is required to develop it to commercial scale (Kumar *et al.*, 2009). Chemical pretreatment methods can refine biomass under a lower temperature than physico-chemical pretreatment leading to lower energy consumption. Yet, the toxicity of the chemicals and the energy consumed to make them needs to be carefully assessed in order to provide a truly sustainable source of energy.

5.6 Biological pretreatment

Biological pretreatment uses microorganisms to disrupt the molecular structure of biomass. White- brown- fungi, and multiple bacteria have been investigated as a pretreatment process. The advantages are the low energy requirements, that no chemicals are needed and the mild condition which better preserve the material (Menon and Rao, 2012). The microbes can decompose the lignin in the biomass without consuming cellulose material. Multiple biomass sources, reaction conditions and microbes have been tested however no large scale pilot plants have been commenced (Saritha and Arora, 2012). The yields are currently very low, it is time-consuming, difficult to control and the microorganism can consume some of the useable parts of the biomass (Zheng *et al.* 2009, Kumar *et al.*, 2009 Talebnia *et al.* 2010, Menon and Rao, 2012). It is a promising technology because it can be a very sustainable method of pretreatment but much more research will be needed to make this commercially attractive (Menon and Rao, 2012).

5.7 Hydrolysis

Pretreated lignocellulose biomass needs to undergo hydrolysis to convert the (hemi)cellulose into fermentable sugars. The hydrolysis step converts the complex carbohydrates of biomass into simple sugar monomers (Sarkar *et al.* 2011, Singhania *et al.* 2012). The process can yield multiple types of sugars depending on the characteristics of the biomass and processing techniques used. Glucose (C₆ sugar) is the main target product of the conversion process since it is an important intermediate product for further conversion into fuels or chemicals. The main source of glucose is the cellulose in the biomass but the hemicellulose is next to glucose also converted into xylose (C₅ sugar), arabinose (C₅ sugar), galactose (C₄ sugar) and mannose (C₂ sugar). These sugars cannot be efficiently processed into fuels via biological conversion but the C₅ sugars can act as an intermediate product for the production of chemicals such as furfural. The hydrolysis is done in an aquatic media via an enzymatic or acid treatment. Total sugar yields of hydrolysis are usually over 90% of the theoretical limit (Balat *et al.* 2007, Lestari *et al.* 2009). The

efficiency of the reaction is affected by the type of pretreatment e.g. level of inhibitor and biomass source e.g. lignin content (Huang *et al.* 2011). Dilute acidic hydrolysis is one of the most currently used methods of hydrolysis. It is done at a temperature of 120 to 200 °C with a pressure of 15 psi to 75 psi. The reaction times range from 30 minutes to 2 hours (Kumar *et al.*, 2009). However, the process leads to the formation of many fermentation inhibitors. These need to be washed off before further processing leading to higher production costs (Limayem and Ricke, 2011). Concentrated acid hydrolysis can be performed under milder temperature close to atmospheric pressure but also leads to the formation of toxic compounds (Kumar *et al.*, 2009).

Enzymatic hydrolysis is more favorable compared to acid hydrolysis due to the milder process conditions, lower levels of inhibitor formation, lower energy requirements and less equipment corrosion (Kumar *et al.* 2009, Limayem and Ricke, 2011, Zhang *et al.* 2012,). It has a slower reaction rate than acid hydrolysis but can lead to very high yields. However, the high costs of the enzymes remain an important barrier for the economics of this process (Geddes *et al.*, 2012). Currently large amounts of enzymes are needed for conversion (Singhania *et al.*, 2012). The costs of have been reduced substantially over the last years but further improvements are needed (Balat *et al.*, 2007). The efficiency of enzymatic hydrolysis can be increased by adding a catalysts e.g. surfactants, polymers, or proteins to the reaction vessel. These compounds can reduce the rate of enzyme deactivation leading to higher yields. Research is has also focused on novel enzymes which are able to achieve high yields with lower loading (Lee *et al.* 2008, Huang *et al.* 2011). For instance, the use of thermophilic bacteria and thermostable enzymes which can work at higher temperatures can reduce the need for high enzyme loadings (Miller and Blum 2010, Bhalla *et al.* 2012). Increasing the recyclability of the enzymes e.g. via filtration can also make the process more economical (Huang *et al.*, 2011). Cost effective hydrolysis remains a major limitation to the economic viability of second generation biofuels (Limayem and Ricke, 2011).

5.8 Concluding remarks

Lignocellulose biomass needs to undergo pretreatment before it can be transformed into fuel and chemicals. The biomass first needs to be chopped into a finer particle size to allow further conversion and increase transportation efficiency. The copped biomass can be directly converted via thermal conversion into fuels and chemicals. However, pelletisation or torrefaction techniques can also be applied to increase the efficiency of the thermal conversion processes as well as to improve the storage properties of the biomass. More extensive pretreatment techniques are required to allow lignocellulose biomass to be processed via biological conversion. The presence of lignin and hemicellulose can lead to the formation of weak acids during pretreatment which act as inhibitors for later fermentation (Carvalho *et al.*, 2008, Menon and Rao, 2012). The separation of lignin early in the conversion process can increase the efficiency of biological conversion. Furthermore, lignin is also an interesting raw material for a range of products. The efficient separation of biomass into its main components before processing can thus increase the viability of second generation biomass technologies (Busch *et al.*, 2006, Menon and Rao, 2012, Gullón *et al.*, 2012). However, efficient and cost effective separation techniques have not yet been developed (De Wild *et al.*, 2011). Pretreatment technologies which are able to separate biomass into its individual components as well as make the cellulose molecules accessible for hydrolysis are highly desirable.

The (hemi)cellulose contained in the biomass are converted via enzymatic or acid hydrolysis into simple sugars. This first requires the disruption of the molecular bounds within the biomass to allow the acids or enzymes to access the (hemi)cellulose molecules. Figure 5.2 provides an overview of the most promising pretreatment technologies for biological conversion. Diluted acid pretreatment is one of the most developed technologies and can provide high sugar yields. However, the acid is toxic, inhibitors are created during processing and lignin cannot be effectively removed. Hydrolytic pretreatment method are less effective but more environmentally friendly. Steam-explosion is a well-developed concept and currently a good candidate for biomass pretreatment (Carvalho *et al.* 2008, Talebnia *et al.* 2010). The use of ionic liquids, biological pretreatment and pulsed-electricfield (PEF) pretreatment could potentially

provide more cost effective and environmentally friendly methods of pretreatment. However, more research will be needed to develop these technologies into a commercially viable scale.

Each pretreatment process has certain advantages and disadvantages (Talebnia *et al.*, 2010). For instance, low cost treatments are often associated with high costs for catalysts recovery and inhibitor removal (Menon and Rao, 2012). The effectiveness of the pretreatment process depends on the type of biomass and purpose of the final product. Several aspects are important when selecting a pretreatment process. It should be able to increase sugar yields and preferably use a low temperature to reduce product degradation and capital requirements (Zhang, 2008). Other important factors to consider are the formation of inhibitors, possibility to recover valuable co-products and sustainability of the catalyst that is used. Furthermore, a good understanding of the molecular structure of the biomass is needed to select the most appropriate pretreatment method (Menon and Rao 2012). Enzymatic hydrolysis is the most favorable technology for the conversion of (hemi)cellulose into sugars but its high costs are a major limitation for commercialization.

Thermal conversion processes require relative simple pretreatment processes such as chopping, shredding, drying or pelletisation to allow further conversion. The pretreatment of lignocellulose biomass to allow biological conversion is more costly. Currently none of the pretreatment methods is able to provide an economically viable method (Zheng *et al.* 2009, Menon and Rao 2012). There is a need to significantly increase its efficiency to make biological conversation more competitive (Yang and Wyman 2007, Zhang, 2008, Menon and Rao, 2012, Chiamonti et al. 2012). Important obstacles for wider implementation are the sufficient separation of the (hemi)cellulose and lignin as well as the formation of fermentation inhibitors, the use of toxic chemicals and/or the energy efficiency of the process. Steam-explosion is currently one of the main candidates for a commercial pretreatment, the use of ionic liquids or supercritical fluids are interesting medium to long term alternatives. The development of more cost effective pretreatment and hydrolysis methods are an essential element for the wider implementation of second generation biofuels.

Figure 5.2: Overview of pretreatment methods

Method of pre-treatment	Sugar yield	Inhibitor formation	Byproduct generation	Reuse of chemicals	Applicability to different feedstock's	Equipment cost	Success at pilot scale	Advantages	Limitations & disadvantages
Mechanical	L	Nil	No	No	Yes	H	Yes	Reduce cellulose crystallinity	High Power consumption than inherent biomass energy
Mineral acids	H	H	H	Yes	Yes	H	Yes	Hydrolysis of cellulose and hemicellulose, alters lignin structure	Hazardous, toxic and corrosive
Alkali	H	L	H	Yes	Yes	Nil	Yes	Removal of lignin and hemicellulose, increases accessible surface area	Long residence time, irrecoverable salts formed
Liquid hot water	H	H	L	No	—	—	Yes	Removal of hemicellulose making enzymes accessible to cellulose	Long residence time, less lignin removal
Organosolv	H	H	H	Yes	Yes	H	Yes	Hydrolyze lignin and hemicellulose	Solvents needs to drained, evaporated, condensed and reused
Wet oxidation	H or L	Nil	L	No	—	H	—	Removal of lignin, dissolves hemicellulose and causes cellulose decrystallization	—
Ozonolysis	H	L	H	No	—	H	No	Reduces lignin content, no toxic residues	Large amount of ozone required
CO ₂ explosion	H	L	L	No	—	H	—	Hemicellulose removal, cellulose decrystallization, cost-effective	Does not modify lignin
Steam explosion	H	H	L	—	Yes	H	Yes	Hemicellulose removal and alteration in lignin structure	Incomplete destruction of lignin—carbohydrate matrix
AFXE	H	L	—	Yes	—	H	—	Removal of lignin and hemicellulose	Not efficient for biomass with high lignin content
Ionic liquids	H/L	L	—	Yes	Yes	—	—	Dissolution of cellulose, increased amenability to cellulase	Still in initial stages

H:- High and L:- Low.

Source: Menon and Rao 2012

Chapter 6 - Biomass conversion

Biomass can be converted into value added products via multiple conversion methods. Biomass with a moisture below 50% can directly be combusted for electricity or heat production. However, the profit margins and conversion efficiency (20-40% for electricity production) for this form of utilization is low (Demirbas 2006, Sims *et al.* 2009). The conversion of biomass into higher value products such as liquid fuels and chemicals can provide a greater return on investment. There are three main reactions i.e. chemical, thermal and biological reactions, by which the chemical composition of biomass can be altered. In many processes a combination of the available reaction pathways is used to transform biomass into value added products. Biological conversion is currently the main method of making ethanol from sugar crops and is intensively studied (Mohammadi *et al.*, 2011). Thermal conversion i.e. pyrolysis and gasification are currently the main conversion methods for second generation biomass sources. An important aspect in choice for conversion technology is the chemical composition of the original feedstock. Biological conversion is not able to react with lignin and the compound acts as inhibitor during fermentation. It needs to be filtered out before processing or biomass with a low lignin content e.g. sugars, grasses or waste should be used. Thermal stresses are able to break down lignin into gasses or liquid products. The thermal conversion of biomass, often in combination with a chemical catalyst, has a long history of research and many similarities with current petrochemical conversion processes. These processes are able to produce a wider range of products such as heavy fuels and aromatics compared to biological conversion (Mohammadi *et al.*, 2011). The success of biomass derived products will partly depend on their utility for current applications. The properties of bio-oils from pyrolysis are however different and more variable than current petroleum products chemicals. One of the main differences between bio-oils and fossil fuels is the oxygen content of the fuel. Additional upgrading steps are therefore often required to make bio-oils suitable for use in conventional applications (Anitescu and Bruno, 2012). This section will present a review of the technologies able to upgrade biomass into more usable products.

6.1 Chemical conversion

This section will discuss the chemical conversion of seed oil into fuel which is the main method employed to produce bio-diesel. Biodiesel production has become popular due to government incentives and the relative low cost of the conversion process. The oil can be extracted from the seeds by mechanical pressure (seeds usually preheated to 40-50 °C), a reaction with a solvent, or by a combination of these techniques (Lestari *et al.* 2009, Mata *et al.* 2010). The oil is further processed via a transesterification reaction into biodiesel which is a more energy dense fuel than ethanol. The triglycerides molecules contained in the oil are converted to diesel via a reaction induced by an alcohol and alkali catalyst. Separate layers are formed in the reaction vessel where after the products can be extracted (Mata *et al.*, 2010). Solid catalyst can increase the ease of product separation and prevent the erosion of equipment (Naik *et al.*, 2009). Heterogeneous catalysts have also been developed to combine the reaction and separation steps and increase the efficiency of the process (Kiss and Bildea, 2012). Glycerol is the main byproduct of the process and can be converted to additional fuels or chemicals (Mata *et al.*, 2010). The same process can be applied to animal fats collected from animal processing companies. The fats are melted down and filtered to obtain pure fats which are suitable for transesterification (Mata *et al.*, 2010). Biodiesel has a lower sulfur and aromatic content than conventional diesel. The carbon monoxide and particulate matter emissions are reduced but the NO_x emissions are higher compared to conventional oil (Al-Sabawi and Chen, 2012). The limited number of conversion steps needed make seed oil types of biodiesel currently more attractive than converting second generation sources to bio-fuels.

6.2 Fermentation

In this paragraph the methods used to ferment i.e. using microorganisms, C5 and C6 sugar molecules into value added products. The sugar molecules undergo a molecular change due to the activity of micro-organisms. The process can be done under aerobic condition (in the presence of oxygen) or under anaerobic (without oxygen) depending on the type of organism used (Naik *et al.* 2009). Multiple fermentation methods have been developed which are capable of convert sugars into acid, ethanol, triglyceride, olefins or hydrogen. Ethanol can directly be used while other products usually need to be further upgraded e.g. into diesel fuels (Westfall and Gardner, 2011). Ethanol derived from first generation sources is predominately made via a fermentation process. During this fermentation process the sugars are mixed in large tanks with water and the microorganisms forming a so called 'fermentation broth'. The fermentation broth is kept under anaerobic conditions and elevated temperature (30 °C) for several hours (Limayem and Ricke, 2011). The microorganisms can be separated from the fermentation broth and re-use in a new production cycle (Sanchez and Cardona, 2007). The microorganism *Saccharomyces cerevisiae* is currently the most used for ethanol production. The use of yeasts does however lead to large amounts of CO₂ emissions and nitrogen needs to be added to increase reaction rate (Balat *et al.* 2007, Limayem and Ricke, 2011). The main method of ethanol recovery is via distillation (Banerjee *et al.*, 2009).

Second generation biomass requires extensive pretreatment to make the sugar accessible for fermentation (Frigon and Guiot, 2010). The hydrolysis of lignocellulose biomass yields multiple sugar molecules, those originating for cellulose and those from hemicellulose. The fermentation of mixed sugars is more complex and less efficient than the fermentation of only glucose molecules. Organisms used for the fermentation of sugarcane or corn cannot ferment xylose and galactose sugars effectively (Limayem and Ricke, 2011). Efficient mixed sugar fermentation is needed to make lignocellulose biomass fermentation commercially attractive (Kim *et al.* 2012). However, only a limited number of microbes are able to convert hemicellulose and its monomers into ethanol (Kumar *et al.* 2009). The mixed sugar fermenters also need to be able to cope with high levels of ethanol and process inhibitors contained in biomass. Multiple microbes are researched but organism capable of fermenting these sugars with high efficiency have not yet been discovered (Madhavan *et al.* 2010, Jordan *et al.* 2012). It is still an immature technology and genetic engineering may be needed to make microbes with high mixed sugar yields (Banerjee *et al.* 2009, Chen 2010). An alternative to ethanol is to make hydrogen gas from second generation sources. However, the efficiency of this process is currently low and major technological hurdles remain (Hallenbeck and Ghosh, 2009). Thermodynamic and metabolic constraints of naturally occurring microorganisms limit the hydrogen yield via fermentation. Genetic engineering is needed to increase the hydrogen production capabilities of microbes (Kumar *et al.* 2009, Hallenbeck and Ghosh, 2009, Patel and Kalia 2012).

Multiple reaction setups have been developed to convert second generation biomass into fuel via fermentation. These include, separate hydrolysis and fermentation (SHF), partial saccharification and cofermentation (PSCF), simultaneous saccharification and fermentation process (SSF), and consolidated bioprocessing (Sanchez and Cardona 2007, Balat *et al.* 2007, Menon and Rao, 2012). SHF is the standard process in which the biomass is first converted into sugars and than fermented into ethanol. The advantage is that the reaction conditions can be made optimal for both processes (Menon and Rao, 2012). PSCF is a method of fermentation in which both reactions are conducted in a single vessel but in separate stages. The conditions are first optimized for the enzymes where after the conditions are altered to suit the fermentation process (Kumar *et al.* 2009). However, the integration of the hydrolysis and fermentation steps in a single reaction is more favorable. SSF can perform the enzymatic hydrolysis and the fermentation simultaneously in a single vessel. It can reduce processing costs as well as increase the efficiency of hydrolysis process (Limayem and Ricke, 2011). A higher efficiency can be achieved if the glucose molecules are directly converted into ethanol. The sugars molecules act as inhibitors during hydrolysis so lower concentration can increase the efficiency of enzymatic hydrolysis (Balat *et al.* 2007) SSF is one of the most efficient strategies for ethanol production (Menon and Rao, 2012). Consolidated

bioprocessing is a novel approach first proposed in 1996. It makes use of microbes able to perform both sugar production and fermentation simultaneously to directly convert cellulose to ethanol reducing the need for costly enzymes (Sarkar *et al.* 2011). It is seen as the best configuration for low cost fermentation of cellulosic biomass (Elkin *et al.* 2010, Olson *et al.* 2011). However, there are no naturally occurring microbes able to achieve high yields, fast conversion rates and also have a high tolerance for process inhibitors (Xu *et al.*, 2009). Genetic engineering is needed to make more efficient microbes for this process (Banerjee *et al.* 2009, Menon and Rao, 2012).

The biological conversion of biomass has a favorable environmental performance compared to thermo-chemical conversion methods. It is the primary conversion method for first generation sources due to the high selectivity and low energy demand. To make the fermentation of second generation sources economically viable novel microorganisms need to be discovered or developed via genetically engineering. Genetically engineered organisms can increase yields but they can also pose a threat to the environment and public health. The risks of novel organism needs to be carefully assessed e.g. with biotechnology risk assessment protocols to make them safe for use (Limayem and Ricke, 2011). Improved separation processes are also desirable since distillation is an energy intensive process (Banerjee *et al.*, 2009). The fermentation of second generation biomass is currently not economically viable due to the need for extensive pretreatment and the lack of co-fermenting microorganisms. The development of organism capable of fermenting mixed sugars e.g. a combination of immobilized cell cultures and consolidated bioprocessing can potentially lead to low cost and efficient conversion of second generation biomass (Lee *et al.*, 2008). Major breakthroughs are needed in developing novel organisms capable of significantly lowering the costs second generation biomass fermentation to make this route more commercially viable.

6.3 Pyrolysis

This section discusses the technique of pyrolysis which can be used to convert biomass into value added products. Pyrolysis refers to a process in which thermal energy is applied to materials in the absence of oxygen. The thermal conversion of biomass via pyrolysis is done with fast or flash pyrolysis processes in which the reaction times are very short (Naik *et al.*, 2009). During flash pyrolysis the biomass is heated to 400–600 °C in 0.5 till 3 seconds followed by rapid cooling (Verma *et al.* 2011, Robbins *et al.* 2012). The long molecular chains in the biomass break down into gasses, condensable vapors (tar and oil) and char. The different components of biomass react at different rates and due to multiple mechanisms e.g. cracking, isomerization and dehydrogenation (Vamvuka, 2011). The main products of flash pyrolysis are bio-oil (70-75%), char (10-15%) and gas (10-15%) (Butler *et al.*, 2011). The pyrolysis vapors are condensed into bio-oil which is a complex mixture of several hundred organic compounds (Xiu and Shahbazi, 2012). The biggest difference between petroleum and bio-oil is the oxygen content; bio oil has 10 up to 45% oxygen where petroleum has almost no percentage of oxygen (Russo *et al.*, 2012). The Bio-char can be used as fertilizer so a substantial portion of the minerals and nutrients can be recycled back to the soil (Verma *et al.* 2011).

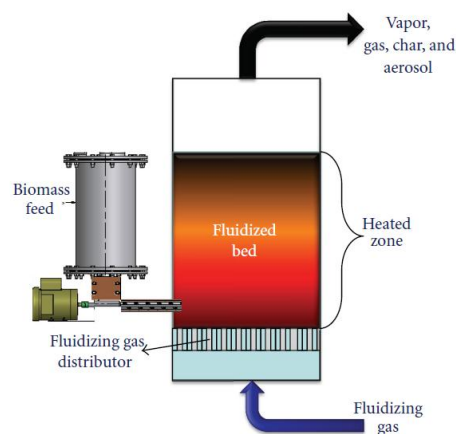
Pyrolysis can use many types of feedstocks and all the components of the biomass are converted. The biomass has to have a moisture content below 10-15% and a finely grounded particle size of 2–3mm efficient conversion (Bridgwater 2006, Verma *et al.* 2011, Jahirul *et al.* 2012). The temperature and reaction time can have a significant influence on the properties of the end product (Robbins *et al.*, 2012). The structure of the feedstock is also an important determinant for oil quality. Cellulose is the main source of bio-oil whereas lignin is mainly converted to char (Jahirul *et al.*, 2012). Yet, some of the lignin is also converted to oil which increases the molecular weight of the end product (Robbins *et al.*, 2012). Woody biomass has high amounts of lignin and generally delivers the highest quality oil. It has lower oxygen content leading to higher heating values of the oil compared to bio-oil from grasses and agricultural residues (Butler *et al.*, 2011). The hemicellulose content also influences the conversion process. Hemicellulose is terminally the least stable molecule. High hemicellulose containing biomass leads to

larger quantities of char and gas and lower bio-oil yields (Butler *et al.*, 2011). Furthermore, residues and grasses have a high ash content which leads to the increased formation of water and gas during the pyrolysis reaction. A maximum of 3% ash is recommended for efficient conversion. The ash content can potentially be decreased with a water or acid pretreatment process. Biomass with high cellulose and moderate lignin content is the most favorable raw material for pyrolysis (Jahirul *et al.*, 2012). The bio oil can be directly used as a fuel but the properties of the oil i.e. high acidity, corrosiveness, high water content, relative poor heating values, instability, heterogeneous composition and high viscosity limit the direct use in many applications (Butler *et al.* 2011, Al-Sabawi and Chen 2012).

Multiple reactor types have been developed for the flash pyrolysis process. The fluidized beds reactors, see figure 6.1, are currently the only commercial available reactors. They come in two varieties, the bubbling fluidized (BFBs) and circulating fluidized beds reactors (CFBs). CFBs are well understood since they are also used in the petrochemical industry. The reactors are now redesigned for use in the biomass industry. Fluidized beds reactors produce a high quality product and can yield between 70-75% liquid oil (Butler *et al.*, 2011). The reactors are popular due to their reliability, simplicity and ease of scaling up (Bridgwater 2006, Vamvuka 2011). Other reactors are also being developed. The Auger reactor has the potential for mobile use to compress biomass and increase transportation efficiency (Verma *et al.*, 2011). It can have a large commercial potential but it is still in the development phase (Xiu and Shahbazi, 2012). Vacuum pyrolysis reactors are also considered to be potential technology for commercialization (Goyal *et al.* 2006, Verma *et al.* 2011).

Several commercial and research reactors are under construction but issues remain with scaling up the technology (Butler *et al.* 2011, Xiu and Shahbazi, 2012). Additional research is needed to improve the reliability of the reactors, the quality of the oil and finding methods to increase supply chain efficiency (Jahirul *et al.*, 2012). The use of catalysts during the pyrolysis reaction can increase the selectivity of the process yielding high-octane oils more suited for direct applications (Zhou *et al.*, 2011). The use of microwaves to heat biomass has also been researched. It leads to rapid heating and allows for lower process temperatures. It can reduce the need for pretreatment because large particles size can be used and a higher moisture content can be tolerated (Yin 2012, Macquarrie *et al.* 2012). The yields depend on the properties of the feedstock because the material must be able to absorb the microwave energy. Additives can be used to increase the microwave energy absorption. It can provide a more energy efficient method of pyrolysis but has not been extensively studied (Yin, 2012).

Figure 6.1: General representation of fluidized bed reactor used for pyrolysis



Source: Verma *et al.*, 2011

To allow wider utilization the bio-oil has to be upgraded. There are two main routes available to upgrade bio-oil, hydrogenation and catalytic cracking (Butler *et al.*, 2011). Hydrogenation takes place at an elevated pressure and temperature under the influence of a chemical catalysts and high levels of hydrogen.

This results in the removal of oxygen and the creaking of the large molecules into lighter fuel (Butler *et al.*, 2011). It is widely used in the petroleum industry to remove impurities from crude oil such as sulfur and nitrogen (Melero *et al.* 2012, Al-Sabawi and Chen 2012). Catalytic hydroprocessing is a well-developed technology able to deliver high value products. It is a viable option for bio-oil upgrading and can yield 30–50% refined bio-oil which is more stable, energy dense, and less corrosive than crude bio-oil. The remaining mass is converted to solids, gasses and water. However, high costs of the equipment and hydrogen make it commercially unattractive (Mortensen *et al.* 2011, Xiu and Shahbazi, 2012 Ko *et al.* 2012) Reducing hydrogen consumption is therefore an important topic of research (Melero *et al.*, 2012). Novel catalyst and reaction step ups are being developed to increase the efficiency of the process (Huber *et al.*, 2006, Al-Sabawi and Chen, 2012).

Hydrogen free catalytic upgrading is also possible but there is a lack of catalysts specifically designed for bio-oil upgrading (Melero *et al.*, 2012). Catalytic vapor cracking removes oxygen via a zeolite catalyst at elevated temperature under atmospheric pressure. However, the yields are relatively low (34% of the feed) and large quantities of cokes are formed (Huber *et al.*, 2006). Furthermore, the difficulty of recovering the catalysts limits the commercial potential of this form of upgrading (Butler *et al.*, 2011). The heterogeneous nature of bio-oil makes catalytic upgrading reactions very complex. Multiple catalysts are under investigation but a better understanding of the reaction mechanics is needed to design more effective catalysts (Mortensen *et al.* 2011, Alonso *et al.*, 2012). The oil can also be mixed with ground char to yield slurry oil suited for gasification via stream reforming (Huber *et al.* 2006, Robbins *et al.* 2012). Steam reforming makes syngas which can be converted to a range of high and low value products. However, steam reforming has low thermal efficiency and high costs (Huber *et al.*, 2006). Esterification (a reaction with an alcohol) can be used to reduce the chemical instability and acidity of bio-oil. The best results are obtained by using an acid catalyst but the resulting bio-oil remains of relative low quality (Butler *et al.* 2011). It is however one of the most practical methods for upgrading due to low costs and simplicity (Xiu and Shahbazi, 2012). Emulsion can also be used which involves the adding of crude diesel to upgrade the quality of the oil. However, the process leads to highly corrosive fuels and the emulsifying agents are expensive. Useful chemicals can also be directly separated from the bio-oil but more reliable and low cost separation techniques are needed (Xiu and Shahbazi, 2012). The economical upgrading of bio-oil is one of the biggest challenges for the commercialization of pyrolysis technologies (Xiu and Shahbazi, 2012).

Biomass pyrolysis reactions are not yet fully understood but it is currently an active area of research (Vamvuka, 2011, Mettler *et al.*, 2012). Significant advancements have been made and pyrolysis is close to becoming a commercial biomass conversion technology. The flash pyrolysis process has shown to be one of the most cost effective thermal conversion methods. It also provides an opportunity to increase the efficiency of decentralized biomass production since it allows for more efficient transporting (Butler *et al.* 2011, Robbins *et al.* 2012). Pyrolysis oil contains around 70% of the energy and 83% of the mass of the original biomass (Zhou *et al.*, 2011). Between 53% and 63% of the original energy remains after upgrading, additional refining further decreases the energy yields (Huber *et al.*, 2006). The fuel upgrading technologies are however not yet available on a commercial scale which is a major limitation for the commercial success of pyrolysis. Pilot project of large scale upgrading technologies have just recently started (Butler *et al.*, 2011). The direct use of bio-oil for electricity generation is one of the main short term opportunities (Jahirul *et al.*, 2012). Flash pyrolysis is still in development and many test installations suffer from limited operational hours. The operational reliability of large scale pyrolysis installations needs to increase. Furthermore, the energy demand of pyrolysis is relatively large due to the high temperatures and the need for finely grounded biomass (Vamvuka, 2011, Jahirul *et al.* 2012). Improvements are needed in the heat transfer efficiency, the feedstock flexibility and the quality of the bio-oil to allow wider commercial application of pyrolysis conversion (Venderbosch and Prins 2009, Butler *et al.* 2011, Jahirul *et al.*, 2012).

6.4 Liquefaction

Liquefaction, also called hydrous pyrolysis, refers to the hydrothermal upgrading of biomass. The process uses a pyrolysis reaction (applying thermal energy without oxygen) at high pressures using sub-critical or supercritical liquids. It was originally designed to convert coal into liquid fuels (Xiu and Shahbazi, 2012). Hydrothermal upgrading can be used as pretreatment step, for the direct conversion of biomass into liquids or for upgrading bio-oils (Zang 2010, Yeh *et al.* 2012). Biomass first needs to be converted into a paste via heat and/or acid treatment before processing. The reaction temperatures range from 250-300 °C at pressures of 120-180 bars for 10-60 minutes, usually in the presence of a catalyst. The large molecular structures in the biomass disintegrate under these extreme conditions and recombine into new molecules. Both batch and continuous production processes have been developed (Xiu and Shahbazi, 2012). The reaction is very complex involving multiple reactions such as dehydration, dehydrogenation, deoxygenation, and decarboxylation (Verma *et al.*, 2011). Multiple catalysts have been tested to increase the efficiency of the process but the mechanics of the process and the influence of catalysts are not yet fully understood (Zhou *et al.* 2011, Verma *et al.* 2011). The process yields a bio-crude (yields of up to 45%-60% of total biomass) which has a reduced oxygen content of 10-15% (Naik *et al.* 2009, Robbins *et al.* 2012). The oil is of a higher quality than the bio-oil produced by fast pyrolysis. The by-products are gasses, char and some organic compounds (Xiu and Shahbazi, 2012). The main advantage of the process is that biomass with a high moisture content (up to 80%) can be used so the technique is well suited for the processing of algae biomass and organic waste e.g. manure. Furthermore, the biomass is completely sterilized which can be an advantage for storage (Peterson *et al.*, 2008). The process is less suited for woody biomass or agricultural residues. High amounts of lignin lead to lower yields and more char formation. The oil can be further upgraded by e.g. hydrodeoxygenation into diesel fuel but this has not been extensively researched (Xiu and Shahbazi, 2012).

Supercritical water gasification (SCWG) is a related process in which biomass is processed in water above its supercritical point (374 C and 22.1MPa). Operating temperatures above 500 °C produce a hydrogen rich gas where as temperatures around 400 °C produce a methane-rich gas. Multiple reactor types and reaction conditions have been tested (Wen *et al.*, 2008). The process can quickly convert the biomass into a new product but it is not yet commercially attractive due to high costs, clogging of reactors and catalyst inactivity. Better heat and catalyst recovery processes as well as improved reactor designs are needed to make the process commercially viable (Peterson *et al.* 2008, Wen *et al.* 2008).

The high pressures required for liquefaction has proven to be an obstacle for large scale development. The high-pressure equipment leads to technical difficulties and increases the capital cost needed for the conversion technique. Some demonstration projects are running but the process is still in the early stages of development (Huber *et al.* 2006, Xiu and Shahbazi, 2012). The primary reaction mechanics are not yet fully understood and the role of the catalysts remains difficult to determine (Zang 2010, Xiu and Shahbazi, 2012). The yields are currently relatively low, the catalysts de-activate quickly and the oil solidifies at 80 °C which may limit its application (Robbins *et al.* 2012, Xiu and Shahbazi, 2012, Yeh *et al.* 2012). The technology can potentially be scaled up to large scale facilities but yields need to increase and the energy demand reduced to make the process more commercially attractive (Xiu and Shahbazi, 2012). It is unlikely that liquefaction can be commercialized for bio-oil production in the short term (Huber *et al.* 2006, Verma *et al.* 2011).

6.5 Gasification

This paragraph will discuss the technique of gasification which is one of the most studied methods to convert lignocellulose biomass into value added products via biological or thermal conversion. The possibility to produce ethanol from syngas has been studied since the 1920s but the high costs have not made the process commercially attractive (Munasinghe and Khanal, 2010). The fermentation of manure, sewage sludge, and other organic waste into methane is already a commercial industry e.g. in Germany (Cantrell *et al.*, 2008). Second generation sources need to undergo pretreatment and hydrolysis to

effectively convert the biomass via fermentation into syngas. This is currently not a viable route commercially due to the large number of conversion steps required (Mohammadi *et al.*, 2011, Chandra *et al.* 2011). The most studied gasification process for second generation sources is thermo-chemical conversion. In this process the biomass is heated to 800–1000 °C (or higher) in the presence of controlled amount of air, oxygen or steam leading to the partial combustion of the biomass (Damartzis and Zabaniotou 2010). The biomass decomposes into four main gasses: carbon monoxide (20-30%), methane (10-15%), carbon dioxide (20-30%), hydrogen (30-40%) and small amounts of ethylene (1%), water vapor (6%) and nitrogen (1%). The quantities of different gasses released depend on the characteristics of the biomass, the type of reactor and the process conditions (Robbins *et al.*, 2012).

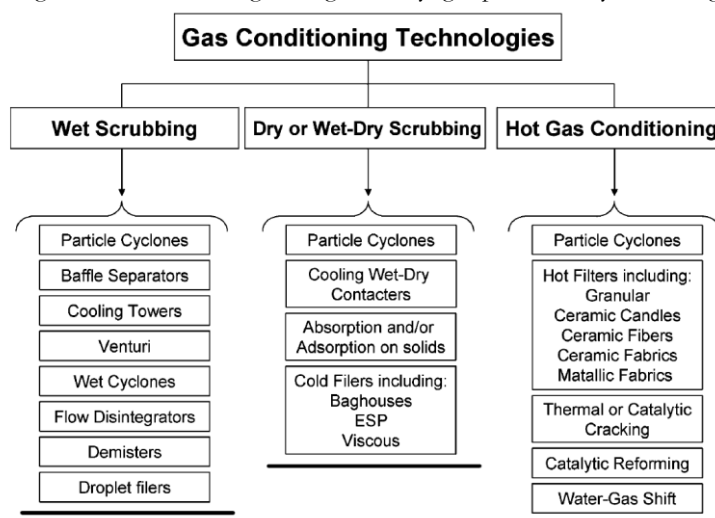
All types of biomass can be used for gasification but the maximum moisture content is 30%. A moisture content below 15% is recommended for efficient conversion (Daniell *et al.* 2012, Robbins *et al.* 2012). The gasification is done in four main steps, size reduction and drying, gasification, cleaning of gas and gas upgrading. Torrefaction has shown to be an efficient pretreatment method for gasification especially for entrained flow gasification which operates at high temperature (Swain *et al.*, 2011). The gasification can be done with or without a catalyst. A non-catalytic process requires higher operating (1300 °C) temperatures whereas a lower temperature can be used in the presence of a catalyst. However, lower temperatures lead to the incomplete combustion of biomass which increases the formation of char and tar. Tar is a mixture of ring structured hydrocarbons and causes corrosion of engines and turbines, catalyst deactivation and emission of potential carcinogenic elements (Damartzis and Zabaniotou 2010, Pereira *et al.* 2012). Control, conversion and limiting tar formation is a key issue for gasification processes (Pereira *et al.*, 2012). The tar can be removed during processing by using high temperatures (above 1000 °C) or by adding processes catalysts and via filtration after processing (Pereira *et al.* 2012). High temperatures increase the costs of processing so the removal of tar at lower temperatures via a catalyst is more attractive (Huber *et al.*, 2006, Zhou *et al.* 2011).

Different types of reactors have been developed for the gasification process. The temperature, pressure and type of feedstock all influence the properties of the gas. The operating temperature has been found to have the biggest influence on the end product (Güell *et al.*, 2011). A high sulfur and ash content in biomass has shown to increase the need for gas cleaning and can reduce the life time of a reaction vessel (Huber *et al.*, 2006). The three main reactors types for gasification are fluidized bed, fixed bed and entrained flow reactors (Kumar *et al.*, 2009_b). The fluidized bed reactors are the most commonly used type and commercially the most attractive (Mohammadi *et al.* 2011, Daniell *et al.* 2012). The required particle size for the reactor is around 8 mm and they can operate at variable loads leading to high flexibility. Fluid bed reactors are an attractive reactor type due to the low cost and ease of scaling up. However, the energy efficiency of the reactor is relatively low and the gas requires extensive cleaning before further processing. Entrained flow gasifiers operate at higher temperatures (1200–1600 °C) and pressures (2–8MPa) and can process both solid and liquid fuels. The higher temperature leads to improved gas quality and higher gas yields. However, this also negatively affects the lifetime of the reactor and the product gas requires additional cooling. The process is therefore more expensive than fluid bed reactors and only cost effective in large scale facilities (Güell *et al.*, 2011). One of the latest developments is the transport reactor gasifier which is a combination of a fluidized bed and an entrained bed gasifier (Mondal *et al.*, 2011). Yet, there is currently no dominant reactor design. New gasification project are often plagued by the cost of tar removal which is usually greater than expected (Kumar *et al.*, 2009_b). More effective tar removal is therefore needed to increase the commercial viability of gasification (Kumar *et al.*, 2009).

The cleaning of syngas is needed before upgrading because, next to tar, the gas can contain alkali compounds, nitrogen and sulfur which can cause erosion of equipment (Kumar *et al.*, 2009_b). Fig 7.2 shows multiple gas cleaning strategies used for the removal of impurities from syngas (Huber *et al.*, 2006). Mechanical methods such as cyclones, various types of filters, and water scrubbers are the most commonly used technologies (Munasinghe and Khanal 2010). The use of membrane-based biogas cleaning processes is attractive but this is currently not available on a commercial scale (Munasinghe and

Khanal 2010, Scholz *et al.* 2012). Thermal cracking is currently one of the most efficient methods for gas cleaning (Kumar *et al.*, 2009). Gas cleaning significantly drives up the cost of production and is one of the least developed aspects of gasification (Pereira *et al.*, 2012).

Figure 6.2: Gas cleaning strategies for syngas produced by biomass gasification



Source: Huber *et al.*, 2006

Cleaned syngas is still of low quality and thus needs to be upgraded to allow wider use. It can be converted to liquid products via fermentation, a Fisher-Tropsch synthesis, methanol synthesis and isosynthesis or converted into hydrogen via a water gas-shift reaction (Huber *et al.*, 2006). The two key processes to upgrade syngas are the Fischer-Tropsch (FT) process and fermentation. FT makes use of a metal catalyst to thermo-chemically convert the syngas into a liquid using a pressure of 20 to 40 bars and a temperature between 180–250 °C (Kumar *et al.*, 2009_b). It can be performed in short times and has been extensively studied (Mohammadi *et al.*, 2011). The process can be performed in a conventional fixed bed, fluidized bed or slurry bubble column reactor. The bubble column reactors have the best efficiency but the separation of the catalyst from the products is difficult. Alternative reactor configurations are under development e.g. by integrating processes to increase the efficiency of conversion (Demirbas, 2006). The F-T process can produce heavy fuels which are very similar to current petroleum fuel (Robbins *et al.*, 2012). It is an attractive conversion method because it can be used to make a wide range of high molecular paraffins and olefins (Damartzis and Zabaniotou 2010). However, it is a complex process, the production costs are high and the process is sensitive to contamination resulting in catalyst de-activation (Daniell *et al.*, 2012). Better catalysts are needed to increase the efficiency of the process (Damartzis and Zabaniotou 2010).

Biological conversion is less vulnerable to contamination and can more selectively convert the gas leading to higher yields and simplified downstream processing (Mohammadi *et al.* 2011, Daniell *et al.* 2012). Yet, impurities in the gas can affect the efficiency of the fermentation process so gas cleaning is still needed before fermentation. Multiple microorganisms have been identified which are able to ferment syngas into usable products (Munasinghe and Khanal 2010). The microbes use CO and/or CO₂ as a carbon source and derive their energy from the hydrogen (Mohammadi *et al.*, 2011). The fermentation takes place at temperatures between 37 and 40 °C or between 55 and 80 °C if thermophilic microorganisms are used. The continuous stirred-tank reactor is the most commonly used syngas fermentation reactor. The ethanol is extracted from the fermentation broth via evaporation although this has high energy costs (Munasinghe and Khanal, 2010). Other reactors such as bubble column reactors, bonolithic biofilm reactors and trickle-bed reactors have also been studied. Ethanol is the main target product of syngas fermentation. The advantages of producing ethanol from second generation sources via

gasification is that no enzymatic or acid pretreatment is required, all types of biomass can be used and the whole biomass is converted to useable products (Munasinghe and Khanal 2010). Biological conversion has the potential to significantly lower the energy demand of syngas conversion and produces higher conversion rates (Mohammadi *et al.*, 2011). The process is however still in the pre-commercial phase although several pilot facilities are being constructed (Tirado-Acevedo *et al.*, 2010). The long residue times, low yields and the limited number of compounds which can be efficiently produced inhibit commercial implementation of syngas fermentation (Munasinghe and Khanal 2010, Mohammadi *et al.* 2011, Daniell *et al.* 2012). More efficient microbes are needed, the product recovery process needs to become more cost effective, the product quality needs to increase as well as the energy efficiency of the process to make gas fermentation more economically feasible (Munasinghe and Khanal 2010).

The main advantages of biomass gasification are that all of the biomass is converted into usable products, limited pretreatment (other than drying and size reduction) or hydrolysis is required and high value products can be produced via the FT process. The thermal conversion of biomass into gas is well developed but the high costs of gas cleaning and upgrading currently limit its commercial application (Kumar *et al.* 2009b, Verma *et al.* 2011). Especially the presence of tar in the gas is problematic for process efficiency. Syngas fermentation offers the potential for lower cost syngas conversion compared to the FT process but it is not well developed (Munasinghe and Khanal, 2009). The yields are currently low and the process mainly produces ethanol whereas the FT process can make diesel, aviation fuels and other heavy carbon atoms. Gasification has the potential to become an important conversion method for biomass due to its higher selectivity compared to pyrolysis and the possibility to produce heavy fuels. However, improved catalysts and gasification reactors are needed to reduce tar formation and lower operational costs to make it a more attractive option for biomass conversion.

6.6 Concluding remarks

Biomass can be converted via three main methods i.e. chemical, thermal and biological conversion, into a range of products. The optimal conversion route depends on the intended application of the product as well as the chemical composition of the original biomass. Seed-oil biodiesel is currently the main source of biofuel in Europe partly due to the relative ease of the production method. The utilization of second generation sources is more complicated since additional conversion steps are required. The economic viability of the biological transformation of second generation sources is hindered by a lack of microbes able to ferment non-glucose sugars into ethanol. The biological transformation of second generation biomass is currently not economical viable but significant cost reductions are expected (Sims *et al.*, 2009). Novel microorganisms and integrated reactor design could significantly increase the efficiency of the process as well as reduce production costs. Biological conversion can be considered the most ideal conversion method. Yet, thermal conversion technologies are more mature and currently the most attractive conversion method for second generation biomass sources.

Pyrolysis is a well-developed and low cost technology able to achieve high oil yields (70% -75%). The process can be used for all types of biomass with a moisture content below 10-15%. The process is close to becoming a commercially available technology although the pyrolysis reaction and the influence of catalysts are not yet fully understood. The quality of the bio-oil produced is however low and needs to be further upgraded to allow wider use. This is a major challenge for the implementation of pyrolysis technologies since bio-oil upgrading technologies are currently not commercially available (Xiu and Shahbazi, 2012). Liquefaction is a hydrothermal conversion method which also utilizes a pyrolysis reaction to convert biomass into oil. The use of sub-critical or supercritical liquids can yield higher quality oil than pyrolysis reactions but the oil yields are substantially lower (45%-60%). Furthermore, additional upgrading steps are still required to allow wide scale use of the oil. Liquefaction is not likely to be commercialized on a short term due to the high cost, technical difficulty and lack of understanding of the reaction and influence of catalysts. The thermal conversion of biomass via gasification is currently more attractive since it is a well-developed technology. Yet, gasification requires multiple conversion steps i.e. gasification, gas

cleaning and gas upgrading. The high costs of cleaning and upgrading syngas are currently a major limitation for the commercialization of gasification. The two main methods for syngas upgrading are the Fischer-Tropsch synthesis and biological transformation via syngas fermentation. A major advantage of syngas fermentation is that pretreatment and hydrolysis are not required. The fermentation of syngas is not well developed but can be a very effective method for ethanol production from second generation biomass. The Fischer-Tropsch process is a well-understood conversion method already used in the petrochemical industry. The main advantage of the process is that a wide range of products can be produced such as diesel, aviation fuels and other heavy carbon atoms. The costs are however high due to the extensive gas cleaning which is required as well as the costs of the equipment and process catalysts.

Thermal conversion technologies are the most advanced technologies for second generation biomass conversion. They are currently close to becoming commercialized but the possibilities for significant cost reductions are limited. The biological conversion of second generation sources is less well developed but has far greater cost reduction potential. However, biological conversion is mainly focused on the production of ethanol whereas thermal conversion is able to produce a wider range of products. The economic viability of the conversion technology thus heavily depends on the intended application of the product. A range of conversion technologies is likely to become commercialized in the future targeting different segments of the current petrochemical market.

Chapter 7 - Bio-chemicals

Chemicals are currently mostly derived from fossil resources such as natural gas and petroleum (Maher and Bressler, 2007). The majority of the chemicals produced are based on a small number of basic building blocks⁵, the so called platform chemicals (Haveren *et al.* 2007, Cukalovic and Stevens, 2008). The bio-chemical industry is still in its infancy and has not yet been able to identify the most cost-effective alternative bio-chemical platform molecules (Bozell and Petersen, 2009). There are more than 300 chemical compounds which can be derived from biomass (Werpy and Petersen, 2004). The source of biomass and the chosen conversion technologies determines which type of chemical can be produced. The technology for the production of bio-chemicals is still developing which makes it difficult to predict which compounds will become the platform chemicals for the bio-chemical industry (Bozell and Petersen, 2009). It could be new types of chemicals or compounds which are very similar to those used by the petrochemical industry (Kamm and Kamm, 2004). Currently the focus lies on the production of similar compounds as those used by the petrochemical industry due to the ease of integrating them into the existing infrastructure. Yet, biomass can also be used to produce high-value products for the pharmaceutical or food industry (Busch *et al.*, 2006). There is an overabundance of potential candidates which poses a challenge to the bio-chemical industry (Bozell and Petersen, 2009). In 2004 the Department Of Energy from the United States of America (DOE) published a review of the chemicals which can be produced from biomass. The study identified twelve high potential candidates for the bio-chemical industry. Since 2004 a number of additional reviews were published on the potential of bio-chemicals (e.g. Haveren *et al.* 2007, Corma *et al.* 2007, Bozell and Petersen 2009, Marshall and Alaimo 2010, Erickson *et al.* 2011, Cherubini and Strömman 2011, Gallezot 2012, Clomburg and Gonzalez 2012). The technological advancements made since 2004 have altered the economics of bio-chemical production. Some of the chemicals listed by the DOE are now less favorable while others that were not included in the top twelve seem more viable. No definitive list can be given since the technology is still rapidly developing (Bozell and Petersen, 2009). This section will discuss how chemicals can be derived from biomass and introduce some of the most studied bio-chemical compounds.

7.1 The production of bio-chemicals

This section introduces production processes for bio-chemicals and intends to provide a general understanding of the steps required to derive chemicals from biomass. The production of bio-chemicals is a complicated issue and it is one of the least developed aspects of bio-refining (Bozell and Petersen, 2009). There are a number of ways to derive chemicals from the biomass. Some bio-chemicals can be gathered by directly separating the chemical out of processed biomass sludge. For instance, PHA bio-plastic can be made from a compound separated from biomass e.g. switch grass without the need for further processing (Snell and Peoples, 2009). Biomass can also contain small amounts of proteins and valuable waxes which can be used in nutritional and medical applications if they can be efficiently separated from the process streams (Haveren *et al.* 2007, Clark *et al.* 2008). However, glucose is the main raw material for most of the generally cited bio-chemicals and requires further processing to derive bio-chemicals (Serrano-Ruiz *et al.*, 2010).

There are three main methods available to produce chemicals from biomass: biological transformation, chemical modification and thermal-catalytic processing. Some chemicals can be produced via multiple methods while others are limited to one conversion technology (Gallezot 2012, Dapsens *et al.*, 2012). C5 and C6 sugars are the preferred starting material for bio-chemicals due to the ability to selectively produce a large number of chemical compounds (Dapsens *et al.*, 2012). Glycerol, a by-product

⁵ ethylene, propylene, butanes, butylenes, butadiene and BTX (benzene, toluene, and xylenes)

from bio-diesel production, and ethanol are also widely investigated starting materials for bio-chemicals. Pyrolysis oil (bio-oil) can potentially be used as a starting material as well. However, the bio-oil consists of a large number of organic compounds which are difficult to separate (de Wild *et al.* 2011, Dapsens *et al.* 2012). Furthermore, the technology yields only a limited number of chemical compounds i.e. acetic acid, furfural and levoglucosan in significant quantities (de Wild *et al.*, 2011). Gasification leads to the complete destruction of the original chemical structures within the biomass. Yet, the syngas can be subsequently upgraded via e.g. Fisher-tropsch synthesis into formaldehyde, acetic acid, propylene, various esters or ammonia but this requires multiple steps and is expensive (Maher and Bressler 2006, de Wild *et al.* 2011). The high energy requirements of gasification make it a less desirable method for the production of bio-chemicals (Gallezot, 2012).

The production of bio-chemicals via thermal-chemical modification usually requires multiple steps. The starting point for chemical transformation is a liquid derivative from biomass such as glucose, ethanol or glycerol. First the oxygen content needs to be reduced; this is usually done via hydrogenolysis, dehydration or hydrogenation. Some oxygen is maintained to serve as a reactive center for further reactions (Serrano-Ruiz *et al.*, 2010). The high oxygen content of biomass is an advantage for the production of oxygen-rich chemicals such as ethylene glycol, acetic acid, and acrylic acid. The next step is upgrading the compound into a chemical via e.g. oxidation, reduction or etherification. Most of these processes have been used in the petro-chemical industry for decades. The choice of technology will determine which derivatives can be produced (Bozell and Petersen, 2009). Thermal-catalytic transformation plays an essential role in most of these processes. Catalytic reactions are processes in which a catalyst is used to cause a transformative reaction within a substance. The efficiency of the production process can be increased by coupling catalytic processes so that the number of processing steps is reduced (Simonetti and Dumesic, 2009). For instance, some bi-functional catalyst can perform the dehydration/hydrogenation and C–C coupling steps in a single reaction (Serrano-Ruiz *et al.*, 2010). The development of effective (bio)catalytic technologies is an important step in the realization of bio-chemical production (Zakzeski *et al.*, 2010). Catalytic-chemical processing has the potential to become a broad based processing technique for bio-chemical production (Dapsens *et al.*, 2012).

Microbiological transformation is one of the most interesting production methods which uses microorganisms to ferment sugars e.g. glucose or xylose into a chemical. It is the preferred method for the production of a number of chemicals such as ethanol or sunninic acid (Clark *et al.*, 2008, Gibbons and Hughe, 2009). Two different types of organisms can be employed, homofermentative microorganisms which produce one type of chemical or heterofermentative organisms which produce more than one product (Tokiwa and Calabia, 2008). The advantages of microbiological transformation are its energy efficiency and low environmental impact. Furthermore, the reaction conditions are mild which is beneficial for product quality. The disadvantages are that large spaces are required, that the residue times are long, that it generates large amounts of potentially hazardous salt solutions and that downstream processing is difficult. For instance, the recovery and purification costs are a large part of the total production costs of biological produced sunninic acid (Cukalovic and Stevens, 2008). The fermentation process can be optimized by developing more efficient strains of microorganisms, the optimization of fermentation conditions and increasing the level of process integration (Lin *et al.*, 2011). Genetically engineered *E. Coli* bacteria have received a lot of attention due to their ability to ferment raw materials into a wide range of products. However, a potential problem of genetically engineered organisms is their possible pathogenicity (Almeida *et al.*, 2012). Novel microorganisms could have unpredictable effects if they leak into the environment (Tokiwa and Calabia, 2008). More research is needed to develop the genetic tools and biological understanding to make a wider range of safe micro-organisms able to efficiently ferment biomass into chemicals. The production of biochemical is still in its infancy but has the potential to become a very sustainable method for chemical production. In the next paragraphs, some of the most cited chemical products derived from biomass will be discussed.

7.2 Oleo-chemicals

Oleo-chemicals are chemicals which are made from the oil derived from plant seeds or animal fat. This is already a large commercial sector, the major sources of oil are palm, soybeans, rapeseed and sunflower. The products are now primarily processed into high value applications for the cosmetic and food industry. They can also serve as an important renewable feedstock for bio-chemicals due to their biodegradability and limited eco-toxicity (Gallezot, 2012). The oil has a higher molecular weight than oil derived from sugars crops or lignocellulose biomass. The properties of the oil are therefore entirely different and more similar to fossil oil (Dyer *et al.*, 2008). Their long hydrocarbon chains make them attractive for the chemical industry (Chikkali and Meching, 2012). The oil contains high amounts of fatty acids which are a good starting point for many products. Furthermore, the oil can contain rare but nutritionally important fatty acids which can be of great economic value (Dyer *et al.*, 2008). Plant seeds or animal fat can be processed into chemicals via three main routes: micro-emulsification, transesterification, and pyrolysis (Thermal cracking) (Maher and Bressler, 2007). Some technologies e.g. the metathesis process and catalytic reactions can provide well-developed methods for the production of oleochemicals (Maher and Bressler 2007, Chikkali and Meching, 2012). The main limitation for the production of these chemicals is the availability of the raw material. The highest yielding plants are restricted to tropical regions and a growing amount of oil is used for biodiesel production, thereby limiting their availability (Gallezot, 2012). More versatile and higher yielding crops are needed to be able to produce significant amounts of oleochemicals in an environmentally sustainable way (Dyer *et al.*, 2008).

7.3 Ethanol and Glycerol

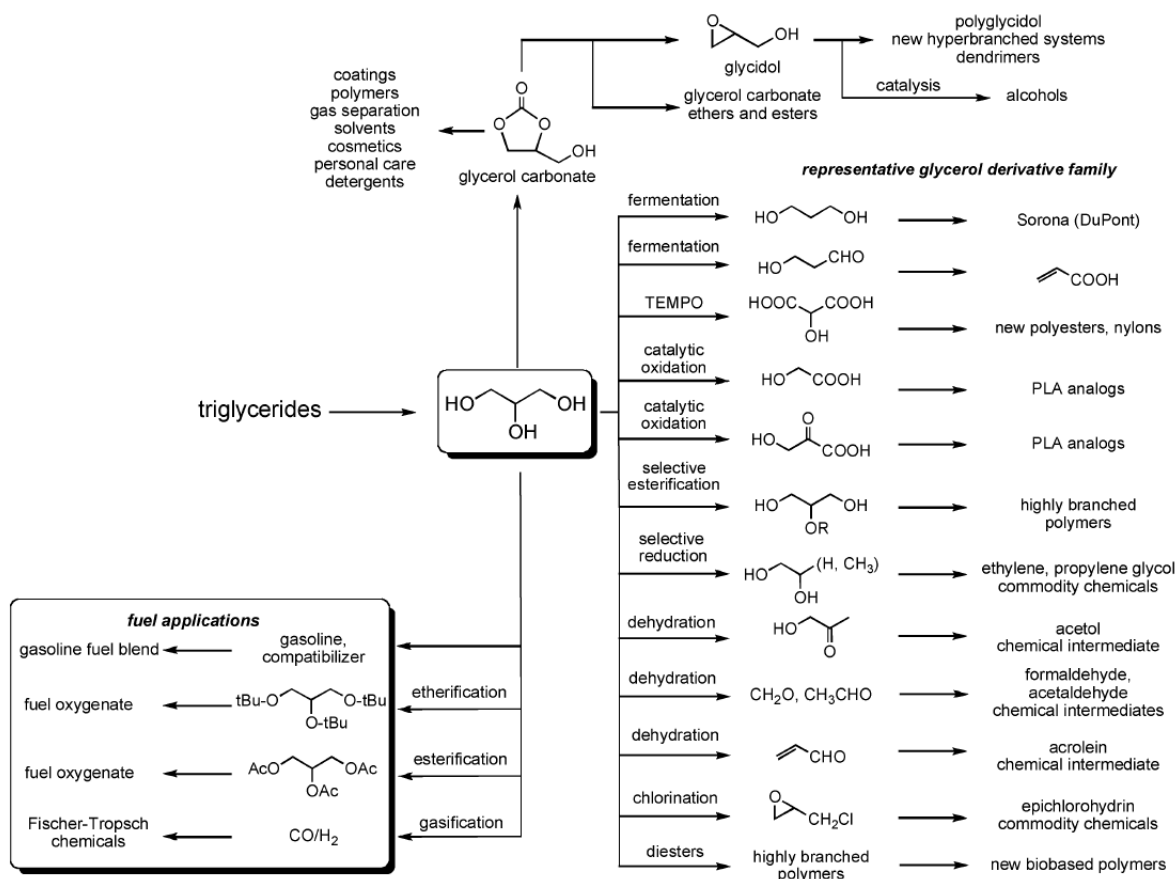
Ethanol is widely used as a biofuel but it can also serve as a platform chemical. In the early 20th century ethanol was the main source of ethylene, one of the most used chemical compounds in the world. The process became uneconomical due to the advancements made in petro-chemical refining. There is now a regained interest in bio-ethylene due to the rise of oil prices. Ethanol can be efficiently converted via dehydration to ethylene, there are no technological hurdles for this process. There are projects underway in Brazil to build large ethanol-to-ethylene plants. Ethanol can also serve as a feedstock for butadiene production which is another major bulk chemical (Haveren *et al.*, 2007). The main limitations are however the price, availability and sustainability of the feedstock. The use of ethanol as important chemical feedstock is for now restricted to places where ethanol is widely available such as Brazil and the US (Bozell and Petersen, 2009).

Glycerol is one of the main byproducts from the production of biodiesel. The conversion of glycerol to chemicals has received much attention over the past years (Bozell and Petersen, 2009, Khanna *et al.* 2012, Almeida *et al.* 2012). It can be processed via chemicals methods e.g. reduction, dehydration, oxidation or biological fermentation into a range of products, see figure 7.1 (Zheng *et al.* 2008, Bozell and Petersen 2009, Almeida *et al.* 2012). The most studied process is the conversion of glycerol to 1,3-propanediol (1,3-PDO), used in a variety of products e.g. carpets, textile fibers and thermoplastics (Almeida *et al.*, 2012). The conversion of glycerol to 1,3-propanediol is done on a commercial scale via biological fermentation (Erickson *et al.*, 2011). Other derivatives which are expected to become of commercial interest are butanol, propanediol and succinic acid (Almeida *et al.*, 2012). The biological conversion of glycerol is more efficient than the conversion of sugars to chemicals due to lower loss of CO₂ during processing (Clomburg and Gonzalez, 2012).

The technology for the conversion of glycerol into chemicals compounds is reasonably advanced (Almeida *et al.*, 2012). However, the amount of products which can be derived from glycerol via biological fermentation is currently limited. The *E. coli* bacteria are widely studied for glycerol fermentation because bioengineered strains are able to make a number of products with relative high efficiency (Clomburg and Gonzalez, 2012). Microalgae have also shown to be able to grow effectively on glycerol to produce polyunsaturated fatty acids which are of high nutritional and medical value (Abad and Turon, 2012). Glycerol has the potential to become an important platform chemical. A major limitation is however that

it is mainly produced as a byproduct of first generation biofuel production. More abundant source of glycerol e.g. from algae will need to become available to make the use of glycerol as major platform bio-chemical economically viable (Gallezot, 2012).

Figure 7.1: The derivatives of glycerol via multiple conversion processes.



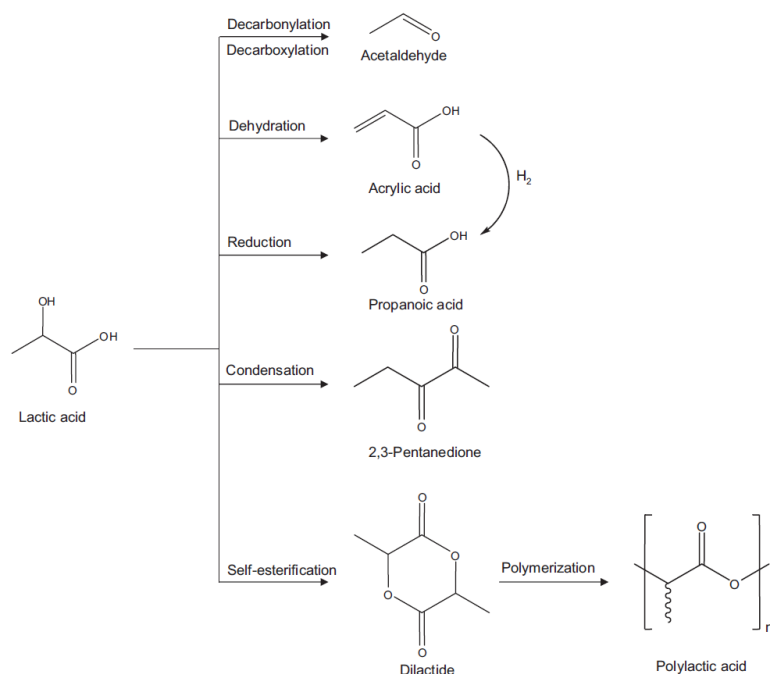
Source: Bozell and Petersen, 2009

7.4 Lactic acid

Lactic acid is a naturally occurring acid e.g. in milk which has been in food related application for a long time. Recently, lactic acid has attracted interest for the production of bio-plastics (Bozell and Petersen, 2009). The starting materials for the production of lactic acid from biomass are molasses or glucose sugars and glycerol (Haveren *et al.*, 2007, Tokiwa and Calabia, 2008). However, the use of low cost biomass is preferred because pure glycerol is too expensive to be an economically attractive source of lactic acid (Gallezot, 2012). Lactic acid is a building block for chemicals such as 2,3-pentanedione, acrylic acid and lactic acid esters, see figure 7.2 (Gallezot, 2012). The esters are of interest for the production of new “green” solvents but the implementation of this technology is limited by the low yield of the dehydration process (Bozell and Petersen, 2009). Lactic acid can also be used to produce propylene glycol which is an important platform chemical (Haveren *et al.*, 2007). Lactic acid can be extracted from biomass chemically but recent advancements in biotechnology made the biological production of sugars into lactic acid the preferred method (Almeida *et al.*, 2012). The direct fermentation of biomass waste into lactic acid is also possible and could provide a cost effective source of lactic acid in the future (Tokiwa and Calabia, 2008). However, a neutralization step is required to accomplish a high level of pure lactic acid, thereby increasing the cost of production. Alternative separation and purification are under investigation to eliminate the need for a neutralization step (Gallezot, 2012). One step catalytic processes have been developed to efficiently upgrade lactic acid to other chemicals. The development of more efficient

catalytic reactions is an important step for the viability of lactic acid as an important biochemical (Serrano-Ruiz *et al.*, 2010). Improved fermentation and purification methods are also needed to make lactic acid an economically viable platform molecule (Gallezot, 2012).

Figure 7.2: The derivatives from lactic acid according to the method of processing.

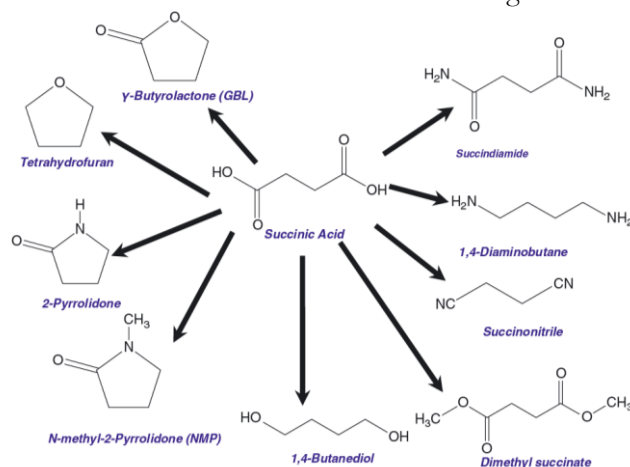


Source: Serrano-Ruiz *et al.*, 2010

7.5 Succinic acid

Succinic acid has strong potential as a platform bio-chemical because it can easily be converted into a number of well-established chemicals such as 1,4-butanediol, γ -butyrolactone and tetrahydrofuran, see figure 7.3 (Bozell and Petersen, 2009, Lin *et al.* 2011, Clomburg and Gonzalez, 2012). Maleic acid is one of the major petrochemicals which succinic acid derivatives can replace (Cukalovic and Stevens 2008, Bozell and Petersen, 2009). Bio-chemically produced succinic acid will have to be able to compete with petro-chemically produced succinic acid (Tokiwa and Calabia, 2008). The most common method to derive succinic acid from biomass is via fermentation of glycerol, sucrose or glucose (Cukalovic and Stevens, 2008). High yields can be obtained via biological transformation with little byproduct formation (Bozell and Petersen, 2009). Succinic acid is further processed via chemical transformation into a range of products e.g. pharmaceuticals, antibiotics, amino acids, vitamins, green solvents or biodegradable plastics (Lin *et al.* 2011, Almeida *et al.* 2012, Clomburg and Gonzalez 2012). A major issue for the economic viability of the fermentation route is the costs of recovery and purification (Cukalovic and Stevens, 2008). Multiple steps are required to derive pure succinic acid from a fermentation broth including removal of microbial cells, removal of impurities, primary product separation and final purification (Cheng *et al.*, 2012). Multiple separation techniques are under investigation such as direct crystallization, liquid-liquid extraction and membrane filtration-electrodialysis (Lin *et al.*, 2011). However, the efficiency of further processing is currently reduced by even very small amount of impurities. Robust catalysts and catalyst reactivation methods are therefore needed which are resistant to the deactivation caused by impurities (Gallezot, 2012). Furthermore, commonly used catalysts such as sulfuric acid, dry HCl (gas), and p-toluenesulfonic acid (PTSA) are hazardous to the environment. There is thus a need to develop more environmentally friendly catalysts (Corma *et al.*, 2007). Another key challenge is to make the separation more cost effective on an industrial scale so that biological succinic acid production is able to compete with petro chemically produced succinic acid (Cheng *et al.*, 2012).

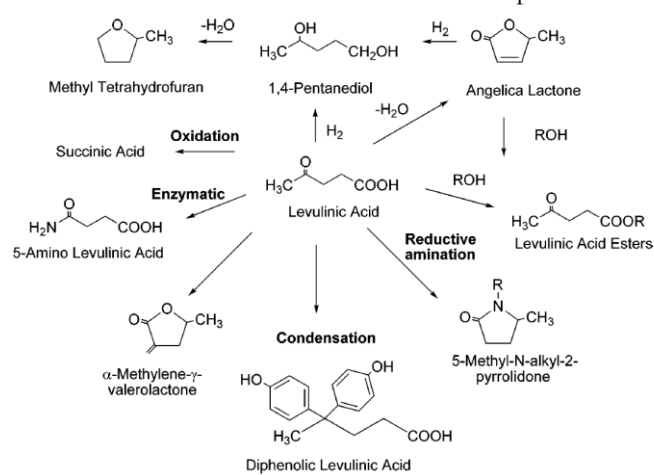
Figure 7.3: Transformation of succinic acid into high value chemicals.

Source: Lin *et al.* 2011

7.6 Levulinic acid

Levulinic acid is a bio-chemical which can be derived from glucose or xylose sugars (Gallezot, 2012). It has the potential of becoming a low cost platform chemical for a variety of products, see figure 7.4 (Serrano-Ruiz *et al.*, 2010). It can be used as a solvent and food flavoring agent or it can be converted into other chemical compounds e.g. methyltetrahydrofuran, various levulinate esters and 1,4-butanedioic acid, see figure 8.4 (Corma *et al.*, 2007). Investigations are also underway to use levulinic acid as a basis for bio-based monomers used in solvents, polymers and thermoplastics (Bozell and Petersen, 2009). In the past years the production of γ -valerolactone (GVL) via the hydrogenation of levulinic acid has received much attention. GVL can be used as a solvent or an intermediate product for the chemical industry (Gallezot, 2012). 5-Aminolevulinic acid (ALA) is another interesting derivative which is made via the oxidation of levulinic acid. This is used as an herbicide, insecticide and plant growth regulator but the production process is currently not cost effective. Investigations are underway to see if some genetically modified microorganisms could be able to cost effectively produce ALA (Corma *et al.*, 2007). Several technologies have been developed which are able to produce levulinic acid at a large scale (Corma *et al.*, 2007). First simple sugars undergo dehydration in an acidic media to form 5-HMF which is subsequently converted into levulinic acid by hydration. Heterogeneous catalysts have not been widely studied for levulinic acid production although catalytic one pot reactions are possible (Corma *et al.* 2007, Serrano-Ruiz *et al.* 2010). The efficiency of levulinic acid production has increased over the past years making the commercialization of levulinic acid a realistic possibility (Corma *et al.* 2007 Gallezot, 2012).

Figure 7.4: The derivatives from levulinic acid via multiple conversion methods.

Source: Corma *et al.*, 2007

7.7 5-hydroxymethylfurfural (5-HMF)

5-HMF is identified as a promising intermediate chemical for the production of levulinic acid, 2,5-bis(hydroxymethyl)-furan (2,5-BHF), 2,5-diformylfuran (2,5-DFF) and 2,5-furandicarboxylic acid (2,5-FDCA) (Gallezot, 2012). These products could replace petrochemical-based monomers for the production of e.g. plastics, polyesters, and solvents (Corma *et al.* 2007, Stahlberg *et al.* 2011). The preferred raw material is fructose because it can efficiently be converted to 5-HMF. However, glucose or polysaccharides can also be used (Corma *et al.* 2007, Gallezot, 2012). The raw materials are converted via dehydration reactions into 5-HMF. Multiple catalytic processes have been investigated to try and increase the yields of 5-HMF (Corma *et al.*, 2007, Bozell and Petersen, 2009). The use of ionic-liquids in combination with a catalyst has also been tested which makes it possible to use less expensive raw materials. However, the ionic-liquids are costly and their use increases the complexity of the production process due to the need to recover the product after processing (Corma *et al.* 2007, Bozell and Petersen, 2009, Gallezot, 2012). 5-HMF can be further processed via oxidation or reduction into other chemical compounds. Researchers are searching for the most efficient catalytic system for the production of 5-HMF (Corma *et al.* 2007, Bozell and Petersen, 2009, Stahlberg *et al.* 2011). 5-HMF is a promising bio-chemical because it can serve as an intermediate for a range of products. It has received much attention over the past years but improvements in separation and catalytic processing are needed to make production economically viable (Bozell and Petersen, 2009, Gallezot, 2012).

7.8 Furfural

Furfural is one of the few biomass derived chemical which is already produced on an industrial scale. The chemistry of the furfural production and further processing is well understood. The price of the product is within the range of petrochemicals such as benzene and toluene (Corma *et al.*, 2007). Agricultural or forestry wastes are usually used as the starting material. The C5 sugar (xylose) contained in the material can be processed via dehydration into furfural. This can then be directly used as a product e.g. lubricating oil or can be converted into other chemical compounds such as furfuryl alcohol, furan and tetrahydrofuran (Gallezot, 2012). The main method employed to derive furfural from biomass is via concentrated sulfuric acid hydrolysis. There are however some serious drawbacks to this process. The acid is extremely corrosive and toxic, it is difficult to separate and recycle and side reactions occur resulting in a lower furfural yield. Improvements are needed to increase the cost effectiveness and environmental sustainability of furfural production. Multiple methods and alternative catalysts are under investigation to improve the process (Corma *et al.* 2007, Bozell and Petersen, 2009, Gallezot, 2012). Furfural can be further processed via oxidation, hydrogenation, reduction or decarbonylation into a range of chemical compounds e.g. furfuryl alcohol, furfurylamine and furoic acid (Corma *et al.* 2007, Gallezot 2012). Furfural is a promising biochemical because there is already a considerable market for the product and the conversion processes are well understood. The main challenge is to increase the cost effectiveness e.g. one pot reactions and environmental sustainability of the production method.

7.9 Sorbitol and Xylitol

Sorbitol is a chemical compound which is produced on an industrial scale via the catalytic hydrogenation of glucose. It is used in food, pharmaceutical and cosmetic industries (Corma *et al.* 2007, Gallezot, 2012). The chemical transformation of biomass to sorbitol is well established. Bi-functional catalysts can be used to convert starch to sorbitol in a one pot reaction (Corma *et al.* 2007). Recently high yielding biological transformation methods have also been developed (Corma *et al.* 2007, Gallezot, 2012). Sorbitol can also be converted into isosorbide via a double dehydration process. Isosorbide is a versatile platform chemical which can be used in a variety of applications such as personal care products, pharmaceuticals or it can be further converted to polymers (Rose and Palkovits, 2012). Isosorbide is an attractive bio-chemical because it has no direct synthetic counterpart and can be derived from low cost sources of biomass with a low environmental impact (Gallezot, 2012). Sorbitol is a promising intermediate

chemical which can easily be integrated with the existing petro chemical infrastructure (Bozell and Petersen, 2010).

Xylitol is a chemical compound which is used as a sweetener. It has no insulin requirements and a lower caloric content making it attractive as a sugar substitute or special sweetener e.g. for diabetics. Xylitol is manufactured on a large scale via the chemical reduction of woody biomass. The xylose obtained from biomass is transformed via catalytic hydrogenation into xylitol (Corma *et al.*, 2007). Ultrasound irradiation can be used to increase the efficiency of the process (Gallezot, 2012). However, costly purification and separation steps are needed to obtain pure xylitol. Biological transformation is also possible but this is not yet able to compete with the chemical methods (Bozell and Petersen, 2009). The advantages of biological transformation are that crude biomass sources can be used rather than isolated xylose (Bozell and Petersen, 2009). Xylitol is a well-established high value product for which advanced processing techniques are available.

7.10 Concluding remarks

Biomass can potentially replace fossil resources as the major raw products for the production of chemicals. The development of bio based chemicals is an important step for the biofuel industry because the sale of chemical compounds can increase the economic viability of biomass refineries (Zhang 2008, Almeida *et al.* 2012). The production of bio based chemicals is however still in its infancy and many of the bio based chemicals are not yet competitive in the market. A small number of products i.e. ethanol, furfural, glycerol and sorbitol are already derived from biomass on an industrial scale. Major technological limitation inhibit the economic viability of other compounds for now (Bozell and Petersen, 2009). The production is limited by the lack of broad based processing techniques able to process a feedstock into a range of chemicals (Bozell, 2008). Key technological barriers for bio chemical production are more efficient separation and purification techniques, effective and environmentally friendly catalysts, higher yielding microorganisms for fermentation and increasing the level of process integration. Furthermore, the availability of the raw materials currently places limits on the viability of the large scale production of bio based chemicals (Bozell *et al.* 2007, Bozell and Petersen 2009, Zakzeski *et al.* 2010, Zhang *et al.* 2011, Gallezot 2012, Cheng *et al.*, 2012). The expansion of the bio chemical industry will depend on the speed of the implementation of second and third generation biomass sources.

The field of bio-based chemical is highly complex due to the large number of products which can be made from biomass. Two broad approaches can be used to identify which chemical to produce from a given biomass source. The target-driven approach implies that a platform molecule is identified after which the best technological pathway to produce the molecule is selected (Gallezot, 2012). The limitation of this approach is that many of the bio based platform chemicals are not yet able to compete with fossil based chemicals. Furthermore, the pre-identification can have a short life cycle since the technology is still rapidly developing which could make other products more attractive to produce (Bozell and Petersen, 2009). The process-driven approach selects products on the basis of the available conversion technologies (Gallezot, 2012). The choice of chemical is based on the most cost effective and convenient conversion method for a given biomass. The disadvantage of this approach is that it is a higher risk strategy because the economic returns on a given chemical are not the main selection criteria (Bozell and Petersen, 2009). The selection, standardization and production of high volume bio-based platform chemicals which can be used in the existing infrastructure will require time. More broad based conversion technologies will need to become available to allow a shift from petrochemical to bio-based platform molecules. The most viable short term strategy is to convert biomass into higher value functional products such as food additives, cosmetics, lubricants etc. for which there are no petrochemical alternatives (Vennestrom *et al.* 2011, Gallezot 2012, Dapsens *et al.* 2012).

Chapter 8 - PESTEL analysis

The success of biomass as an alternative energy source does not only depend on technological advancements within the sector. The theories on innovation discussed in chapter three point towards the importance of wider social, economic and political developments which can influence patterns of innovation. Technological development does not follow pure engineering logic but is deeply shaped by macro environmental trends such as consumer preferences, political alliances and the sunk costs of capital goods. Specific technological pathways can emerge because firms engage in a cumulative process of innovation and social preferences become aligned with technologies. The PESTEL analysis is a strategic planning technique which is used to analyze the external pressures on organizations. It will serve as a basis for identifying the macro environmental factors which influence the patterns of innovation within the biomass sector. The analysis will give insight into the main driving forces behind the desire to develop a biomass industry in Europe. Furthermore, recent social and economic developments are discussed as well as some potential competitors within the clean energy sector. The last paragraph of the PESTEL analysis will review the legal framework around the biomass industry. In the final section of the chapter the results of the assessment on biomass innovations will be discussed in light of the theoretical background and the insights from the PESTEL analysis. The information will be used to answer the main research question i.e. “What is the most effective strategy to increase the sustainability of energy and chemical production in North-Western Europe via the utilization of biomass”?.

8.1 Political

This section discusses the political framework around the utilization of biomass and will assess the effectiveness of governmental policies. The energy market has always been closely linked with political power. The control over the oil supply is high centralized with around four-fifths of the reserves being controlled by state owned companies (Mastny, 2007). The oil trade has considerable economic and political power e.g. oil is used as a political instrument via oil embargos or price manipulation. The majority of the oil is located in Middle Eastern and North African countries. These regions have become increasingly destabilized due to social uprisings, insurgent groups and militant organizations e.g. in Nigeria, Libya, Iraq and Syria. Energy security is an important incentive for nations to diversify their energy supply and these developments are likely to increase interest in alternative energy sources (Mastny, 2007). Energy policies are predominately aimed at securing a low energy price with minimum volatility while also reducing the environmental damage of energy consumption (Steenbilk, 2007). Biomass has a central place in the renewable energy policies of the EU (de Jager *et al.*, 2011). Bio energy programs have received a lot of interest since they are seen as a method to increase energy security, provide an economy stimulus and reduce CO₂ emissions at the same time (Steenbilk, 2007, Pacific *et al.* 2010, Bloomberg 2010). Especially the French and German governments have shown much support for biofuels due to the importance of agriculture for their economies. Biofuels are also seen as a method for absorbing agricultural surpluses thereby stabilizing commodity prices. Farmers and foresters are among the most important stakeholders in the biofuel industry (Mastny, 2007).

Governmental policies have been instrumental in setting up the biofuel industry in Europe. Subsidies have led to a fast growth in biofuel production over the past decades (Mastny, 2007 Pacific *et al.*, 2010). In 2011 the sector was supported with between 9.3 and 10.7 billion euros in the EU. The main support programs take the form of price tax exemptions and blending quota. Tax exemptions are the most costly policy instrument leading to around 5,5 billion euros of lost revenue in 2011 (Charles *et al.*, 2013). Other support measures for biofuels are e.g. reduced registration fees or tax reductions for biofuel-compatible cars, free parking or subsidies for gas stations that provide the fuels. Furthermore, governments invest in their own car fleets to make them compatible with biofuels (Charles *et al.*, 2013). Blending mandates are becoming increasingly popular since it lowers the costs for governments by shifting the burden onto consumers (Gerasimchuk *et al.*, 2012). Producers of biofuel feedstock's are also

indirectly supported by the Single Payment Scheme (SPS) of the EU Agricultural Policy. The scheme provides payments to farmers based on the area of land they cultivate. There is no direct support for biofuels but biofuel producers receive money from the fund since any cultivative land is eligible for SPS support. This does not mean the expenses of the program would be lower if no biofuels were produced because farmers would then probably grow other crops. However, the agricultural policies are intended to increase food security and affordability in Europe and not as a measure to support biofuel production. The support measures mean that ethanol is effectively subsidized with between 0.48 and 0.54 E/l and biodiesel between 0.44 and 0.51 E/L in Europe (Charles *et al.*, 2013). Furthermore, biofuel research and development efforts are supported by multiple programs from the European Union. The horizon 2020 subsidy program is a recent EU initiative which combines the support programs of, the Framework Programmes for Research and Technical Development, Competitiveness and Innovation Framework Programme (CIP) and the European Institute of Innovation and Technology (EIT). The program has a proposed budget of 80 billion euros and will be launched on the first of January in 2014. However, the still evolving budget negotiations within the EU could lead to a reduction of the budget for the program to around 69 billion euros⁶. Other EU funding programs such as the Intelligent Energy Europe program, Technical Cooperation Funds Programme and European Local Energy Assistance also provide grants to renewable energy projects. A significant proportion of these funds are allocated to the development of biomass technologies (Jager *et al.*, 2011).

Substantial amounts of public money have been invested in the biomass industry but the reporting on the magnitude and effectiveness of the policies has been limited (Gerasimchuk *et al.*, 2012). Biofuels are an important focus of the policy measures but the effectiveness of support policies on reaching the stated objectives have been unclear and seem to be marginal in many instances (Charles *et al.*, 2013). There are benefits for farmers and the rural economy but money is increasingly flowing to non-EU suppliers of biofuels. Only around half of the feedstock for the biofuels consumed in the EU is grown by EU farmers. Around 3-4 billion euros worth of feedstock e.g. palm oil, soybean oils and oilseeds was imported from tropical countries. Increasing imports is not in line with the EU desire to increase the domestic production of energy (Charles *et al.*, 2013). Furthermore, after years of support in Europe only around 4% of the transportation fuels are currently bio-fuels. This means the policies were able to replace just 2 or 3 large fossil fuel refineries with a limited effect on overall energy security (Charles *et al.*, 2013). The EU is likely to remain heavily dependent on energy imports in the medium to long term (Bloomberg, 2010). It also seems to be an expensive and ineffective method to reduce CO₂ emissions even without considering indirect effects on land use. The European Commission estimated that, if the indirect land impacts are taken into account, conventional biodiesel does not reduce CO₂ emissions and can even lead to higher emissions than fossil fuels. Ethanol does lead to emissions saving reduction but at a high cost of between 432 E and 493 E per ton CO₂ (Charles *et al.*, 2013). Demand side measures e.g. stimulate walking, using a bicycle or car sharing are largely ignored although they could provide a more cost effective measure to reduce CO₂ emissions (Steenbilk, 2007, Charles, *et al.* 2013). The economic benefits in terms of the number of jobs created in the sector is not monitored and thus difficult to quantify but an estimated 121.911 jobs, including direct, indirect and induced jobs, were created in the biofuel sector in Europe in 2011 (Charles *et al.*, 2013).

The development of the biofuel industry is largely the result of political decisions (Steenbilk 2007, Alain *et al.* 2010, Charles *et al.* 2013). The opportunity costs of biofuels policies are however increasingly scrutinized under pressure from the economic downturn. The money needed for the subsidies needs to be borrowed, collected via increased revenues or via the reduction of spending elsewhere (Charles, *et al.* 2013). Yet, a cleaner and more secure transportation system is urgently needed. Biofuels are a proven technology which can be directly used in the current transport system (Steenbilk, 2007). It is therefore likely that the political support will be maintained even though the effects of the policies appear to be

⁶ <http://www.universityworldnews.com/article.php?story=20130208170945405>

limited. Governments in the EU are now starting to focus on the development of second generation biomass sources (Alain *et al.*, 2010).

8.2 Economic

This paragraph will discuss the economic factors which affect the implementation of biomass as an alternative energy source. The demand for energy is projected to increase due to rising population numbers and fast economic growth of emerging economies like China and India. The fast economic development in these regions is raising concerns about the stability of the energy prices (Pacific *et al.*, 2010). Crude oil remains the most important source of energy for the transportation sector. There are currently over 650 refineries in 116 countries which have a combined production capacity of 86 million barrels of oil a day. The price of oil is deeply related to almost all economic activity and also determines the economic viability of biofuels (Arora *et al.*, 2012). Higher oil prices lead to growing trade imbalances in Western nations and slower economic growth and thus raise interest in biofuels (Mastny, 2007). Falling oil prices, on the other hand, pose a risk to investors in biofuel production since lower prices limit the ability of biofuels to be competitive (Pacific *et al.*, 2010). Commodity prices on the agricultural market also affect the biofuel industry. The increase in food prices over the last years has contributed to the lower profit margins of ethanol production (Alain *et al.*, 2010). The prices are also important since farmers will only be willing to plant energy generation crops if they cannot provide an equal or greater return on investment compared to food crops. Many of the second generation sources are currently not able to provide a good return on investment for farmers. The production of food crops will likely remain more attractive to farmers without subsidies or significant cost reduction in processing, especially if food prices continue to stay high (Steenbilk, 2007).

The global economic growth has slowed down during the past years and Europe is currently in a major economic recession. The financial crisis of 2008 coupled with continuing turmoil in the Middle East and a governmental debt crisis led to falling economic growth in the Europe Zone (Arora *et al.*, 2012). The slower economic growth and relative high value of the euro lead to lower oil prices (Arora *et al.*, 2012). The banking sector in Europe has traditionally been the main financier for renewable energy projects. However, since the financial crisis the credit ratings of banks have worsened which reduced the access to capital for entrepreneurs. Banks are increasingly cautious with providing loans to business. Biomass is seen as a high risk investment due to novelty of technology, its high capital costs and dependency on subsidies (Jager *et al.*, 2011). Even at high oil prices governmental support will be needed to develop the next generation biofuels (Sims *et al.*, 2008). Developing a bio refinery infrastructure requires large investments (between 125 -250 USD for a 100 Ml/yr plant) which have a long payback. Large scale processing would also require up to 600 000 tons of biomass a year. Investments are thus needed to develop the logistics networks as well as to provide an ample supply of feedstock (IEA, 2010). Onshore wind and solar are currently considered to be safer investments and have fewer problems attracting capital (Arora *et al.*, 2012). Governments need to take up part of the risks to increase private investment in the biofuel sector (Sims *et al.*, 2008). The European Investment Bank (EIB) tries to fill up the gap left by private banks by increasing the capital available to renewable energy projects (Arora *et al.*, 2012).

Agricultural residues are currently not used to their full potential for the production of bioenergy (Bloomberg, 2010). The increased use of residues can provide additional income to farmers as well as provide a cost effective source of biomass (IEA, 2010). However, residues will not be able to supply large volumes of oil and their use might also help to sustain the dominance of conventional biofuels. The production of first generation sources becomes more efficient with increased residue use while investments are diverted from more advanced methods of production (Gerasimchuk *et al.*, 2012). The greatest potential for biofuel production can be found in tropical regions. The favorable climate combined with cheap lands and low cost labor makes them very suitable for bio fuel production. Sugar cane production in these countries is very attractive since the feedstock price is such an important determinant in bio fuel prices (Mastny, 2007 Charles, *et al.* 2013). It has been estimated that sugar cane alone could

potentially provide for 10% of the world's gasoline supply (Pacific *et al.*, 2010). International competition is making it more difficult for farmers in Europe to be competitive (Cohen 2012, Charles *et al.* 2013). Biofuels are currently a small player in the market for transportation fuels (Charles *et al.*, 2013). The sector is heavily dependent on governmental support to be able to compete with fossil fuels. The renewable energy is the fastest growing market within the energy sector but investing in bio-energy production in Europe is currently highly risky (Arora *et al.*, 2012). The use of biomass e.g. forest residues for electricity generation in a co-firing plant provides a well-tested and cost effective application of biomass. However, the major challenge is to develop an alternative to liquid fuels for the transportation sector. Yet, the production of bio-fuels in Europe is currently commercially non-viable in many cases without governmental intervention (Arora *et al.*, 2012). The current economic climate i.e. relative low energy prices and increased budgetary problems for governments will make it more difficult for biofuels produced in NW-Europe to enter the market.

8.3 Social

This section will investigate the social trends which affect the introduction of biofuels. The use of residues for heat and electricity production is not considered to be a major social issue. Liquid fuels are a relative price inelastic good because most consumers own cars with an internal combustion engine. Consumers depend on liquid fuels so prices increases will affect demand slowly. The price inelasticity of liquid fuels is an advantage for the introduction of biofuel. Low levels of biofuel/gasoline blends result in limited difference in the product utility. Most of the bio-fuels currently in Europe are sold as an E5 (5% biofuels and 95% gasoline). The standard EU legislation limits the use of ethanol to E10 and biodiesel to B7 for standard cars⁷. There are also regions where higher blends e.g. E85 or B30 are sold but this requires flex fuel cars on the road. Research indicates that most cars can use biofuel blends of up to 20% without any or minor changes needed to the engines (Knoll et al. 2009, NREL, 2011). Yet, the uptake of E10 blends has been relatively slow partly due to the public perception on the increased risk of damage to cars caused by higher fuel blends (Cohen, 2012). Furthermore, higher level blends e.g. E85 lead to a decrease of the mileage of cars due to the lower energy content of biofuels compared to fossil fuels (Knoll et al., 2009). Safety issues and a decrease in mileage can negatively affect consumers' perception about biofuels and slow down the uptake of the fuels.

The environmental and social benefits of biofuels have been a topic of discussion ever since the start of the industry. Multiple organizations and individuals from NGOs, academia and governments have proclaimed that biofuel policies need to be reconsidered due to several socio-economic concerns (Gerasimchuk *et al.*, 2012). Planners and economists are often skeptical on biofuels and argue that it is an expensive way to achieve the policy objective (Steenbilk, 2007). Other groups have raised concerns about the environmental effects of monocultures, genetic engineering and the possible exploitation of poorer nations. In India and the EU there is a reluctance to accept genetically modified (GM) crops so they could potentially block GM products from the market (Mastny, 2007). The food vs. fuel debate has also shaped the public perception on biofuels. The Food and Agricultural Organization (FAO) published a report in 2011 entitled "Price Volatility in Food and Agricultural Markets" which points to the possibility of increasing the volatility of agricultural markets due to government-imposed biofuel mandates. They called for the removal of governmental imposed mandates in case of high food prices (Gerasimchuk et al., 2012). The impacts on the food supply are dependent on the local situation but overall the effects seem to be limited for now. The food security of an average EU citizen will not be threatened by biofuels although low income countries are more susceptible to food price increases (Rathmann et al. 2010, Charles et al. 2013). Yet, the foods vs. fuel debate led to little enthusiasm for the 'first generation' bio-fuels in Asia and Europe where the population densities are much higher than in the Americas (Ghatak, 2011).

⁷ http://ec.europa.eu/energy/renewables/events/doc/2009_03_19/session3/biofuels_quality.pdf

Biofuel proponents often point to the possible benefits of biofuels for developing countries. It is seen as a method of poverty reduction and improving the North-South trade relations (Langeveld *et al.*, 2010). However, the ownership model of a potential biofuel industry is important to consider when assessing the potential social benefits of biofuels. Large scale production of biofuels owned by investors and large companies can limit the positive effects of rural communities in developed but especially in developing nations. Large international companies can acquire lands at the expense of the poorest and least powerful groups (Gerasimchuk *et al.*, 2012). The biofuel industry may result in a same concentration of power with the similar social, economic and environmental issues as the current petroleum industry. There is a danger that large multinational cartels emerge which replace unsustainable oil production with unsustainable biofuels to maximize profits (Mastny, 2007). Overall, the main trends within society are not highly supportive of developing a large scale biofuel sector.

8.4 Technologic

This paragraph will assess the main competitors of biomass energy and will discuss private sector investments into biofuel research and development. Alternative energy technologies are currently an intensively studied topic. Multiple technological pathways are being explored aimed at making the energy supply more sustainable. Biomass energy is currently the most used sustainable energy resource in the world. It is used to derive biofuels but large volumes of biomass (e.g. residues of the wood industry) are also combusted to generate heat and electricity (European Commission, 2013). The two main competing sustainable technologies for electricity generation are solar and wind energy. Solar power is currently a small sector but it is projected to be the faster growing renewable energy sector. The price of solar panels is rapidly falling and they will become cost competitive without subsidies in the short to medium term (Devabhaktuni *et al.*, 2013). Wind energy, especially land based installations, is also gaining importance as an alternative source of electricity and can already be cost effective in some parts of the world (Arora *et al.*, 2012). These alternative sources appeal to social trends in more localized energy generation and are important competitors to biomass energy for electricity production. However, conventional sources such as coal plants are likely to remain important in the coming decades due to the sunk costs of the installations. Co-firing of biomass is therefore an interesting alternative energy source for heat and electricity generation as long as the plants are operational. An additional benefit of biomass is that it can supply a constant stream of energy whereas wind and solar are dependent on the sun and wind to be available.

Alternative fossil fuel energy resources such as heavy oil, tar sands, methane hydrate, gas-to-liquids and coal-to-liquids technologies are also being developed. Heavy-oil and tar sands are competitive with an oil price of around 65\$/bbl (Sims *et al.*, 2008). These sources provide an alternative with limited need for radical change (FAO, 2008). The sources are however more costly to extract and can pose additional environmental concerns compared to conventional oil. Yet, the development of shale gas and the potential of methane hydrate from the sea floor have led to optimism about the available natural gas supplies. This increased the interest into natural gas power stations as well as heavy-duty vehicles which can run on natural gas. Gas powered power stations have a high efficiency and are relatively low cost to construct. The lack of infrastructure and technical issues are however major limitations to wider use of heavy duty gas power vehicles (Arora *et al.*, 2012). Gas is likely to remain an important fuel for energy and heat production in the coming decades. A cleaner alternative is the production of liquid fuels from CO₂ via electro-catalytic conversion. The technology is still in the development phase but the potential benefits are great. It can become a major competitor to biofuels if the technology can become commercially viable e.g. see airfuelsynthesis.com (Olah *et al.* 2009, Benson *et al.* 2009).

Liquid fuels are an important market for clean energy since they have the advantage of being compatible with the current infrastructure. Developing a totally different transportations system is a costly affair due to the sunk cost of the current infrastructure. To make alternatives vehicles such as electric cars or hydrogen fuel cells more attractive the problem of what comes first, the alternative fuel infrastructure

or the vehicles, needs to be addressed (Alain *et al.*, 2010). Electric cars are an attractive alternative since they have better fuel economy, can improve air quality in cities and they can make use of the electricity infrastructure. Yet, the decision to buy a car is made by people on many more grounds e.g. comfort, performance, style and the purchasing costs. Electric cars are more expensive than fossil fuel cars and there is currently a lack of available infrastructure. Their market share is likely to remain relatively without technological breakthroughs in battery technologies. Furthermore, liquid fuels are a far more attractive power source for heavy duty vehicles such as trucks, planes and ships than electricity due to their higher energy density (Sims *et al.* 2009, Arora *et al.*, 2012). Hydrogen fuel cell or electric cars provide a more radical departure from the current fossil fuel industry but are much harder to implement widely. Biofuels are an important short to medium term alternative for liquid transportation fuels since the internal combustion engine is likely to continue to be the most important technology for transportation in the foreseeable future (Alain *et al.*, 2010). However, more cars will need to become compatible with higher bio-fuel blends to further increase the use of biofuel (Mastny, 2007).

The private sector has made considerable investment into the research and development of biofuel over the past years. The main focus has been on short-term or high-payoff research (Mastny, 2007). The biodiesel industry in Europe is characterized by two main types of companies. There are a few large companies focusing on large scale production and a large number of small firms usually owned by farmers (e.g. see the European Biodiesel Board) (Steenbilk, 2007). Smaller scale bio-fuel companies are privately held so their R&D budgets are difficult to determine. However, major publicly held bio-chemical companies such as Monsanto, Syngenta, and DuPont have also recognized the profitability of biofuels. They are developing new strains of maize, sugarcane and new energy crops (e.g. Switchgrass and miscanthus) by in-house research or acquisition and investment in small biotech companies. In 2008, Monsanto bought two of the leading Brazilian sugarcane breeding and biotechnology companies and spend 32 million dollars on sugar cane R& D. It is estimated that in 2008 alone a total of \$240 million was spent on sugar cane research and development in Brazil. Some of the largest companies in the US are also making substantial investments into biofuels. Companies such as Algenol, Sapphire, Solayzmes, Neste Oil and Synthetic Genomics are spending around 200 million dollars annually on third generation bio-fuel development. Furthermore, ExxonMobil has announced in 2009 that it will invest 600 million dollars in the coming years into algae research. The other major privately owned fossil fuel companies made a combined investment of around 680 million (a conservative estimate) into biofuel research in 2009 (Pray *et al.*, 2011). The companies Novozymes and Genencor Diversa are the biggest supplier of enzymes for biofuel production. Their total R& D investments in 2009 were around 65 million dollars. Most startups focus on converting biomass into green gasoline or diesel known as drop-in fuels. The production of identical products to gasoline or diesel makes sure that the product easily distributed. The total private-sector investment in biofuel R&D is estimated to be around 1.47 billion dollar for the year 2009. The majority of the investments are currently directed toward reducing the costs of second generation fuels. They are however not expected to have a significant impact on ethanol production for 12 till 16 years (Pray *et al.* 2011). The use of biomass for the production of electric energy is faced with increased competition from alternative energy sources such as wind and solar power. Biomass is however likely to remain one of the most important sources for the production of liquid fuels.

8.5 Environmental

The section will briefly discuss the environmental developments which affect the biofuel industry. The sustainability of biomass energy sources has also been addressed in previous sections e.g. see section 9.1. The Kyoto protocol and the reports from the intergovernmental panel on climate change put greenhouse gas emission high on the international agenda (Alain *et al.*, 2010). The conference in Copenhagen in 2009 on the negotiation to expend the Kyoto protocol largely failed. Yet, there is a general understanding among the public that the economy should move in a more sustainable direction. Climate change policies are likely to be implemented worldwide even without international agreement (Pacific *et*

al., 2010). Companies are increasingly driven to report on the sustainability of their production systems. Biomass is seen as a sustainable source of energy since it can be grown yearly and are thought to be climate neutral. Yet, over a third of the global land area and around 70% of the available freshwater is already devoted to agriculture. The effects of biofuels on the water supply and their direct and indirect impacts on land use are therefore important to consider (Charles, *et al.* 2013). Regions which already experience water stress could be negatively affected when increasing the production of biofuel (Gerasimchuk *et al.*, 2012). Furthermore, biofuel production is vulnerable to natural or manmade disasters. The effects of climate change are expected to lead to more frequent extreme weather events (Gerasimchuk *et al.*, 2012). This may pose a threat to prices stability in the biofuel market because there is a natural time lag between prices change and biofuel production. Farmers cannot easily increase production so the price of biofuel can become volatile in years in which harvests are limited. Concerns over fertilizers and pesticide use can also arise even if second generation sources are used (Mastny 2007, Steenbilk 2007). Sugar cane from Brazil is recognized as being a fairly sustainable source of liquid fuel with relative high emission savings. The additional benefits of second generation are yet to be determined since there is still a lot of uncertainty due to the lack of data from commercially operating plants (Gerasimchuk *et al.*, 2012). The environmental benefits of biofuels remain highly uncertain.

8.6 Legal

This section will assess the legal framework surrounding the use of biomass which is mainly focused on biofuels. The European Union is the main legislative body supporting the implementation of biofuels in Europe. The European Commission views the development of a bio-based economy as a key element for green growth in Europe. The most important pieces of legislation are the Renewable Energy Directive 2003/30/EC; The Biomass Action Plan of 2005; the Renewable Energy Directive 2009/28/EC; the Energy Taxation Directive 2003/96/EC and the Fuel Quality Directive 2009/30/EC (Alain *et al.*, 2010). In the Renewable Energy Directive of 2009 an overall target of 20% renewable energy by 2020 was set for all EU members. Nation states can choose their own pathways for reaching this target but they are obligated to reach at least 10% in the transportation sector by 2020 (EU, 2009). Biofuels are expected to be the major technology for reaching these targets (Jager *et al.*, 2011). The 10% target is founded on the assumption that second generation sources will become commercial during this decade (Alain *et al.*, 2010 EU, 2010). In 2012 an amendment to the energy directive was proposed to limit the use of food crops to a maximum of 5%. Member states who use first generation fuels above the 5% target cannot take them into account for the energy targets. The subsidies for first generation biofuels should be reduced to zero by 2020 as much as possible (EU, 2012_b). Next generation sources will count double for the 10% target so only 5% second generation fuels are needed to reach the target (Charles *et al.*, 2013). The directive also includes performance criteria to ensure the sustainability of the biofuels. The greenhouse gas emissions savings of a new biofuel installation should now be at least 35%, from 2017 the saving should be 50% and from 2018 onward savings of at least 60% for new installations (EU directive 2009). Other criteria to assess the sustainability of biofuels are; biodiversity value of the cultivate land, carbon stock of used land and agro-environmental practices of cultivation. Discussion is still going on within the EU on how to fully assess and integrate the impacts on indirect land use changes in these performance criteria (Flach *et al.* 2012). The sustainability criteria apply to domestically produced fuels as well as imported biofuels. The Directive on the Quality of Petrol and Diesel Fuels is also important since biofuels must be able to meet quality standards to be allowed wide use of the products (Mastny, 2007). EU legislation limits the blending of ethanol to a maximum of 10% ethanol for standard cars. The 10% blending quota might limit the possibilities to increase to the share of biofuels on the market in the future (Bloomberg, 2010).

The development of a carbon market is intended to make alternative energy technologies more competitive (Sims *et al.*, 2008). The European Union enacted the first large scale emissions trading scheme in the world, the European Union Emissions Trading System (EU ETS). It was launched in 2005 and intends to raise taxes on carbon emissions and re-invest the revenues into the development of cleaner

technologies. However, there is currently a large over supply of carbon credits on the market reducing their price and thereby the effectiveness of the scheme. The carbon market is currently having limited effect on stimulating the price competitiveness of alternative energy technologies. This might drive policies makers to intervene in the market in the future but no decisions have yet been taken (Scott, 2013).

International agreements can also affect the trade in biofuels (Mastny, 2007). Biofuels have been an ongoing topic of discussion during the WTO trade negotiations. The classification of biofuels into environmental, agricultural or chemical products determines under which trade agreement they fall (Steenbilk, 2007). Biodiesel is currently classified as a “products of chemical and allied industries (HS 382490)” and bioethanol is considered to be an agricultural product under the category of “beverages, spirits and vinegar”⁸. The possible classification of biofuels into the environmental goods will lead to more liberal trade of the products (Steenbilk, 2007). The EU currently imposes trade tariffs on fuels imported from outside the EU but the tariffs are not the same in all countries. Tariffs for un-denatured ethanol (low level blends) are around 30% of the market price in most EU countries (the UK and the Netherlands impose lower tariffs) (Cohen, 2012). Recently countervailing (CvD) and anti-dumping (AD) duties were imposed on US imports and Spain has implemented import quotas. These measures are all intended to protect EU biofuel producers for international competition (Flach *et al.* 2012). The WTO negotiations are intended to address these issues and any outcome will affect the biofuel industry. An agreement on the lowering of subsidies and a reduction of trade barriers could increase international trade in biofuels and help developing countries. However, the biofuel sector is heavily supported by governments so protectionist measures can also be expected in case local producers are affected by cheap imports (Steenbilk, 2007).

Non-economic trade barriers are also in place such as regulations on the chemical and physical characteristics of biofuels and regulations on biohazard control or genetically engineered organisms. These regulations are complex and still evolving but important to consider especially for the next generation biomass sources (Alain *et al.*, 2010). With regard to the production of bio-chemicals no specific European directives have been prepared. Like all other chemicals, the production of bio-based chemicals is regulated under the Regulatory framework for the management of chemicals. The Registration, Evaluation, Authorization and Restriction of Chemical substances (REACH) directive is an integrated system aimed to register, evaluate, authorize and if necessary restrict the production of chemicals within the European market. It is interesting to note that substances are exempted from the REACH directive if they are naturally occurring substances and not chemically modified. Although these definitions are interpreted very strictly the exemption could be important for some biomass processing techniques (Anfuso, 2012). The reduction of non-economic trade barriers is important to allow wider application of biotechnology into the liquid fuel sector (Alain *et al.*, 2010). Yet, there is a large support framework in place to support the development of renewable energy technologies. The mandates targets of the EU are likely to lead to a rising demand for biofuels in the near to medium term future. The next page will present a summary of the results of the PESTEL analysis.

⁸ http://www.wto.org/english/tratop_e/envir_e/climate_challenge_e.htm, May 2013

Table 8.1: Summary of PESTEL results

<p>Political:</p> <ul style="list-style-type: none"> • Energy policies are highly politicized. • Biofuels receive large amount of financial support in the EU. • Biofuels are seen as a means to increase energy security, support the rural economy and a method to reduce greenhouse gas emission. • Governments are now focusing on second generation sources. • However, the effects of biofuels policies on the stated policy goals appear to be limited. 	<p>Economic:</p> <ul style="list-style-type: none"> • Demand for energy is projected to increase. • Price of oil and food affects the viability of biofuel industry. • Economic slowdown makes it harder for biofuel projects to attract capital. • Southern regions have a significant competitive advantage for the production of biomass. • Residues can be a cost effect source of biomass energy • The use of dedicated energy crops for large scale biofuel production is not economically viable without governmental support.
<p>Social:</p> <ul style="list-style-type: none"> • Liquid fuels are a relative price inelastic good. • Low level biofuel/gasoline blends result in limited difference in product utility compared to standard liquid fuels. • Consumers are concerned about the safety of higher level blend in standard cars. • The environmental and social benefits of biofuels are questioned by multiple organizations and individuals. • There is a danger of that large multinational cartels emerge with negative effects on rural communities. 	<p>Technologic:</p> <ul style="list-style-type: none"> • Co-firing of biomass remains an interesting alternative as long as coal plants remain operational. • Solar energy and wind energy can become cost competitive without subsidies in the near term. • Liquid fuels are an important market due to the dominance of the internal combustion engine • Alternative such as electric cars or hydrogen fuels cell are difficult to implement. • Electro-catalytic conversion of CO₂ can provided a very sustainable source of liquid fuel. • Fossil fuel based alternatives such as heavy oil, tar sands, methane hydrate and shale gas are also being developed.
<p>Environmental:</p> <ul style="list-style-type: none"> • The Kyoto protocol and other international agreements increased interest in biomass energy. • Companies are increasingly driven to report on the sustainability of their products. • Biomass energy can affect the water supply as well as have direct and indirect impacts on land use. • Biofuel energy production is vulnerable to natural disasters. • Climate change is expected to lead to more frequent extreme weather events 	<p>Legal:</p> <ul style="list-style-type: none"> • European Union is the main legislative body supporting the implementation of biofuels in Europe. • Renewable Energy Directive of 2009 sets an overall target of 20% renewable energy by 2020. • At least 10% renewable energy in the transportation sector by 2020. • A maximum of 5% food crop based fuels. • Sustainability criteria will apply to domestically produced as well as imported biofuels. • The carbon market largely failed thus far. • Trade tariffs and import quota are applied in the EU to imported biofuels. • WTO trade negotiations can impact the legal status of biofuel commodities.

8.7 Synthesis of results

This section will first provide a short summary of the results of the PESTEL analysis where after the main research question will be answered. The main focus of the PESTEL analysis has been on the biofuel sector since it is considered to be the most important niche market for biomass energy. The biofuel sector can be seen as a mature niche market in the liquid fuel sector wherein a number of actors share similar expectations based on tangible experimental results. A broad coalition of actors is supportive of the biofuel sector with an active network of research and development activities in place facilitating the learning process. The regime actors are able to shape a favorable social-technological landscape for the development of agricultural based biofuels. The bio-fuel sector in Europe would not have existed without

the financial support of governments. Biomass energy research projects are among the greatest recipients of research and development funding provided by governments. Yet, the effects of stimulating biofuels on energy security, economic development and greenhouse gas emissions reductions appear to be limited (Charles *et al.*, 2013). The European Commission decided to focus on the development of second generation sources in order to improve the economic and environmental benefits of biofuels. However, the previous chapters showed that many innovations are still needed to make a biofuel industry based on second generation sources possible. There is a lack of practical knowledge about the yields of second generation sources in North Western Europe, pretreatment and conversion technologies are currently not commercially available and the development of the bio-chemical industry is still in its infancy. Large scale investments are needed in different parts of the supply chain to make second generation sources competitive. Furthermore, the additional environmental benefits of second generation are yet to be determined. There is still a lot of uncertainty about the economic and environmental benefits of second generation biofuels due to the lack of data from commercially operating plants (Gerasimchuk *et al.*, 2012).

The uncertainties about the benefits of biofuels make it crucial to critically assess support programs because once they are granted they are politically difficult to take away (Mastny, 2007). For instance, the fossil fuel sector continues to be supported with subsidies even though this is counterproductive for developing cleaner alternatives (Visser *et al.*, 2011). Incumbent actors can use their influence to steer the economic and political agenda into a direction where there is limited need for major reforms (Mastny, 2007). Petro-chemical technologies are currently very important for economic activity. Biofuels are complementary to fossil fuel since they need to be used as blends and not likely lead to radical change in the transportation sector (Steenbilk, 2007). Agricultural based biofuel are well aligned with important social values and offer a politically stable alternative due to their potential economic benefits and the limited need for radical changes in the energy supply. The social-technological regime surrounding alternative energy technologies is usually supportive for biofuels. This affects the R&D spending on other alternatives making it harder for them to become competitive. Agricultural biofuels are a proven technology and can be implemented on a relative short time scale. The ratification of the EU's Renewable Energy Directive of 2009 is likely to lead to further investments into the biofuel sector. However, the opportunity costs of biofuel development in NW-Europe need to be considered. The theories on innovation discussed in the second chapter point towards the cumulative nature of technological development, see paragraph 2.1. Large scale biofuel production based on second generation sources will require significant amounts of money at the expense of investments in developing other alternatives. The support for the sector can become a powerful barrier for new players to enter the market. It will be very expensive to switch to another energy source once the biofuel infrastructure is built. Investing substantial amounts of money in biofuel infrastructure can thus result in a new 'lock-in' in a suboptimal energy system.

The theory of strategic niche management (SNM) presented in chapter two is intended as a tool to stimulate innovations which are socially desirable on a long-term and constitute a radical novelty. According to the theory, 1) innovations need to have major technological opportunities, 2) must exhibit increasing rates of return or great learning opportunities 3) must be compatible with important users' needs and values that are already present in society 4) need to be an attractive option for some applications in the current market. Second generation sources are able to meet requirement three and four but do not score well on point one and two. Second generation sources mostly represent an incremental innovation compared to first generation sources and are not a radical departure from the current system. The technological opportunities are moderate since biofuels will not be able to replace all liquid-fuels, can only be phased in slowly and they help to sustain the dominance of the internal combustion engine. The industry does not present the pattern of 'creative destruction' wherein a radical new idea is introduced which is able to attract a large market share. The biofuel sector is heavily dependent on the support of governments and the return on investments in terms of environmental benefits seem to be moderate (Gerasimchuk *et al.* 2012, Charles *et al.* 2013). Moreover, SNM stresses the importance of developing a

diverse portfolio of technological solutions and not pick winners beforehand. It seems though that there is a bias in governmental policies to the support of biofuels. SMN also argues that policies need to be implemented temporary in order to generate selection pressures on technologies. Yet, the development of a biofuel sector in Europe has received long term financial support from governments. Large scale production of biofuels in NW-Europe via the use of dedicated energy crops is a costly strategy to increase the sustainability of the transportation systems. From the perspective of SNM the development of agricultural based biofuels cannot be considered an effective policy for steering the economy into a more sustainable direction. SMN argues that more radical alternatives e.g. third generation sources or the synthesis of oil from CO₂ via electro-catalytic conversion should be supported by governments.

So what can be considered an effective strategy to increase the sustainability of energy and chemical production in NW-Europe via the utilization of biomass? Production systems based on the use of waste streams or agricultural residues do meet the criteria of SNM. Using waste streams as a feedstock does not compete with food production, has low feedstock costs, can deliver clear environmental benefits and can be used as a means to deal with waste. These technologies are often first developed on a small scale, depending on the opportunities of a specific location, and are well aligned with important values within society e.g. dealing with waste and increase income for farmers. The production of bio-chemical e.g. from residues streams or dedicated crops to derive specific chemicals is also a niche market able to meet the criteria of SNM. The bio-chemical production is still in its infancy and there are major technological opportunities to improve production methods. The field exhibits great learning opportunities due to the large array of possible target chemicals and conversion methods. Focusing on bio-chemical production in NW-Europe is a sensible strategy since the lower biomass yields in Northern Europe will make it difficult for large scale biomass energy production to become competitive. Bio-chemicals are compatible with important users needs and values in society e.g. demand for more sustainable products and can be an attractive option for companies which seek to develop a sustainable product line. The multiple technological pathways which can be explored make it possible to create a diverse portfolio of solutions and can help to create the variation and selection pressures needed for effective SNM. Novel third generation sources e.g. algae or duckweed are also eligible for support from the perspective of SNM. They hold great promise for increasing the sustainability of liquid fuels, have great learning opportunities and are well aligned with needs and values present in society e.g. small impact on food production. The building of a vision, the creation of social networks and stimulating learning can help to increase the uptake of these technologies. Much of this research has focused on describing means to derive products from second generation sources since it is currently the main focus of EU policy. The research indicates that numerous innovations and support policies are needed to make large scale energy production from second generation sources economically viable. The results suggest that the opportunity costs of developing these technologies are too high. It can be concluded that, from the perspective of SNM, the support policies should rather be aimed at developing more radical alternative technologies.

Chapter 9 – Conclusions

Biomass is considered to be one of the most important energy sources for Europe. Residues are the least expensive source of biomass and currently an important sustainable energy (European commission, 2013). The technologies needed to utilize forestry or agricultural residues for the production of electricity, bio-gas or heat are commercially available. However, the amount residues are not expected to increase significantly in the future (Scarlat *et al.* 2009, Fischer *et al.* 2009_a). Dedicated energy crops are needed in order to maintain the position of biomass as an important alternative energy source (Bentsen and Felby, 2012). Europe has decided to focus on using second generation sources such as Willow, Poplar, Miscanthus and Switchgrass for liquid fuel production, see chapter 4. These crops can produce higher yields with lower levels of input compared to first generation sources i.e. food crops. Yet, the environmental, economic and social benefits of agricultural based biofuel are uncertain (Petersen *et al.* 2007, Jaeger and Egelkraut, 2011). Numerous innovations are needed to make the production of energy from second generation crops commercially viable. Lignocellulose biomass stemming from second generation sources is much more difficult to process than the sugars derived from food-crops. Additional pretreatment is required to process lignocellulose biomass into value added products. Thermal conversion methods such as combustion, pyrolysis and gasification require only limited pretreatment. The biomass needs to be dried (in case of high moisture content) and chopped into a finer particle size to allow more efficient transportation as well as to increase the thermal conversion efficiency. More extensive pretreatment is needed to allow lignocellulose biomass e.g. agricultural residues or Switchgrass to be converted to fuels and chemicals via biological transformation. The (hemi)cellulose contained in the biomass needs to be converted via chemical (acid) or biological (enzymes) hydrolysis into fermentable sugars. To make the (hemi)cellulose molecules accessible for the hydrolysis process the biomass first needs to be pretreated via physico-chemical, chemical or biological treatment. There are currently no pretreatment methods commercially available for making lignocellulose biomass suitable for biological conversion, see paragraph 5.8.

Biomass can be processed into value added products via three main reaction pathways i.e. chemical, thermal and biological reactions. The optimal conversion route depends on the intended application of the product as well as the chemical composition of the original biomass. Thermal conversion i.e. pyrolysis and gasification are currently the main conversion methods for second generation sources. They are among the most mature technologies for biomass conversion and close to becoming commercially available e.g. flash pyrolysis. Biological conversion methods are hindered by the lack of commercially available pretreatment methods and microbes able to ferment non-glucose sugars into ethanol. However, the products produced by pyrolysis and gasification are of low quality and need to be further upgraded to allow wider use. This represents a major challenge for the implementation of thermal conversion technologies since the upgrading technologies are currently not commercially available (Xiu and Shahbazi, 2012). Biological conversion can produce products more selectively reducing the need for further upgrading. It has a greater cost reduction potential compared to thermal conversion technologies due to the lower input requirements e.g. lower energy demand, no chemicals needed and greater product selectivity. Yet, thermal conversion technologies are able to produce a wider range of products e.g. aromatic oils. A range of conversion technologies will need to be commercialized to be able to replace different segments of the current petrochemical market, see paragraph 6.6.

Biomass can also provide the raw materials needed for the production of chemical products. There are more than 300 chemical compounds which could potentially be derived from biomass (Werpy and Petersen, 2004). The abundance of potential candidates poses a challenge to the bio-chemical industry and research institutes (Bozell and Petersen, 2009). A small number of products e.g. furfural, glycerol and sorbitol are already derived from biomass on an industrial scale. Major technological limitations inhibit an economically viable supply of other bio-chemical compounds for now, see paragraph 7.10 (Bozell and Petersen, 2009). Key technological barriers for bio-chemical production are efficient separation and

purification techniques, more effective and environmentally friendly catalysts, higher yielding microorganisms for fermentation and decreasing the number of processing steps required. The development of bio-based chemicals is an important step for the biomass industry. Chemicals are high value products, their sale can increase the economic viability of biomass refineries (Zhang 2008, Almeida *et al.* 2012). Some bio-chemicals can be gathered by separating the chemical out of processed biomass sludge e.g. PHA bio-plastic. However, C5 (xylose) and C6 (glucose) sugars are the main raw materials for most of the generally cited bio-chemicals and require further processing steps (Serrano-Ruiz *et al.*, 2010). There are three main methods for deriving chemicals from these intermediate products: biological transformation, chemical modification and thermal-catalytic processing. The choice of technology determines which bio-chemical product can be produced. This study discussed some of the most cited bio-chemical compounds in the literature but no definitive list can be given (Bozell and Petersen, 2009). The technology is still rapidly developing, future process innovations will determine which bio-chemical compound can be commercially produced, see chapter 7 (Vennestrøm *et al.* 2011, Gallezot 2012, Dapsens *et al.* 2012). Figure 9.1 provides an overview of the biomass supply chains discussed in this research.

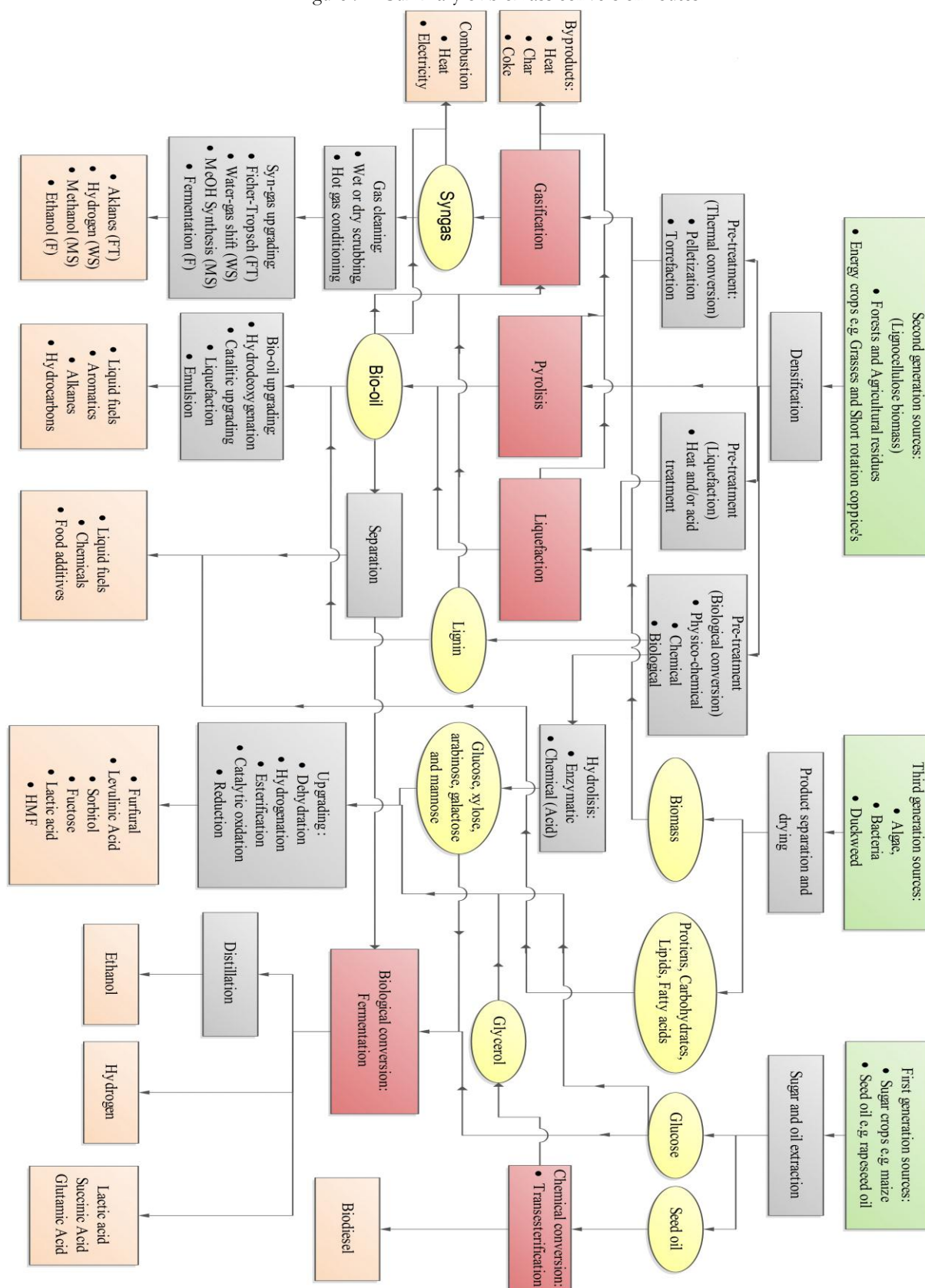
The research used the framework of a PESTEL (Political, Economic, Social, Technological, Environmental and Legal) analysis to investigate wider macro environmental factors influencing the bio-energy sector. Political support has been one of the main drivers behind the biofuel industry. Governments view biofuels as a means to increase energy security, provide an economy stimulus and reduce CO₂ emissions at the same time. Subsidies have led to a fast growth in biofuel production in Europe over the past decades. In 2011 the sector was supported with between 9.3 and 10.7 billion euros in the EU, see paragraph 8.1 (Mastny, 2007 Pacific *et al.*, 2010). The energy targets set by the European Union are likely to lead to further investments into the biofuel sector. However, it seems that the support for biofuels has had limited effect on the stated policies goals of energy security, economic development and greenhouse gas emissions reductions (Gerasimchuk *et al.*, 2012 Charles *et al.*, 2013). The policies are also been criticized due to several socio-economic concerns e.g. the food vs. fuel debate and the ownership models, see paragraph 8.3 (Gerasimchuk *et al.*, 2012). Second generation sources are seen as a means to address these issues but investing in them is currently risky. The economic downturn in Europe made banks increasingly cautious with providing loans to businesses. Biofuels project are capital intensive and have long payback times which makes attracting capital for bio-refining projects more difficult. The economic, social and environmental benefits of second generation biofuels are still uncertain.

The main research question for the study was “What is the most effective strategy to increase the sustainability of energy and chemical production in North-Western Europe via the utilization of biomass”? Strategic Niche Management (SNM) provided the theoretical background for identifying effective strategies biomass utilization, see paragraph 2.2. The theory is aimed at stimulating radical innovations which are able to significantly increase the sustainability of current production methods. The results of the study indicate that second generation energy crops are mostly an incremental innovation compared to first generation sources. The technological opportunities are moderate, the sector is heavily dependent on the support of governments and the environmental benefits are relatively small. The most effective strategies for biomass utilization in NW-Europe from the perspective of SNM are supporting the use of residues stream, the production of bio-chemicals and the development of novel third generation sources. However, biofuels are a proven technology which can be implemented on a relative short time scale. More radical alternatives are uncertain which is problematic for policy makers. Large scale investments are now needed in order to reach the energy targets set by the EU. Yet, the opportunity costs of developing biofuels need to be carefully considered because once billions of euros have been invested there is a strong incentive to continue along the same path. There is a danger that the energy targets set by the EU create a new ‘lock-in’ into a suboptimal energy system. It is therefore important to increase the diversity of governmental support policies for alternative energy solution and not pick a winner beforehand. Future policies need to be based on solid scientific evidence about the possible effects and benefits of biofuels as well as the technological opportunities of alternative technologies. A better

understanding of the opportunity costs of developing large scale bio-energy projects is needed to ensure that cost-effective policies are implemented to increase the sustainability of energy supply. The following recommendations are based on the finding of the research:

- ✓ The environmental benefits of agricultural based biofuels are uncertain. An increased understanding is needed about the potential for CO₂ emissions reductions and the net energy gains of second generation bio-energy crops.
- ✓ Farmers are important stakeholders in an energy system based on biomass. It is recommended that the attitude of farmers against bioenergy projects is carefully considered.
- ✓ Residue streams are a low cost and sustainable source of biomass. They will not be able to provide a major alternative energy source but can be developed into viable business cases.
- ✓ Biological conversion methods can be considered the most favorable conversion method for lignocellulose biomass e.g. residues due to its potentially favorable economic and environmental performance.
- ✓ The cultivation of dedicate crops or use of waste streams for the production of chemical products is an effective biomass utilization strategy for Northern Europe. SNM can be used to develop knowledge networks around the topic of bio-chemicals.
- ✓ Third generation sources offer the potential of delivering high environmental benefits. SNM can be used to accelerate the development of more radical alternative sources of biomass e.g. algae, bacteria or duckweed.

Figure 9.1: Summary of biomass conversion routes*.



*Green boxes are biomass sources, Red boxes are main conversion steps, Yellow boxes are intermediate products, Grey boxes are intermediate conversion step and Orange boxes represent potential end-products

Reference

- Abad, S., and Turon, X. (2012). Valorization of biodiesel derived glycerol as a carbon source to obtain added-value metabolites: Focus on polyunsaturated fatty acids. *Biotechnology advances*, 30(3),
- Afas *et al.*, N. Al, Marron, N., Van Dongen, S., Laureysens, I., & Ceulemans, R. (2008). Dynamics of biomass production in a poplar coppice culture over three rotations (11 years). *Forest Ecology and Management*, 255(5-6), 1883–1891.
- Agbor *et al.* V. B., Cicek, N., Sparling, R., Berlin, A., & Levin, D. B. (2011). Biomass retreatment: fundamentals toward application. *Biotechnology advances*, 29(6), 675–85.
- Aitken, D., and Antizar-Ladislao, B. (2012). Achieving a Green Solution: Limitations and Focus Points for Sustainable Algal Fuels. *Energies*, 5(12), 1613–1647. doi:10.3390/en5051613
- Almeida *et al.* J. R. M., Fávoro, L. C. L., & Quirino, B. F. (2012). Biodiesel biorefinery: opportunities and challenges for microbial production of fuels and chemicals from glycerol waste. *Biotechnology for biofuels*, 5(1), 48.
- Alonso *et al.* D. M., Wettstein, S. G., & Dumesic, J. a. (2012). Bimetallic catalysts for upgrading of biomass to fuels and chemicals. *Chemical Society reviews*, 41(24), 8075–98.
- Al-Sabawi M., and Chen, J. (2012). Hydroprocessing of Biomass-Derived Oils and Their Blends with Petroleum Feedstocks: A Review. *Energy & Fuels*, 26(9), 5373–5399.
- Amaro *et al.* H. M., Macedo, Â. C., & Malcata, F. X. (2012). Microalgae: An alternative as sustainable source of biofuels? *Energy*, 44(1), 158–166.
- Anderson *et al.* E., Arundale, R., Maughan, M., Oladeinde, A., Wycislo, A., & Voigt, T. (2011). Growth and agronomy of *Miscanthus x giganteus* for biomass production. *Biofuels*, 2, 167–183.
- Anfuso M. (2012) *European legislation for the sector of the bio-based products*, BioChem. Inc.
- Anitescu, G. and Bruno, T. J. (2012). Liquid Biofuels: Fluid Properties to Optimize Feedstock Selection, Processing, Refining/Blending, Storage/Transportation, and Combustion. *Energy & Fuels*, 26.
- Arai *et al.* K., Smith, R. L., & Aida, T. M. (2009). Decentralized chemical processes with supercritical fluid technology for sustainable society. *The Journal of Supercritical Fluids*, 47(3), 628–636.
- Arbor (2012) *website of the Arbor project*: <http://www.arbornwe.eu> > Home
- Atkinson, C. J. (2009). Establishing perennial grass energy crops in the UK: A review of current propagation options for *Miscanthus*. *Biomass and Bioenergy*, 33(5), 752–759. doi:10.1016/j.biombioe.2009.01.005
- Awudu, I., and Zhang, J. (2011). Uncertainties and sustainability concepts in biofuel supply chain management: A review. *Renewable and Sustainable Energy Reviews*, 16(2), 1359–
- Aylott *et al.* M. J., Casella, E., Tubby, I., Street, N. R., Smith, P., & Taylor, G. (2008). Yield and spatial supply of bioenergy poplar and willow short-rotation coppice in the UK. *The New phytologist*, 178(2), 358–70. doi:10.1111/j.1469-8137.2008.02396.x
- Balat *et al.* M., Balat, H., & Öz, C. (2007). Progress in bioethanol processing. *Progress in Energy and Combustion Science*, 34(5), 551–573.
- Balezentiene *et al.*, L., Streimikiene, D., & Balezentis, T. (2012). Fuzzy decision support methodology for sustainable energy crop selection. *Renewable and Sustainable Energy Reviews*, 17, 83–93.

- Banerjee *et al.* S., Mudliar S., Sen R., G. B. (2009). Commercializing lignocellulosic bioethanol : technology bottlenecks. *Biofuels, Bioprod. Bioref.*, 4, 77–93.
- Benson, E. E., Kubiak, C. P., Sathrum, A. J., & Smieja, J. M. (2009). Electrocatalytic and homogeneous approaches to conversion of CO₂ to liquid fuels. *Chemical Society reviews*, 38(1), 89–99. doi:10.1039/b804323j
- Bentsen, N. S., and Felby, C. (2012). Biomass for energy in the European Union - a review of bioenergy resource assessments. *Biotechnology for biofuels*, 5(1), 25. doi:10.1186/1754-6834-5-25
- Bhalla *et al.* A., Bansal, N., Kumar, S., Bischoff, K. M., & Sani, R. K. (2012). Bioresource Technology Improved lignocellulose conversion to biofuels with thermophilic bacteria and thermostable enzymes, 128, 751–759.
- Boehmel *et al.* C., Lewandowski, I., & Claupein, W. (2008). Comparing annual and perennial energy cropping systems with different management intensities. *Agricultural Systems*, 96(1-3), 224–236.
- Bonin, C., and Lal, R. (2012). Bioethanol Potentials and Life-Cycle Assessments of Biofuel Feedstocks. *Critical Reviews in Plant Sciences*, 31(4), 271–289.
- Bozell *et al.* J. J., Holladay, J. E., White, J. F., and Johnson, D. (2007). Top Value-Added Chemicals from Biomass Volume II — Results of Screening for Potential Candidates from Biorefinery Lignin, II(October). Department of Energy USA.
- Bozell J. J. (2008) *Feedstocks for the Future Biorefinery - Production of Chemicals from Renewable Carbon*. CLEAN - Soil, Air, Water, 36(8), 641–647
- Bozell, J. J., and Petersen, G. R. (2009). Technology development for the production of biobased products from biorefinery carbohydrates—the US Department of Energy’s “Top 10” revisited. *Green Chemistry*, 12(4), 539.
- Brennan, L., and Owende, P. (2009). Biofuels from microalgae—A review of technologies for production, processing, and extractions of biofuels and co-products. *Renewable and Sustainable Energy Reviews*, 14(2), 557–577.
- Breschi *et al.* S., Malerba F. and Orsenigo L. (2000) Technological regimes and schumpeterian patterns of innovation, *The Economic Journal*, 110 (April), 388-410.
- Bridgwater, T. (2006). Biomass for energy. *Science food and agriculture*, 1768(December 2005),
- Briner R, and Denyer D. (2010) *Systematic Review and Evidence Synthesis as a Practice and Scholarship Tool*, Chapter in Denise Rousseau (Ed.) *Handbook of Evidence-Based Management: Companies, Classrooms, and Research*, Oxford University Press.
- Brosse *et al.* N., Lorraine, U. De, Dufour, A., Lorraine, U. De, Meng, X., Sun, Q., & Ragauskas, A. (2012). Miscanthus : a fast- growing crop for biofuels and chemicals production. *Biofuels, Bioprod. Bioref.*, 6.
- Bruun H. and Hukkinen J. (2003) Crossing Boundaries: An Integrative Framework for Studying Technological Change, *Social Studies of Science* 33/1(February 2003) 95–116
- Busch *et al.*, R., Hirth, T., Liese, A., Nordhoff, S., Puls, J., Pulz, O., Sell, D., *et al.* (2006). The utilization of renewable resources in German industrial production. *Biotechnology journal*, 1(7-8), 770–6. doi:10.1002/biot.200600057
- Butler *et al.* E., Devlin, G., Meier, D., & McDonnell, K. (2011). A review of recent laboratory research and commercial developments in fast pyrolysis and upgrading. *Renewable and Sustainable Energy Reviews*, 15(8), 4171–4186.
- Cantrell *et al.* K. B., Ducey, T., Ro, K. S., & Hunt, P. G. (2008). Livestock waste-to-bioenergy generation opportunities. *Bioresource technology*, 99(17), 7941–53.

- Carlsson A., Möller, Ralf, van B. J. B., & Clayton, D. (2007). *Micro- and macro-algae: utility for industrial applications*. CPL Press.
- Carvalho et al., F., Duarte, L. C., & Gírio, F. M. (2008). Hemicellulose biorefineries : a review on biomass pretreatments. *Journal of Scientific & Industrial Research*, 67(November), 849–864.
- Casler, M. D., and Undersander, D. J. (2006). Selection for Establishment Capacity in Reed Canarygrass. *Crop Science*, 46(3), 1277.
- Casler et al. M. D., Cherney, J. H., & Brummer, E. C. (2009). Biomass Yield of Naturalized Populations and Cultivars of Reed Canary Grass. *BioEnergy Research*, 2(3), 165–173.
- CEFIC (2011) *Facts and Figures 2011: The European chemical industry in a worldwide perspective*, The European Chemical Industry Council
- Chandra et al. R., Takeuchi, H., & Hasegawa, T. (2011). Methane production from lignocellulosic agricultural crop wastes: A review in context to second generation of biofuel production. *Renewable and Sustainable Energy Reviews*, 16(3), 1462–1476.
- Chandy R.K and Tellis G.J. (2000) The Incumbent's Curse? Incumbency, Size, and Radical Product Innovation, *Journal of Marketing* Vol. 64 (July 2000), 1–17
- Chen, Y. (2010). Development and application of co-culture for ethanol production by co-fermentation of glucose and xylose: a systematic review. *Journal of industrial microbiology & biotechnology*, 38(5), 581–97.
- Cheng et al. K.-K., Zhao, X.-B., Zeng, J., Wu, R.-C., Xu, Y.-Z., Liu, D.-H., and Zhang, J.-A. (2012). Downstream processing of biotechnological produced succinic acid. *Applied microbiology and biotechnology*, 95(4), 841–50.
- Cherubini, F., and Strømman, A. H. (2011). Chemicals from lignocellulosic biomass : opportunities , perspectives , and potential of biorefi nery systems. *Biofuels, Bioprod. Bioref.*, (7491),
- Chiaromonti et al. D., Prussi, M., Ferrero, S., Oriani, L., Ottonello, P., Torre, P., & Cherchi, F. (2012). Review of pretreatment processes for lignocellulosic ethanol production, and development of an innovative method. *Biomass and Bioenergy*, 46, 25–35.
- Chikkali, S., and Mecking, S. (2012). Refining of plant oils to chemicals by olefin metathesis. *Angewandte Chemie (International ed. in English)*, 51(24), 5802–8.
- Christian et al. D. G., Riche, a B., & Yates, N. E. (2001). The yield and composition of switchgrass and coastal panic grass grown as a biofuel in southern England. *Bioresource technology*, 83(2), 115–24.
- Ciolkosz, D., and Wallace, R. (2011). A review of torrefaction for bioenergy feedstock, *Biofuels, Bioprod. Bioref.*, 5:317–329.
- Clark et al. J. H., Deswarte, F. E. I., and Farmer, T. J. (2008). The integration of green chemistry into future biorefineries. *Biofuels, Bioprod. Bioref.*, 3, 72–90.
- Clomburg, J. M., and Gonzalez, R. (2012). Anaerobic fermentation of glycerol: a platform for renewable fuels and chemicals. *Trends in biotechnology*, 31(1), 20–8.
- Corma et al., A., Iborra, S., & Velty, A. (2007). Chemical routes for the transformation of biomass into chemicals. *Chemical reviews*, 107(6)
- Cosentino, S. L., Testa, G., Scordia, D., & Alexopoulou, E. (2012). Future yields assessment of bioenergy crops in relation to climate change and technological development in Europe. *Italian Journal of Agronomy*, 7(2). doi:10.4081/ija.2012.e22

- Cukalovic, A., and Stevens, C. V. (2008). Feasibility of production methods for succinic acid derivatives : a marriage of renewable resources and chemical technology. *Biofuels, Bioprod. Bioref.*, 2, 505–529.
- Czarnitzki et al. D., Hussinger K. and Leten B. (2010). The market value of blocking patents, Paper presented at the Pacific Rim Innovation Conference, Melbourne.
- Damartzis, T., and Zabaniotou, A. (2010). Thermochemical conversion of biomass to second generation biofuels through integrated process design—A review. *Renewable and Sustainable Energy Reviews*, 15(1), 366–378.
- Daniell *et al.* J., Köpke, M., & Simpson, S. (2012). *Commercial Biomass Syngas Fermentation*. *Energies* (Vol. 5, pp. 5372–5417).
- Dapsens, *et al.* P. Y., Mondelli, C., & Pe, J. (2012). Biobased Chemicals from Conception toward Industrial Reality : Lessons Learned and To Be Learned. *American Chemical society*, 2, 1487–1499.
- Daroch *et al.* M., Geng, S., and Wang, G. (2013). *Recent advances in liquid biofuel production from algal feedstocks*, *Applied Energy*, 102, 1371–1381.
- Day *et al.* J. G., Slocombe, S. P., & Stanley, M. S. (2012). Overcoming biological constraints to enable the exploitation of microalgae for biofuels. *Bioresource technology*, 109, 245–
- de Visser *et al.* E., Winkel T., de Jager D., de Vos R., Blom M., Afman M. (2011) Overheidsingrepen in de energiemarkt Onderzoek naar het Nederlandse speelveld voor fossiele brandstoffen, hernieuwbare bronnen
- De Wild *et al.* P., Reith, H., and Heeres, E. (2011). *Biomass pyrolysis for chemicals*. *Biofuels* Vol. 2, pp. 185–208.
- De Wit, M., and Faaij, A. (2009). European biomass resource potential and costs. *Biomass and Bioenergy*, 34(2), 188–202. doi:10.1016/j.biombioe.2009.07.011
- Deckmyn *et al.*, G., Laureysens, I., Garcia, J., Muys, B., & Ceulemans, R. (2004). Poplar growth and yield in short rotation coppice: model simulations using the process model SECRETS. *Biomass and Bioenergy*, 26(3), 221–227.
- Deleuran, L. C., and Flengmark, P. K. (2005). Yield Potential of Hemp (*Cannabis sativa* L.) Cultivars in Denmark. *Journal of Industrial Hemp*, 10(2), 37–41.
- Demirbas, a. (2006). Progress and recent trends in biofuels. *Progress in Energy and Combustion Science*, 33(1), 1–18.
- Demirbas, A. (2009) *Biorefineries Current activities and future developments*, *Energy Conversion and Management*, 50, 2782–2801.
- Devabhaktuni *et al.* V. Alam A., Depuru S., Green R., Nims D. and Near C. (2013) Solar energy: Trends and enabling technologies,
- Djomo *et al.* S. N., Kasmoui, O. El, & Ceulemans, R. (2010). Energy and greenhouse gas balance of bioenergy production from poplar and willow: a review. *GCB Bioenergy*, 3(3), 181–197.
- Dosi, G. (1982) Technological paradigms and technological trajectories. *Research Policy*, 11(3), 147–162.
- Dyer *et al.* J. M., Stymne, S., Green, A. G., & Carlsson, A. S. (2008). High-value oils from plants. *The Plant journal : for cell and molecular biology*, 54(4), 640–55.
- EC (European Commission) (2011) *High level expert group on key enabling technologies*, European commission, Final report 2011
- Kasmoui El, O., and Ceulemans, R. (2012). Financial analysis of the cultivation of poplar and willow for bioenergy. *Biomass and Bioenergy*, 43, 52–64.

- Elkins et al. J. G., Raman, B., & Keller, M. (2010). Engineered microbial systems for enhanced conversion of lignocellulosic biomass. *Current opinion in biotechnology*, 21(5), 657–62.
- Elzen A. and Wieczorek A.T. (2005) Transitions towards sustainability through system innovation, *Technological Forecasting & Social Change* 72 (2005) 651–661
- Ericsson, K., and Nilsson, L. J. (2006). Assessment of the potential biomass supply in Europe using a resource-focused approach, 30, 1–15.
- Erickson *et al.*, B., Nelson, & Winters, P. (2011). Perspective on opportunities in industrial biotechnology in renewable chemicals. *Biotechnology journal*, 7(2), 176–85.
- EU (European Union) (2005) *Biomass action plan*, Communication from the commission, COM (2005) 628 final, Brussels
- EU (European Union) (2009) *On the promotion of the use of energy from renewable sources and amending and subsequently repealing Directives 2001/77/EC and 2003/30/EC*, European Union Directive 2009/28/EC
- EU (European Union) (2010) *Communication from the Commission on the practical implementation of the EU biofuels and bioliquids sustainability scheme and on counting rules for biofuels*, COM 160/02, Official Journal of the European Union
- EU (European Union) (2012_a) *Innovating for Sustainable Growth: A Bioeconomy for Europe*, European commission COM(2012) 60 final, Brussels
- EU (European Union) (2012_b) *Amending Directive 98/70/EC relating to the quality of petrol and diesel fuels and amending Directive 2009/28/EC on the promotion of the use of energy from renewable*, COM(2012) 595 final, Okt 2012 Brussels
- Feltus, F. A., and Vandenbrink, J. P. (2012). Bioenergy grass feedstock: current options and prospects for trait improvement using emerging genetic, genomic, and systems biology toolkits. *Biotechnology for biofuels*, 5(1),
- Fike *et al.* J. H., Parrish, D. J., Wolf, D. D., Balasko, J. a., Green, J. T., Rasnake, M., & Reynolds, J. H. (2006). Long-term yield potential of switchgrass-for-biofuel systems. *Biomass and Bioenergy*, 30(3), 198–206.
- Fischer *at al.* G., Prieler, S., Van Velthuizen, H., Lensink, S. M., Londo, M., & De Wit, M. (2009_a). Biofuel production potentials in Europe: Sustainable use of cultivated land and pastures. Part I: Land productivity potentials. *Biomass and Bioenergy*, 34(2), 159–172.
- Fischer *et al.* G., Prieler, S., Van Velthuizen, H., Berndes, G., Faaij, A., Londo, M., & De Wit, M. (2009_b). Biofuel production potentials in Europe: Sustainable use of cultivated land and pastures, Part II: Land use scenarios. *Biomass and Bioenergy*, 34(2), 173–187.
- Flynn *et al.* K. J., Mitra, A., Greenwell, H. C., Sui, J., Flynn, K. J., Mitra, A., Greenwell, H. C., et al. (2013). Monster potential meets potential monster : pros and cons of deploying genetically modified microalgae for biofuels production Monster potential meets potential monster : pros and cons of deploying genetically modified microalgae for biofuels production. *Interface focus*, 3.
- Frigon, J., and Guiot, S. R. (2010). Biomethane production from starch and lignocellulosic crops : a comparative review. *Biofuels, Bioprod. Bioref.*, 4, 447–458.
- Gallezot, P. (2012). Conversion of biomass to selected chemical products. *Chemical Society reviews*, 41(4), 1538–58.
- Gasol, *et al.* C. M., Martínez, S., Rigola, M., Rieradevall, J., Anton, A., Carrasco, J., Ciria, P., et al. (2009). Feasibility assessment of poplar bioenergy systems in the Southern Europe. *Renewable and Sustainable Energy Reviews*, 13(4), 801–812. doi:10.1016/j.rser.2008.01.010
- Geddes *et al.* C. C., Nieves, I. U., and Ingram, L. O. (2011). Advances in ethanol production. *Current opinion in biotechnology*, 22(3), 312–9.

- Ghatak, H. R. (2011). Biorefineries from the perspective of sustainability: Feedstocks, products, and processes. *Renewable and Sustainable Energy Reviews*, 15(8), 4042–4052.
- Gibbons, W. R., and Hughes, S. R. (2009). Integrated biorefineries with engineered microbes and high-value co-products for profitable biofuels production. *In Vitro Cellular & Developmental Biology - Plant*, 45(3), 218–228.
- Glowacka, K. (2011). A review of the genetic study of the energy crop *Miscanthus*. *Biomass and Bioenergy*, 35(7), 2445–2454. doi:10.1016/j.biombioe.2011.01.041
- Gnansounou *et al.* E., Dauriat, a, Villegas, J., & Panichelli, L. (2009) *Life cycle assessment of biofuels: energy and greenhouse gas balances*, *Bioresource technology*, 100(21), 4919–30.
- Gnansounou, E. (2010). Production and use of lignocellulosic bioethanol in Europe: Current situation and perspectives. *Bioresource technology*, 101(13), 4842–50. doi:10.1016/j.biortech.2010.02.002
- Gnansounou, E., and Dauriat, A. (2010). Techno-economic analysis of lignocellulosic ethanol: A review. *Bioresource technology*, 101(13), 4980–91.
- Goyal *et al.* H. B., Seal, D., & Saxena, R. C. (2006). Bio-fuels from thermochemical conversion of renewable resources: A review. *Renewable and Sustainable Energy Reviews*, 12(2), 504–517
- Güell *et al.* B., Sørum, Lars, S. J. (2011). Gasification of biomass to secondgeneration biofuels: a review. *Conference on sustainable energy, ES2011-541*, 1–11.
- Gullón *et al.* P., Romaní, A., Vila, C., Garrote, G., Parajó, J. C., & Engineering, C. (2012). Potential of hydrothermal treatments in lignocellulose biorefineries. *Biofuels, Bioprod. Bioref.*, 6, 219–232.
- Guo *et al.* F., Fang, Z., Xu, C. C., & Smith, R. L. (2011). Solid acid mediated hydrolysis of biomass for producing biofuels. *Progress in Energy and Combustion Science*.
- Hallenbeck, P. C. and Ghosh, D. (2009). Advances in fermentative biohydrogen production: the way forward? *Trends in biotechnology*, 27(5), 287–97.
- Haveren *et al.* J. Van, Scott, E. L., & Sanders, J. (2007). Bulk chemicals from biomass, *Biofuels, Bioprod. Bioref.* 41–57.
- Heinsoo *et al.*, K., Hein, K., Melts, I., Holm, B., & Ivask, M. (2010). Reed canary grass yield and fuel quality in Estonian farmers' fields. *Biomass and Bioenergy*, 35(1), 617–625.
- Hinchee *et al.*, M., Rottmann, W., Mullinax, L., Zhang, C., Chang, S., Cunningham, M., Pearson, L., *et al.* (2009). Short-rotation woody crops for bioenergy and biofuels applications. *In vitro cellular & developmental biology. Plant : journal of the Tissue Culture Association*, 45(6)
- Hoffmann, D., and Weih, M. (2004). Limitations and improvement of the potential utilisation of woody biomass for energy derived from short rotation woody crops in Sweden and Germany. *Biomass and Bioenergy*, 28(3), 267–279.
- Huang *et al.* R., Su, R., Qi, W., & He, Z. (2011). Bioconversion of Lignocellulose into Bioethanol: Process Intensification and Mechanism Research. *BioEnergy Research*, 4(4), 225–245
- Huber *et al.* G. W., Iborra, S., & Corma, A. (2006). Synthesis of transportation fuels from biomass: chemistry, catalysts, and engineering. *Chemical reviews*, 106(9), 4044–98.
- Hughes *et al.* A. D., Kelly, M. S., Black, K. D., & Stanley, M. S. (2012). Biogas from Macroalgae: is it time to revisit the idea? *Biotechnology for biofuels*, 5(1), 86.
- IEA (International energy agency) (2011) *Technology roadmap: biofuels for transport*, International energy agency 2011

- IPCC (Solomon, S., D. Qin, M. Manning, Z. Chen, M. Marquis, K.B. Averyt, M. Tignor and H.L. Miller) (2007): Climate Change 2007: Assessment Report of the Intergovernmental Panel on Climate Change, *Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 996 pp.*
- IPCC (Intergovernmental Panel on Climate Change) (2011) Special Report on Renewable Energy Sources and Climate Change Mitigation, *United nations*
- Jaeger, W. K., and Egelkraut, T. M. (2011). Biofuel economics in a setting of multiple objectives and unintended consequences. *Renewable and Sustainable Energy Reviews*, 15(9),
- Jahirul *et al.* M., Rasul, M., Chowdhury, A., & Ashwath, N. (2012). Biofuels Production through Biomass Pyrolysis — A Technological Review. *Energies*, 5(12), 4952–5001.
- Jasinskas *et al.* A., Zaltauskas, A., & Kryzeviciene, A. (2008). The investigation of growing and using of tall perennial grasses as energy crops. *Biomass and Bioenergy*, 32(11), 981–987.
- Jessup, R. W., (2009). Development in the United States energy crops. *Vitro Cellular & Developmental Biology. Plant*, 45(3), 282–290.
- Jing, *et al.* Q. Conijn, S. J. G., Jongschaap, R. E. E., & Bindraban, P. S. (2012). Modeling the productivity of energy crops in different agro-ecological environments. *Biomass and Bioenergy*, 46, 618–633.
- Jordan *et al.* D. B., Bowman, M. J., Braker, J. D., Dien, B. S., Hector, R. E., Lee, C. C., Mertens, J. a, et al. (2012). Plant cell walls to ethanol. *The Biochemical journal*, 442(2)
- Kahneman D. (2011) Thinking, Fast and Slow, Farrar, *strauss and Giroux/New York*
- Kamm, B., and Kamm, M. (2004). Principles of biorefineries. *Applied microbiology and biotechnology*, 64(2), 137–45. doi:10.1007/s00253-003-1537-7
- Karp, A., and Shield, I. (2008). Bioenergy from plants and the sustainable yield challenge. *The New phytologist*, 179(1), 15–32.
- Kemp R. *et al.*, Schot J. and Hoogma R. (1998) Regime shifts to sustainability through processes of niche formation: The approach of strategic niche management, *Technology Analysis & Strategic Management* 10 (2) p. 175-198
- Keshwani, D.R., and Cheng, J. J. (2008). Switchgrass for bioethanol and other value-added applications: a review. *Bioresource technology*, 100(4), 1515–23. doi:10.1016/j.biortech.2008.09.035
- Khanna *et al.* S., Goyal, A., & Moholkar, V. S. (2012). Microbial conversion of glycerol: present status and future prospects. *Critical reviews in biotechnology*, 32(3), 235–62.
- Kim *et al.*, S. R., Ha, S.-J., Wei, N., Oh, E. J., & Jin, Y.-S. (2012). Simultaneous co-fermentation of mixed sugars: a promising strategy for producing cellulosic ethanol. *Trends in biotechnology*, 30(5), 274–82.
- Kirrolia *et al.* A., Bishnoi, N. R., & Singh, R. (2012). Microalgae as a boon for sustainable energy production and its future research & development aspects. *Renewable and Sustainable Energy Reviews*, 20,
- Kiss, A. a. and Bildea, C. S. (2012). A review of biodiesel production by integrated reactive separation technologies. *Journal of Chemical Technology & Biotechnology*, 87(7), 861–879.
- Koller *et al.*, M., Salerno, A., Tuffner, P., Koinigg, M., Böchzelt, H., Schober, S., Pieber, S., (2012). Characteristics and potential of micro algal cultivation strategies: a review. *Journal of Cleaner Production*, 37, 377–388.
- Kraan, S. (2010). Mass-cultivation of carbohydrate rich macroalgae, a possible solution for sustainable biofuel production. *Mitigation and Adaptation Strategies for Global Change*, 18(1), 27–46.

- Kratky, L., and Jirout, T. (2010). Biomass Size Reduction Machines for Enhancing Biogas Production. *Chemical Engineering & Technology*, 34(3), 391–399.
- Kumar, *et al.* S., Singh, S. P., Mishra, I. M., & Adhikari, D. K. (2009). Recent Advances in Production of Bioethanol from Lignocellulosic Biomass. *Chemical Engineering & Technology*, 32(4), 517–526.
- Kumar *et al.* A., Jones, D. D., and Hanna, M. a. (2009_b). Thermochemical Biomass Gasification: A Review of the Current Status of the Technology. *Energies*, 2(3), 556–581.
- Labrecque, M., and Teodorescu, T. I. (2005). Field performance and biomass production of 12 willow and poplar clones in short-rotation coppice in southern Quebec (Canada). *Biomass and Bioenergy*, 29(1), 1–9.
- Lam, M. K., and Lee, K. T. (2011). Microalgae biofuels: A critical review of issues, problems and the way forward. *Biotechnology advances*, 30(3), 673–90.
- Lankoski, J., and Ollikainen, M. (2006). Bioenergy crop production and climate policies: a von Thunen model and the case of reed canary grass in Finland. *European Review of Agricultural Economics*, 35(4), 519–546. doi:10.1093/erae/jbn040
- Laureysens, *et al.* I., Pellis, A., Willems, J., & Ceulemans, R. (2005). Growth and production of a short rotation coppice culture of poplar. III. Second rotation results. *Biomass and Bioenergy*, 29(1), 10–21. doi:10.1016/j.biombioe.2005.02.005
- Lee *et al.* J., Parameswaran, B., Lee, J., & Park, S. (2008). Recent developments of key technologies on cellulosic ethanol production, 67(November), 865–873.
- Lee *et al.* A. K., Lewis, D. M., & Ashman, P. J. (2012). Disruption of microalgal cells for the extraction of lipids for biofuels: Processes and specific energy requirements. *Biomass and Bioenergy*, 46, 89–101.
- Lestari *et al.* S., Mäki-Arvela, P., Beltrami, J., Lu, G. Q. M., & Murzin, D. Y. (2009). Transforming triglycerides and fatty acids into biofuels. *ChemSusChem*, 2(12), 1109–19.
- Lewandowski *et al.* I., Clifton-brown, J. C., Scurlock, J. M. O., & Huisman, W. (2000). Miscanthus : European experience with a novel energy crop. *Biomass and Bioenergy*, 19(2000), 209–227.
- Lewandowski *et al.* Iris, Scurlock, J. M. O., Lindvall, E., & Christou, M. (2003). The development and current status of perennial rhizomatous grasses as energy crops in the US and Europe. *Biomass and Bioenergy*, 25(4), 335–361. doi:10.1016/S0961-9534(03)00030-8
- Limayem, A., and Ricke, S. C. (2011). Lignocellulosic biomass for bioethanol production: Current perspectives, potential issues and future prospects. *Progress in Energy and Combustion Science*, 38(4), 449–467.
- Lin *et al.* S. K., Luque R. and Clark J. (2011). Wheat-based biorefining strategy for fermentative production and chemical transformations of succinic acid. *Biofuels, Bioprod. Bioref.*, 6, 88–104.
- LNv (Ministerie van Landbouw, Natuur en Voedselkwaliteit) 2007 Overheidsvisie op bio-based economy in de energietransitie, de keten sluiten, Document prepared by the dutch government.
- Londo *et al.* M., Dekker, J., & Terkeurs, W. (2004). Willow short-rotation coppice for energy and breeding birds: an exploration of potentials in relation to management. *Biomass and Bioenergy*, 28(3), 281–293.
- Lovell, H. (2007) The governance of innovation in socio-technical systems: the difficulties of strategic niche management in practice. *Science and Public Policy*, 34(1), 35–44.
- Macquarrie *et al.* D. J., Clark, J. H., and Fitzpatrick, E. (2012). The microwave pyrolysis of biomass. *Biofuels, Bioprod. Bioref.*, 6, 549–560.

- Madhavan *et al.* A., Srivastava, A., Kondo, A., & Bisaria, V. S. (2010). Bioconversion of lignocellulose-derived sugars to ethanol by engineered *Saccharomyces cerevisiae*. *Critical reviews in biotechnology*, 32(1), 22–48.
- Maier, K. D., and Bressler, D. C. (2007). Pyrolysis of triglyceride materials for the production of renewable fuels and chemicals. *Bioresour technology*, 98(12), 2351–68.
- Marshall, A.-L., and Alaimo, P. J. (2010). Useful products from complex starting materials: common chemicals from biomass feedstocks. *Chemistry (Weinheim an der Bergstrasse, Germany)*, 16(17), 4970–80.
- Mata *et al.* T. M., Martins, A. a., Sikdar, S. K., & Costa, C. a. V. (2010). Sustainability considerations of biodiesel based on supply chain analysis. *Clean Technologies and Environmental Policy*, 13(5), 655–671.
- McKendry, P. (2002). Energy production from biomass (Part 1): Overview of biomass. *Bioresour technology*, 83(1), 37–46.
- McLaughlin, et al. S., Bouton, J., Bransby, D., Conger, B., Ocumpaugh, W., Parrish, D., Taliaferro, C., et al. (1999). Developing Switchgrass as a Bioenergy Crop. In: J. Janick (ed.), *Perspectives on new crops and new uses*. ASHS Press, Alexandria, VA.
- McLaughlin et al., S. B., Kiniry, J. R., Taliaferro, C. M., La, D. De, & Ugarte, T. (2006). Projecting yield and utilization potential of switchgrass as an energy crop. *Advances in Agronomy*, 90(06).
- Melero *et al.* J. Iglesias J. And Garcia A. (2012). Biomass as renewable feedstock in standard refinery units. *Energy & Environmental Science*, 5, 7393.
- Menon, V., and Rao, M. (2012). Trends in bioconversion of lignocellulose: Biofuels, platform chemicals & biorefinery concept. *Progress in Energy and Combustion Science*, 38(4),
- Mettler *et al.* M. S., Vlachos, D. G., & Dauenhauer, P. J. (2012). Top ten fundamental challenges of biomass pyrolysis for biofuels. *Energy & Environmental Science*, 5(7), 7797.
- Miao *et al.* Z., Shastri, Y., Grift, T. E., Hansen, A. C., & Ting, K. C. (2011). Lignocellulosic biomass feedstock transportation alternatives, logistics, equipment configurations, and modeling, *Biofuels, Bioproducts and Biorefining Volume 6, Issue 3, pages 351–362, May/June 2012*
- Miller P. and Blum P. (2010). Extremophile-inspired strategies for enzymatic biomass saccharification. *Environmental science & technology*, 31(8-9), 1005–1015.
- Mohammadi *et al.* M., Najafpour, G. D., Younesi, H., Lahijani, P., Uzir, M. H., & Mohamed, A. R. (2011). Bioconversion of synthesis gas to second generation biofuels: A review. *Renewable and Sustainable Energy Reviews*, 15(9), 4255–4273.
- Mondal *et al.* P., Dang, G. S., and Garg, M. O. (2011). Syngas production through gasification and cleanup for downstream applications — Recent developments. *Fuel Processing Technology*, 92(8), 1395–1410.
- Monti et al. A., Bezzi, G., Pritoni, G., & Venturi, G. (2008). Long-term productivity of lowland and upland switchgrass cytotypes as affected by cutting frequency. *Bioresour technology*, 99(16), 7425–32.
- Mortensen *et al.* P. M., Grunwaldt, J.-D., Jensen, P. a., Knudsen, K. G., & Jensen, a. D. (2011). A review of catalytic upgrading of bio-oil to engine fuels. *Applied Catalysis A: General*, 407(1-2), 1–19.
- Mulrow, C. D. (1994) *Systematic Reviews: Rationale for systematic reviews*, BMJ 309(September 1994), P. 597–599.
- Munasinghe, P. and Khanal, S. K. (2010). Biomass-derived syngas fermentation into biofuels: Opportunities and challenges. *Bioresour technology*, 101(13), 5013–22.

- Naik *et al.*, S. N., Goud, V. V., Rout, P. K., & Dalai, A. K. (2009). Production of first and second generation biofuels: A comprehensive review. *Renewable and Sustainable Energy Reviews*, 14(2), 578–597
- NBS (2011) *Guide to NBS Systematic Reviews*, Network for Business Sustainability.
- Nill, J., and Kemp, R. (2009). Evolutionary approaches for sustainable innovation policies: From niche to paradigm?, *Research Policy*, vol. 38 issue 4.
- NREL (2011) Biodiesel Handling and Use Guide, Fourth Edition. National Renewable Energy Laboratory
- Octave S. and Thomas D. (2009) *Biorefinery: Toward an industrial metabolism*, *Biochimie* Volume 91, Issue 6, June 2009, Pages 659–664
- Olah, G. a, Goeppert, A., & Prakash, G. K. S. (2009). Chemical recycling of carbon dioxide to methanol and dimethyl ether: from greenhouse gas to renewable, environmentally carbon neutral fuels and synthetic hydrocarbons. *The Journal of organic chemistry*, 74(2), 487–98.
- Olson *et al.* D. G., McBride, J. E., Shaw, a J., & Lynd, L. R. (2011). Recent progress in consolidated bioprocessing. *Current opinion in biotechnology*, 23(3), 396–405.
- Parmar *et al.* A., Singh, N. K., Pandey, A., Gnansounou, E., & Madamwar, D. (2011). Cyanobacteria and microalgae: a positive prospect for biofuels. *Bioresourve technology*, 102(22), 10163–72.
- Patel, S. K. S., and Kalia, V. C. (2012). Integrative Biological Hydrogen Production: An Overview. *Indian Journal of Microbiology*, 53(1), 3–10.
- Pellis *et al.* A. Lauresysens I., C. R. (2004). Growth and production of a short rotation coppice culture of poplar I. Clonal differences in leaf characteristics in relation to biomass production. *Biomass and Bioenergy*, 27(1), 9–19.
- Pereira *et al.* E. G., Da Silva, J. N., De Oliveira, J. L., & Machado, C. S. (2012). Sustainable energy: A review of gasification technologies. *Renewable and Sustainable Energy Reviews*, 16(7), 4753–4762.
- Petersen *et al.* J., E. B. W. T. and F. J. and E. U. (2007). Estimating the environmentally compatible bioenergy potential from agriculture. *European Environment Agency*, (12).
- Peterson *et al.* A. a., Vogel, F., Lachance, R. P., Fröling, M., Antal, J. . M. J., & Tester, J. W. (2008). Thermochemical biofuel production in hydrothermal media: A review of sub- and supercritical water technologies. *Energy & Environmental Science*, 1(1), 32.
- Petticrew M. and Roberts H. (2006) Systematic reviews in the social sciences. A practical guide, *Blackwell Publishing*
- Prade *et al.* T., Svensson, S.-E., Andersson, A., & Mattsson, J. E. (2011). Biomass and energy yield of industrial hemp grown for biogas and solid fuel. *Biomass and Bioenergy*, 35(7).
- Ratha, S. K., and Prasanna, R. (2011). Bioprospecting microalgae as potential sources of “Green Energy”—challenges and perspectives (Review). *Applied Biochemistry and Microbiology*, 48(2), 109–125.
- Raven R. and Verbong G. (2007) Multi-Regime Interactions in the Dutch Energy Sector: The Case of Combined Heat and Power Technologies in the Netherlands 1970–2000, *Technology Analysis & Strategic Management*, 19:4, 491-507
- Raven, R. (2005). Strategic Niche Management for Biomass Strategic Niche Management for Biomass, *Technische Universiteit Eindhoven*
- Rehman *et al.* M. S. U., Rashid, N., Saif, A., Mahmood, T., & Han, J.-I. (2012). Potential of bioenergy production from industrial hemp (*Cannabis sativa*): Pakistan perspective. *Renewable and Sustainable Energy Reviews*, 18, 154–164.
- Richard, T. L. (2010). Challenges in scaling up biofuels infrastructure. *Science (New York, N.Y.)*, 329(5993), 793–6. doi:10.1126/science.1189139

- Ridley, *et al.* C. E., Clark, C. M., Leduc, S. D., Bierwagen, B. G., Lin, B. B., Mehl, A., & Tobias, D. a. (2012). Biofuels: network analysis of the literature reveals key environmental and economic unknowns. *Environmental science & technology*, 46(3),
- Robbins *et al.*, M. P., Evans, G., Valentine, J., Donnison, I. S., & Allison, G. G. (2012). New opportunities for the exploitation of energy crops by thermochemical conversion in Northern Europe and the UK. *Progress in Energy and Combustion Science*, 38(2), 138–155.
- Rose, M., and Palkovits, R. (2012). Isosorbide as a renewable platform chemical for versatile applications--quo vadis? *ChemSusChem*, 5(1), 167–76.
- Rowe *et al.*, R. L., Street, N. R., & Taylor, G. (2009). Identifying potential environmental impacts of large-scale deployment of dedicated bioenergy crops in the UK. *Renewable and Sustainable Energy Reviews*, 13(1), 271–290.
- Russo *et al.* D., Dassisti, M., Lawlor, V., & Olabi, a. G. (2012). State of the art of biofuels from pure plant oil. *Renewable and Sustainable Energy Reviews*, 16(6), 4056–4070.
- Saito *et al.* T., Brown, R. H., Hunt, M. a., Pickel, D. L., Pickel, J. M., Messman, J. M., Baker, F. S., *et al.* (2012). Turning renewable resources into value-added polymer: development of lignin-based thermoplastic. *Green Chemistry*, 14(12), 3295.
- Sánchez, O. J., and Cardona, C. a. (2007). Trends in biotechnological production of fuel ethanol from different feedstocks. *Bioresource technology*, 99(13), 5270–95.
- Sanderson *et al.*, M. a., Adler, P. R., Boateng, a. a., Casler, M. D., & Sarath, G. (2006). Switchgrass as a biofuels feedstock in the USA. *Canadian Journal of Plant Science*, 86(Special Issue), 1315–1325.
- Sanderson, M. a, and Adler, P. R. (2008). Perennial forages as second generation bioenergy crops. *International journal of molecular sciences*, 9(5), 768–88.
- Sannigrahi *et al.*, P., Ragauskas A., and Tuskan G. (2010). Poplar as a feedstock for biofuels : A review of compositional characteristics. *Biofuels, Bioprod. Bioref.*, 4, 209–226.
- Saritha, M., and Arora, A. (2011). Biological Pretreatment of Lignocellulosic Substrates for Enhanced Delignification and Enzymatic Digestibility. *Indian Journal of Microbiology*, 52(2), 122–130.
- Sarkar *et al.* N., Ghosh, S. K., Bannerjee, S., & Aikat, K. (2011). Bioethanol production from agricultural wastes: An overview. *Renewable Energy*, 37(1), 19–27.
- Scarlat *et al.* N., Dallemand, J.-F., Skjelhaugen, O. J., Asplund, D., & Nesheim, L. (2011). An overview of the biomass resource potential of Norway for bioenergy use. *Renewable and Sustainable Energy Reviews*, 15(7), 3388–3398.
- Scarlat *et al.* N., Martinov, M., & Dallemand, J.-F. (2010). Assessment of the availability of agricultural crop residues in the European Union: potential and limitations for bioenergy use. *Waste management (New York, N.Y.)*, 30(10), 1889–97.
- Scholz *et al.* M., Melin, T., & Wessling, M. (2012). Transforming biogas into biomethane using membrane technology. *Renewable and Sustainable Energy Reviews*, 17, 199–212.
- Schot J. and Geels F. W. (2008). Strategic niche management and sustainable innovation journeys: theory, findings, research agenda, and policy. *Technology Analysis & Strategic Management*, 20(5), 537–554.
- SER (Sociaal Economische Raad) (2010) *Meer chemie tussen groen en groei: de kansen en dilemma's van een biobased economy*, advies uitgebracht aan de minister van economische zaken landbouw en innovatie.
- Serrano-Ruiz *et al.* J. C., West, R. M., and Dumesic, J. a. (2010). Catalytic conversion of renewable biomass resources to fuels and chemicals. *Annual review of chemical and biomolecular engineering*, 1, 79–100.

- Shastri *et al.* Y, Hansen A. Rodrigues L., T. K. (2012). Switchgrass - practical issues in developing a fuel crop. *CAB Reviews: Perspectives in Agriculture, Veterinary Science, Nutrition and Natural Resources*, 7(037). doi:10.1079/PAVSNNR20127037
- Simonetti, D. a., and Dumesic, J. a. (2009). Catalytic Production of Liquid Fuels from Biomass-Derived Oxygenated Hydrocarbons: Catalytic Coupling at Multiple Length Scales. *Catalysis Reviews*, 51(3),
- Sims *et al.* R., Taylor M., S. J. and Mabee W. (2008). From 1st - to 2nd -Generation BioFuel technologies: An overview of current industry and RD&D activities., *International Energy Agency*
- Sims *et al.* R. E. H., Mabee, W., Saddler, J. N., & Taylor, M. (2009). An overview of second generation biofuel technologies. *Bioresource technology*, 101(6), 1570–80.
- Singh, N. K., and Dhar, D. W. (2010). Microalgae as second generation biofuel. A review. *Agronomy for Sustainable Development*, 31(4), 605–629.
- Singhania *et al.*, R., Kumar, A., Sukumaran, R. K., Larroche, C., & Pandey, A. (2012). Bioresource Technology Role and significance of beta-glucosidases in the hydrolysis of cellulose for bioethanol production. *Bioresource technology*, 127, 500–507.
- Sipos *et al.* B., Kreuger, E., Svensson, S.-E., Réczey, K., Björnsson, L., & Zacchi, G. (2010). Steam pretreatment of dry and ensiled industrial hemp for ethanol production. *Biomass and Bioenergy*, 34(12), 1721–1731.
- Smeets *et al.* E. M. W., Lewandowski, I. M., & Faaij, A. P. C. (2009). The economical and environmental performance of miscanthus and switchgrass production and supply chains in a European setting. *Renewable and Sustainable Energy Reviews*, 13(6-7), 1230–1245.
- Snell, K. D., and Peoples, O. P. (2009). PHA bioplastic : A value-added coproduct for biomass biorefineries. *Biofuels, Bioprod. Bioref.*, 3, 456–467.
- Somerville *et al.*, C., Youngs, H., Taylor, C., Davis, S. C., & Long, S. P. (2010). Feedstocks for lignocellulosic biofuels. *Science (New York, N.Y.)*, 329(5993), 790–2. doi:10.1126/science.1189268
- Ståhlberg *et al.* T., Fu, W., Woodley, J. M., & Riisager, A. (2011). Synthesis of 5-(hydroxymethyl)furfural in ionic liquids: paving the way to renewable chemicals. *ChemSusChem*, 4(4), 451–8.
- Sticklen, M. (2006). Plant genetic engineering to improve biomass characteristics for biofuels. *Current opinion in biotechnology*, 17(3),
- Stražil, Z. (2012). Evaluation of reed canary grass (*Phalaris arundinacea* L .) grown for energy use. *Research in agricultural and engineering*, 58(4), 119–130.
- Struik *et al.* P. C., Amaducci, S., Bullard, M. J., & Stutterheim, N. C. (2000). Agronomy of fibre hemp (*Cannabis sativa* L .) in Europe, 11, 107–118.
- Sun, Y. and Cheng, J. (2001). Hydrolysis of lignocellulosic materials for ethanol production: a review. *Bioresource technology*, 83(1), 1–11.
- Swain *et al.* P. K., Das, L. M., & Naik, S. N. (2011). Biomass to liquid: A prospective challenge to research and development in 21st century. *Renewable and Sustainable Energy Reviews*, 15(9), 4917–4933.
- Tabak J. (2009) *Biofuels*, Energy and the environment, Facts On File, Inc.
- Taheripour *et al.* F., Hertel T.W., Tyner W.E., Beckman J.F. and Birur D.K. (2009) *Biofuels and their by-products: Global economic and environmental implications*, Biomass and Bioenergy 2009.10.017
- Talebnia *et al.* F., Karakashev, D., & Angelidaki, I. (2010). Production of bioethanol from wheat straw: An overview on pretreatment, hydrolysis and fermentation. *Bioresource technology*, 101(13), 4744–53.

- Taylor *et al.*, L. E., Dai, Z., Decker, S. R., Brunecky, R., Adney, W. S., Ding, S.-Y., & Himmel, M. E. (2008). Heterologous expression of glycosyl hydrolases in planta: a new departure for biofuels. *Trends in biotechnology*, 26(8),
- Teece, et al. D. J., Pisano, G., & Shuen, A. (1997) Dynamic capabilities and strategic management, *Strategic Management Journal* 18(7), 509–533, 1997
- Tirado-Acevedo et al., O., Chinn, M. S., and Grunden, A. M. (2010). Production of biofuels from synthesis gas using microbial catalysts. *Advances in applied microbiology*, 70(10), 57–92.
- Tokiwa, Y., and Calabia, B. P. (2008). Biological production of functional chemicals from renewable resources, 555, 548–555.
- Trodd N. (2007) *PESTLE Analysis*, GeoImaging and GeoInformatics (GIGI)
- Tuck *et al.* G., Glendining, M. J., Smith, P., House, J. I., & Wattenbach, M. (2006). The potential distribution of bioenergy crops in Europe under present and future climate. *Biomass and Bioenergy*, 30(3),
- Tumuluru *et al.* J. S., Wright, C. T., Hess, J. R., Kenney, K. L., & National, I. (2011). A review of biomass densification systems to develop uniform feedstock commodities for bioenergy application †, 683–707.
- UN (United Nations) (2012) Report of the United Nations Conference on Sustainable Development, *United Nations Conference on Environment and Development, Rio de Janeiro, Brazil 2012*
- UNEP (United Nations Environment Programme) (2012) Global Chemicals Outlook: Towards Sound Management of Chemicals, *United Nations*
- Urbanchuk J.M. (2012) *Contribution of biofuels to the global economy*, Global Renewable Fuels Association, CardnoEntrix
- US-DOE (U.S. Department of Energy) (2012) Replacing the whole barrel to reduce U.S. dependence on oil, *Office of Energy USA*
- Utterback J.M. and Suhez F.F. (1991) Innovation, competition, and industry Structure, *Research Policy* 22 (1993) 1-21
- Vamvuka, D. Ā. (2011). Bio-oil , solid and gaseous biofuels from biomass pyrolysis processes — An overview, (January), *Int. J. Energy Res.* 2011 835–862.
- Van der Stelt *et al.* M. J. C., Gerhauser, H., Kiel, J. H. a., and Ptasinski, K. J. (2011). Biomass upgrading by torrefaction for the production of biofuels: A review. *Biomass and Bioenergy*, 5.
- Venderbosch R. and Prins W. (2009). Fast pyrolysis technology. *Biofuels, Bioprod. Bioref.*, (1), 178–208.
- Venendaal *et al.* R., Jorgensen U. and Foster C. (1997). European energy crops: a synthesis. *Biomass and Bioenergy*, 13(3), 147–185.
- Vennestrøm et al. P. N. R., Osmundsen, C. M., Christensen, C. H., & Taarning, E. (2011). Beyond petrochemicals: the renewable chemicals industry. *Angewandte Chemie (International ed. in English)*, 50(45), 10502–9. doi:10.1002/anie.201102117
- Venter G. (2012) *The software of life*, Aljazeera
- Verbong, G. *et al.*, Geels, F. W., & Raven, R. (2008). Multi-niche analysis of dynamics and policies in Dutch renewable energy innovation journeys (1970–2006): hype-cycles, closed networks and technology-focused learning. *Technology Analysis & Strategic Management*, 20(5), 555–573.
- Verma *et al.* M., Godbout, S., Brar, S. K., Solomatnikova, O., Lemay, S. P., & Larouche, J. P. (2011). Biofuels Production from Biomass by Thermochemical Conversion Technologies. *International Journal of Chemical Engineering*, 2012, 1–18.

- Verschuren, P. and Doorewaard, H. (2010) Designing a research project, *Eleven International Publishing second ed.*
- Volk *et al.* T., Abrahamson, L., Nowak, C., Smart, L., Tharakan, P., & White, E. (2006). The development of short-rotation willow in the northeastern United States for bioenergy and bioproducts, agroforestry and phytoremediation. *Biomass and Bioenergy*, 30(8-9), 715–727.
- Wang *et al.*, D., Lebauer, D. S., & Dietze, M. C. (2010). A quantitative review comparing the yield of switchgrass in monocultures and mixtures in relation to climate and management factors. *GCB Bioenergy*, 2(1), 16–25.
- Weber, K. M., & Rohrer, H. (2012). Legitimizing research, technology and innovation policies for transformative change. *Research Policy*, vol. 41 issue 6.
- Wei *et al.*, N., Quarterman, J., & Jin, Y. (2013). Marine macroalgae : an untapped resource for producing fuels and chemicals, *Trends in biotechnology* 31(2).
- Wen *et al.* D., Jiang, H., & Zhang, K. (2008). Supercritical fluids technology for clean biofuel production. *Progress in Natural Science*, 19(3), 273–284.
- Werpy, T., and Petersen, G. (2004). Top value added chemicals from biomass, vol. 1. Results of screening for potential candidates from sugars and synthesis gas. *National Renewable energy Lab*
- Westfall, P. J., and Gardner, T. S. (2011). Industrial fermentation of renewable diesel fuels. *Current opinion in biotechnology*, 22(3), 344–50.
- Williams, P. J. L. B., and Laurens, L. M. L. (2010). Microalgae as biodiesel & biomass feedstocks: Review & analysis of the biochemistry, energetics & economics. *Energy & Environmental Science*, 3(5), 554.
- Wright, L., and Turhollow, A. (2010). Switchgrass selection as a “model” bioenergy crop: A history of the process. *Biomass and Bioenergy*, 34(6), 851–868. doi:10.1016/j.biombioe.2010.01.030
- Xiu, S., and Shahbazi, A. (2012). Bio-oil production and upgrading research: A review. *Renewable and Sustainable Energy Reviews*, 16(7), 4406–4414.
- Xu *et al.* Q., Singh, A., & Himmel, M. E. (2009). Perspectives and new directions for the production of bioethanol using consolidated bioprocessing of lignocellulose. *Current opinion in biotechnology*, 20(3), 364–71.
- Yang, B., and Wyman, C. E. (2008). Pretreatment : the key to unlocking low-cost cellulosic ethanol. *Biofuels, Bioprod. Bioref.*, 2, 26–40.
- Yeh *et al.* T. M., Dickinson, J. G., Franck, A., Linic, S., Thompson, L. T., and Savage, P. E. (2012). Hydrothermal catalytic production of fuels and chemicals from aquatic biomass. *Journal of Chemical Technology & Biotechnology*, 88(1), 13–24.
- Yin, C. (2012). Bioresource Technology Microwave-assisted pyrolysis of biomass for liquid biofuels production. *Biore*, 120, 273–284.
- Zakzeski *et al.*, J., Bruijninx, P. C. a, Jongerius, A. L., & Weckhuysen, B. M. (2010). The catalytic valorization of lignin for the production of renewable chemicals. *Chemical reviews*, 110(6)
- Zegada-lizarazu *et al.* Elbersen H. , Cosentino S.I., Zatta A., A. E. and M. A. (2010). Agronomic aspects of future energy crops in Europe. *Biofuels, Bioprod. Bioref.*, (4)
- Zegada-Lizarazu, W., and Monti, A. (2011). Energy crops in rotation. A review. *Biomass and Bioenergy*, 35(1), 12–25.
- Zetl *et al.* C., Gairola, K., Kirsch, C., Perez-Cantu, L., & Smirnova, I. (2011). High Pressure Processes in Biorefineries. *Chemie Ingenieur Technik*, 83(7), 1016–1025.

- Zhang, Y.H.P. (2008) Reviving the carbohydrate economy via multi-product lignocellulose biorefineries, *Journal of industrial microbiology & biotechnology*, 35(5), 367–75.
- Zhang, Y. (2010). Hydrothermal Liquefaction to Convert Biomass into Crude Oil (pp. 201–232). *Biofuels from agricultural wastes and byproducts*.
- Zhang, Y.-H. P. (2011). What is vital (and not vital) to advance economically-competitive biofuels production. *Process Biochemistry*, 46(11),
- Zhang *et al.*, X., Tu, M., & Paice, M. G. (2011). Routes to Potential Bioproducts from Lignocellulosic Biomass Lignin and Hemicelluloses. *BioEnergy Research*, 4(4), 246–257.
- Zhang *et al.* Z., Donaldson, A. a, & Ma, X. (2012). Advancements and future directions in enzyme technology for biomass conversion. *Biotechnology advances*, 30(4), 913–9.
- Zheng *et al.* Y., Chen X., and Shen Y. (2008). Commodity chemicals derived from glycerol, an important biorefinery feedstock. *Chemical reviews*, 110(3), 1807
- Zheng *et al.* Y., Pan, Z., & Zhang, R. (2009). Overview of biomass pretreatment for cellulosic ethanol production. *Int. J. Agriculture and biology*, 2(3), 51–68.
- Zhou *et al.* C., Xia X., Lin C., Tong D., B. J. (2011). Catalytic conversion of lignocellulosic biomass to fine chemicals and fuels. *Chem. Soc. rev*, 40, 5588–5617.
- Zub M. and Brancourt-Hulmel H. (2010). Agronomic and physiological performances of different species.pdf. *agronomy and sustainable development journal*, 30, 201–214.