Making the Biobased Economy Work

Biomass Utilization model in South-Holland

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Executive summary

In this thesis the options for biobased production of products, energy and fuels are reviewed. This review provides an extensive overview of possibilities. These possibilities show that there are a lot of technologies available for biobased production. The most developed and widely used technologies can be found in the energy and fuel sector. While in general there are a lot of developments, the chemical sector is now moving towards biobased production which is shown by the various reviewed pathways for biobased chemical production.

Using the reviewed pathways a model is constructed showing the variety of possibilities. This makes it possible to visualize the developments going on in this sector. In order to demonstrate the possibilities the model is applied to the Dutch Province of South-Holland. Gathering information through qualitative interviews with companies and public institutes the South-Holland region is modelled.

The display of the tool its applicability should stimulate further research in this subject and allow for the model to be used as a tool in providing both companies and regions insight in their biobased status and potential.
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1. Introduction

In the last decades much has been written about Sustainable Development (e.g. Meadows and the Club of Rome, 1972; World Commission on Environment and Development and Brundtland, 1987; Stern, 2007). This development is necessary to preserve the earth for future generations (World Commission on Environment and Development and Brundtland, 1987) and nowadays is associated with a varied amount of topics (World Bank, 2012).

This thesis will go into detail on a specific topic within the topics associated with sustainable development: biomass resources. Fossil resources are diminishing and will be depleted in the future because everything will be used up or the costs of extraction will be too high (Dasgupta and Heal, 1974 – pp 25-27). This implies the necessity to transition into sustainable resources (Daly, 1990 – pp 1). One of the solutions for this transition is the increased use of biomass as resource. Because regional settings can have a big impact (Kromus et al., 2004 pp 11), the research in this thesis will be put into context in the Dutch province of South-Holland.

Biomass can be used as a resource for a wide variety of products (Klass, 1998 pp1 - 651). The focus in this thesis will be the use of biomass for chemicals, fuels & energy. Because fuels and energy have been discussed widely their role will be more limited than the discussion of the non-fuel chemical industry. Biomass its role will be discussed in three sections:

- Biomass resources
  Here the amount of biomass, the different typologies of biomass and important actors will be discussed.

- Biobased production
  In the second part a more in-depth look will be taken through the review of academic literature on the biobased production methods. This will be done through reviewing
the possibilities of biomass for energy, followed by the chemical industry and finishing with biobased fuels.

After these 2 sections the goal is to create a biomass utilization model flowchart which shows the reviewed possibilities in one map. In the following section this model will then be put into context:

- **Biobased in South-Holland**
  By using interview data from important actors in the South-Holland province the results of the review will be placed into regional context. The previously constructed biomass utilization model will be put into regional context showing development paths and important stakeholders.

This thesis should give a concise review of the possibilities for biomass. Using the reviewed papers a model will be constructed to easily identify biomass its possibilities. To test this it will be placed into context for the province of South-Holland allowing objectives for further research to be identified. This thesis does not aim to give a complete overview of every single possibility but serve as a basis for further research and extensions with other possibilities that are not yet discussed in this thesis.
2. Methodology

This thesis is set up along 2 lines of investigation. The first line of investigation is done through a review of existing literature on biobased production. This review is based on existing academic literature, various reports and market studies. The review is supported by a citation analysis that is used to rank chemicals according to the academic interest. Using this review a model is constructed, which in its core is a graphical representation of the review.

Secondly a series of qualitative interviews has been done to assess the situation in the Dutch Province of South-Holland. Using the interview data the reviewed literature will be put into regional context for the South Holland province. This is done by adding the information about South-Holland combined with the expectations expressed during the interviews to the model. This puts the model into context and gives an indication of future possibilities with current expectations expressed by market actors.
3. Biomass as a resource

This chapter starts with an overview of the pathways in the biobased economy; there are several pathways possible from plant to product. This chapter should give a basic understanding of the possible pathways on a general level. In the following chapters for various parts of the pathways I will go more into detail. But first in the following sections an overview of technologies for biomass utilization. Since biomass is not only limited to technologies but also to supply & demand there will also be a short discussion of important actors.

As said the goal of this chapter is to give a broad overview, this is done not only by short textual explanation but also graphically modelling the pathways that can be taken in flowcharts. Where possible these flowcharts can be found in text, for some of the bigger flowcharts please refer to the appendixes.

3.1 Biomass routes

The very first flowchart we start off with is the most basic one that resembles the whole industry, everywhere we have biomass (regardless of its source) it can be processed through various treatment processes into products. This is nothing new and is a representation of process in place since we first started using tools.

![Simple biomass flow - own work](image)

It gets more interesting when we start expanding our flowchart to take more complexities into account, let us first start with the Biomass itself:
Here we there is a distinction between 4 major groups of supply; these 4 groups constitute almost all the biomass we can use for the biobased economy. Because these are used often in literature (e.g. Ligué et al., 2011) they are only shortly explained:

**Waste**

The most common waste we all know as biomass waste is the biodegradable municipal solid waste, all the greens that we throw away in our daily lives. This is a large amount of very heterogeneous biomass waste, there are different kinds of biomass and people do not always separate correctly. Another municipal stream is the green waste that comes from natural resource & landscape management. When municipalities keep parks, forest and other green areas in order they generate a large amount of biomass waste.

Besides municipal waste there is a large amount of Biomass coming from agrarian companies and the food processing industries. These are usually more mono waste streams in which separation is good to very good e.g. farmers grow one type of crop so
have residuals of one crop type as waste. These streams can be called the low hanging fruits since they are easier to transform due to their constant supply and quality. Because of this easier transformation these waste streams are often already used as feed, fuel, resource or other useful purposes. (Liguel et al., 2011, p12-14) The definition of waste is still a very regional sensitive issue. Even within the European Union some countries their recycling rates are very high with only waste streams that are more difficult to use achieving low recycling. While in some other countries most of the waste still goes to landfills. (European Comission, 2012 – pp 1-6)

1st generation biomass

1st generation biomass is generated from plants that grow on arable land and have a high sugar content. They are specifically cultivated to be used as biomass for energy or production purposes although they can sometimes also be used as food. One of the well-known examples is the corn fields in Brazil that produce Ethanol. Here the plant has high starch contents and can easily be processed into energy and/or fuel products. The biggest drawback here is that these plants are also and important feedstock for both humans and animals, so there is a direct competition with our food supply. (Havlik et al., 2011, pp 10) (Sims and Taylor, 2008, pp 16-21, 26-32)

2nd generation biomass

2nd generation biomass can come from all the lignocellulose plants in the world, which is the most abundant biomass resource available, is used as a resource for further processing. The big advantage here is that non arable land can be used and transformation of the whole plant is possible (Harmsen et al. 2010, pp 6) and (Sims and Taylor, 2008, pp 34-35). This means less competition with our food supply (Sims and Taylor, 2008, pp 35). Theoretically using lignocellulose we can provide all the energy we need but there is not yet any clear agreement on this (Berndes et al., 2003, pp 19). The technology is much in development and still has high investment costs (Sims and Taylor, 2008, pp 34). In the next sections more about the technological processes.
Algae

Sometimes also called 3rd generation biomass (Posten and Schaub, 2009, pp 66) algae are one promising route because of their extremely high yields and capability to grow in areas otherwise considered inhabitable (desserts, saline grounds, (salt) water environments) this makes them interesting for both developed and developing countries. They can grow almost anywhere and produce high yields however there is still lots of research to be done and the current reactor designs still require large investments. (Sharma et al., 2011, pp 13)

Supply

While very theoretically we can supply all of our needs by utilizing biomass, some like Saratale and Oh (2012, pp 1003) call it virtually inexhaustible, this only when very high efficiencies in every step are reached. There are various technical limitations which are shown in one of the extensive reviews. This review of different studies on biomass availability results in the following graphic:
As can be seen in the graphic there is not a clear consensus on total amounts that can really be supplied by biomass. It is also clear that most studies do not expect biomass to be the Holy Grail, although it can supply enough whether this is really feasible the opinion differ a lot (Berndes et al., 2003, pp 6, 19). In this thesis the main focus is not on energy, although the possibilities will be reviewed, but on chemicals and products from biomass. Europe uses about 3% of its oil supply for products not including fuels & energy. Including fuels total oil consumption in 2009 was ca. 97.000 TOE which is about 4 Ej. (Eurostat, 2012). This would indicate that biomass can substitute oil not for our complete energy supply but at least for products and fuels. There are however so much insecurities in this field that more research is needed taking a lot more factors into account to be certain of this as was shown by the recent iLUC discussion (more about this later) (Dunkelberg et al., 2011, pp 1). For now the assumption in this thesis is that at least substitution of oil used for chemical production by biomass is feasible. Since there is at least an indication that fuels can be substituted as well these will be taken into account. Furthermore as indicated there will only be a short review of possibilities on the use of biomass for energy. This is important as it is still an option and/or in use for many countries, indicated by the supply of 35 to 55 Ej of bio energy. (Berndes et al., 2003, pp 1-6).

For the biomass supply it is critical to understand the complexity and uncertainty regarding the possible biomass supply (Heinimö, 2007 – pp 39). Berndes et al. (2003) have given a very good overview in 2003 and more recently the review of Offerman et al. (2010) is a good recommendation. But also here the estimates range between 0 and 1600 eJ. Since this thesis is on the possibilities of biomass it is recommended to read Offerman et al. (2010) for more information about the current discussion of biomass supply. It reviews recent studies and shows the complexity of calculating the possibilities (Offerman et al., 2010).
3.2 Supply actors

To come back to the flowchart, we have different forms of biomass and what is good to know are the different possible sources for the various biomass streams in order to get an overall picture of the whole chain:

Agrarians

Already biobased for thousands of years, the agrarian industry is the main provider of food and feed. In the future however it can add the role of resource provider for the biobased industry as well. This can start in this sector by utilizing waste and side streams but if the growth sustains than we will also see a transition here; not only supply food and feed but also supply biomass for industry. The first steps of this transition are already being made, we can see societal unrest about the impact on food prices of this development. Looking at population trends combined with the biobased production possibilities means that the agrarian industry will have to increase yields and utilize locations that are currently not considered arable. There is a wide array of possibilities for them to increase when looking at the differences between developed and developing countries but biobased production can also utilize feedstock that do not compete with food supply. (Sherpa group and European Comission, 2011, pp 8)
**Municipalities**

In South Holland municipalities play a central role in assigning who takes away the waste and therefore gets residual biomass from end consumers (households). This is first of all the waste from private households and the municipalities its own natural resource management. So we have a municipal waste flow and a natural resource management flow of biomass originating from municipalities. This waste stream allows municipalities to exercise control over what has to be done with the waste but sometimes it is also tendered to private parties. (Personal communication Royal HaskoningDHV, 2012)

**Industry**

Industry has a lot of different wastes but due to their usually mono waste type they are often waste for one company and a valuable resource for another company. This is reinforced through rising resource prices giving waste a positive instead of a negative value for companies. Even when the waste has a very low or negative value there are more and more decentralized energy generation options using biomass that can allow companies to create value using their own waste stream. This makes waste less and less a cost for companies but instead can even generate value. (Lehmann, 2011, pp 28 – 32)

**Green Industry**

Besides the previous groups there are also new initiatives that produce biomass specifically for further processing in the biobased economy. These are advanced processes like algae reactors and specific plant strains for direct processing. Furthermore the growing off some specialized energy plants/molecular farming is sometimes also regarded as part of the green industry and seen as a way to further improve processes similar to advances in the food and feed industry (Herrero et al., 2006, pp 18) (Ragauskas et al., 2006, pp 487). Other companies develop processes for turning waste into resources and accept streams that others regard as worthless. But with new technologies it is possible to create a positive cash flow out of wastes that at the moment still have negative value. These companies in turn offer different and/or new resources and products. (Laufenberg et al., 2003, pp 167)
4. Biobased Production

Having established the main categories and sources of biomass we will now look at the other side of our flow chart and identify possible products and their related production processes. First of all we can identify various categories of products that can be made from biomass (Iuguel et al. 2011, pp 10):

- Energy
- Fuels
- Bulk chemicals
- Specialty chemicals/pharmaceuticals
- Fodder
- Food

As one can see this is a wide range of products that can be made, the possibilities are often depending on the local situation. In this thesis the context will be South Holland so processes applicable to this region have been favoured in selecting the examples of processing discussed in this paper. Not all possibilities have been included, but the most discussed and/or market ready technologies have been selected as favourable. This has mainly been done for “new” biobased products as there already is a well-developed food and fodder sector. Furthermore a short summary of energy and fuel possibilities has been included to give the complete overview of “new” possibilities that have been developed since the first oil crisis. Sometimes these are continued developments of processes that are thousands of year’s old but simply regained attention and for the main focus category, being bulk chemicals, the processes that are developed can be really new and have never been seen before. So food, fodder and specialty chemicals have been excluded as they are either well established or so niche specific that their discussion does not help this thesis. Energy and fuels will be discussed but most of the attention will go to the possibilities for bulk chemicals.
4.1 Energy

In this chapter the current and future developments of bio mass to energy technologies will be discussed. This will be done by first looking at the different possibilities currently in use in Europe, followed by looking at its spread throughout the European Union. The chapter will finish with an outlook on future developments in bio energy technologies.

There is a large variety of conversion technologies for biomass to energy; a difference can be made in the process used to transform the biomass into energy. The following processes have been identified (McKendry, 2002, pp. 48-52):

- Combustion
- Anaerobic Digestion
- Gasification
- Fuel production

The focus here is on the biomass that are directly converted into heat and/or electricity so the fuel producing processes will not be discussed.

Combustion

One of the oldest forms of using biomass is by simply burning it, as long as biomass is not too moist (< 50%) it is possible to light it and transform its energy contents into heat. This can be done on a very small and inefficient scale like a small campfire but nowadays also by co-combusting biomass with coals. (McKendry, 2002, pp. 48) Biomass combustion facilities can generate both heat and electricity depending on their configuration. Usually the heat is used to generate electricity and the remaining heat is for example supplied to district heating.
**Direct (small scale) combustion**

We used to have fire stoves to heat our homes; this is a perfect example of direct small scale combustion where biomass is burned up to generate heating in a house or small company. Also here developments have taken place and small scale controlled combustion units are available for burning the biomass and using the heat throughout the house by e.g. a central heating system. As example of such a system we have an image here of the KWB Multifire 50.

This is a small system intended to run on both wood pellets and woody materials. Due to their smaller size there is less research in this area and detailed information is not available. Some studies favor larger scale plants though (Dornburg & Faaij, 2001, pp. 1). Most pellet systems are focused on generating heat only and can be compared to a central heating unit the runs on gas. At the moment only Austria seems to have a large amount of non-industrial wood pellet use. Because of this specific market the discussion of this system is not covered further but should not be forgotten when looking at future developments as there is high growth potential. (Sikkema et al., 2011, pp. 1) More information on this technology and Austrian markets can be found in the proceedings of the second world conference on pellets (Obernberger & Thek, 2006, pp. 31-40).

**Co-combustion**

One of the uses of biomass for generating power and heat is through co-combustion with coals. This way existing and new installation can be used without much effort and the amount of renewable energy in the mix is easily improved. Although this has potential
positive effects in the usage of CO2 and mitigating emissions there are also various problems that can occur. Before we go to the problems, first a description of the technology judged most viable to use for co-firing biomass with coal: fluidized bed combustion followed by the more common grate fired co-combustion. (Saidur et al., 2011, pp. 2277 - 2278) Both methods can also be used for only Biomass but are less efficient and more prone to pollution problems that way (Nussbaumer, 2003, pp. 1). For now task 32 has identified that for the near-term co-combustion is most easily realized and cost-effective. (IEA, 2012)

Fluidized beds

In a fluidized bed coal (and possibly biomass) is combusted inside an airflow that fluidizes the particles. This leads to better performance both in burning the materials and in heat extraction while still being able to maintain an overall lower temperature. Other forms of fluidized beds are also possible depending on the situation this could mean recirculation of particles or using the same principle under pressure. (NREL, 2012)

![Fluidized bed diagram of its functioning](YassineMrabet/Wikipedia, 2012)
Some of the advantages of a fluidized bed according to the Indian Bureau of Energy (2012, pp. 151-152) Efficiency:

- High efficiency

The fluidized bed has a high burning efficiency burning up to 95% leading to overall efficiency rates of about 84%. When combined with pressurized beds efficiencies in power generation can increase even more.

- High flexibility

Due to their design the fluidized beds can effectively burn a lot of different fuels and react quickly on changing parameters.

- Use of low grade fuels

Fluidized beds do not need only high grade fuels; they can also function on low grade, low energy content materials making them well suited to burning various biomasses together with coal. The following picture from Koornneef et al. (2007) gives a good overview of possibilities for Fluidized beds:

Figure 6 - Overview of fuel possibilities for fluidized beds (Koornneef et al., 2007)
One can see that there is a lot possible without (major) challenges. Nonetheless there are some problems that commonly occur with the co-combustion of coals and biomass which have been summarized in the section after the next combustion method; grate fired biomass.

*Grate fired system*

A somewhat more traditional model for firing biomasses is the grate firing system, biomass is put on a grate where it is burned and the heated gases heat super heaters from which the heat can be transported or transformed into e.g. electricity. One of the main differences between systems is the way fuel is added. This can be done by using a sloped grate, travelling grate, reciprocating grate or vibrating grate (Yin, Rosendahl, & Kær, 2008, pp. 728–733).

![Grate fired system diagram](Image)

The differences between the grates are mainly in the amount of control and carbon burning efficiency. The more control and better mixed it is the better; the worst is the sloped grate due to the little amount of control exerted and possible fuel avalanches. This is followed by a travelling grate that improves the amount of possible control. It can be further optimized in the reciprocating grate that improves the mixing process. Finally a vibrating grate still provides good control and mixture while being more economical (Yin et al., 2008, pp. 728 – p733). Some differences between a grate system and a fluidized bed according to Yin et al. (2008 pp. 728 - 733) are:
• Needs to be fed homogeneous fuels, needs more adjustments to accommodate a specific fuel.

• Combustion instability in the bed.

• Insensitive to bed agglomeration that can happen in fluidized beds with certain fuels.

• Both need extra systems to keep emissions under control, although in fluidized beds this can be accommodated by the type of bed that is chosen.

• Partial loading is possible with good results

• Cheaper

_Co-combustion problems_

Baxter & Koppejan (2004, pp. 3-7) give the following problems that may arise from co-combusting biomass with coals:

• fuel preparation, storage, and delivery

Due to Biomass it’s much larger mass to energy ratio you simply need a lot more biomass to generate the same amount of energy as you do with coals. Already at about 10% Biomass instead of coal (compared at output levels) is the mass ratio 1:1. This presents a lot more logistics and feeding than plant was used to or even built to accommodate (Baxter & Koppejan, 2004, pp. 4). Sami et al. (2001, pp. 209) recommend placing the plants close to sources of supply to reduce transport and ensure delivery.

• ash deposition

Due to different ash behavior, fusing of ash happens a lot more quickly with biomass as co input product. Due to the chemistry involved it is hard to predict what exactly will happen but general indexes have already been established that can give rough guidelines
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(Baxter & Koppejan, 2004, pp. 4). The ash deposits that form can lead to reduced combustibility, heat transfer and increased corrosion (Sami et al., 2001, pp. 209). However more recent research by Shao et al. (2010, pp. 1) shows that in fluidized beds specific mixtures of coal and biomass can actually lead to a reduced amount of depositions and more uniform heating temperatures.

- fuel conversion

When the biomass is excessive in size or moisture content they are not converted into heat but it just becomes dried biomass together with the ashes at the bottom. (Baxter & Koppejan, 2004, pp. 4 - 5)

- pollutant formation

Sami et al. (2001, pp. 209) indicate that it is possible to reduce the amount of pollutants associated with traditional coal firing through co-combustion. However, Baxter et al. (2004, pp. 5) also indicate that industry experiences are not yet in line with expected reductions.

- increased corrosion rates of high temperature components

Biomass combustion has the capability to increase temperatures around depositions and through this cause more corrosion. (Sami et al., 2001, pp. 209) The co-firing process reduces this problem due to mitigating factors (sulphur) present in coal (Baxter & Koppejan, 2004, pp. 4 - 5) Still Sami et al. (2001, pp. 209) recommend using biomass with low chlorine and alkali contents.

- fly ash utilization

Fly ash is a co-product from coal fired power plants and in use in the cement Industry, as long as biomass is co-fired with coal up to a 20% w/w than there are no technical issues to prevent this method from continuing. (Grammelis et al., 2006, pp. 1)

- impacts on SCR (selective catalytic reduction) systems
There is evidence suggesting impacts of co-firing biomass on SCR systems, due to the alkali content in the biomass the SCR systems get “poisoned” and do not perform as they are supposed to anymore. This has the potential of increasing NOx emissions but is still under research. (Baxter & Koppejan, 2004, pp. 7).

**Digestion**

The second technology discussed here is digestion of organic materials, this cannot be used for solid materials but organic material that can be reduced to a relatively small size can be digested to form methane gasses. These gasses can subsequently be used for powering a CHP installation or brought up to spec to use as “green gas” either for heating or transport fuel (possibly combined with cryogenic installations). Although the basis remains the same there are differences in approach, digestion can be done both wet and dry and furthermore different temperatures (thermo- vs. mesophilic) and the use of a co-substrate (“co-digestion”) are possibilities. (Wu, 2007, pp. 1-2) Beside these differences there can be differences in design of the installation these are however largely dependent on the previous differences in biomass feed.

**Process**

Digestion processes are well established and work on the process of microorganisms eating organic materials and transforming them into methane and CO2:
This figure from a supplier of digesters shows how the biological process works: First we start with the materials quite intact and just cut/shredded to small pieces but on molecular level still polymers. These polymers can be made up of proteins, starch or fats. Through hydrolytic and acetogenic processes these polymers are broken down into hydrogen, fatty acids, acetates, alcohols and CO2. Through a combination of processing microorganism these are transformed into methane gas. This is still a rich gas and CO2 mixture and through further cleaning high quality green gas can be produced. The final product resulting from the digestion unit are methane gas and digestate, the digestate can be split into a solid and liquid fraction. (Batstone et al., 2002, pp. 65-69) (Mozaffarian et al., 2004, pp. 1).
Design

For the design of an Anaerobic Digestion unit there are various options, each with their positive and negative properties. The various design choices are shortly summarized with a table for each choice summarizing the positives and negatives of each choice.

One of the important choices is whether the digestion process will be done at mesophilic temperatures (ca. 35 degrees) or thermophilic temperatures (ca. 55 degrees). The main advantage of thermophilic temperatures is increased speed of digestion and adhering to EU rules for animal waste minimum requirements to prevent diseases. It is still a more complex, and harder to control, process which makes it more suited for large operations.

<table>
<thead>
<tr>
<th>Thermophilic</th>
<th>Mesophilic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Faster</td>
<td>Less need for control</td>
</tr>
<tr>
<td>Smaller</td>
<td>Lower capital costs</td>
</tr>
<tr>
<td>No pasteurization necessary</td>
<td></td>
</tr>
<tr>
<td>Higher capital costs</td>
<td>Slower</td>
</tr>
<tr>
<td>Optimum balance necessary</td>
<td>Bigger</td>
</tr>
<tr>
<td>Toxicity problems for manure co-digesting</td>
<td>Animal products need pasteurizer</td>
</tr>
</tbody>
</table>

(Batstone et al., 2002) (Juniper, 2007, pp. 7-12)

Secondly there the consideration between a wet or dry process, dry is only relatively dry as the moist percentages can still go up to 50% while wet is a slurry that has been mixed and is digested. The dry process can be done in batches or continuously in a plug flow design (biomass moving through a “tube”).

<table>
<thead>
<tr>
<th>Wet/Mixed</th>
<th>Dry/Batch or plug flow</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixed during digestion</td>
<td>Less wastewater &amp; energy</td>
</tr>
<tr>
<td>Lower investment</td>
<td>Lower operation costs</td>
</tr>
<tr>
<td>Contamination problems</td>
<td>Premixing necessary</td>
</tr>
<tr>
<td>Larger</td>
<td>Higher investment</td>
</tr>
<tr>
<td>Higher operation costs</td>
<td>Higher CO2 impact</td>
</tr>
</tbody>
</table>

(Batstone et al., 2002) (Juniper, 2007, pp. 7-12) (Mata-Alvarez et al., 2000, pp. 3-16)
There are more and more developments in further optimizing digestion reactors and processes but it can take a long time before products arrive on the market with a references chicken and egg problem. Examples of recent entries on the market that claim better digestion technologies and/or very pure gas are Serigas (India) and Bareau (the Netherlands). However it seems to be hard to get proper references about larger than pilot scale projects and up scaling is usually indicated as a serious problem. (Personal communication, various consultants Royal HaskoningDHV)

Gasification

The development of gasifiers dates back more than 200 hundred years ago when biomass was used in blast furnaces and rests upon the conversion of biomass to (energy) gas that is created through an oxidization process. In design the gasifiers can be very similar to a combustion plant however instead of burning an energy rich gas is produced. (Goswami, 1986, pp. 1-2)

The produced gas usually consist of CO2, CO, hydrogen, methane and water, this is combined with various chars & tars that are left behind in the process. The process has been known for a long time and there are various designs for gasifier installations. Despite the long of knowing the process only through the interest during the oil crisis in the 70’s have more efficient and reliable designs been realized. (Stevens, 2001, pp. 3-4)

As indicated by Stevens (2001, pp. 4) one of the high impact choices in design is the choice of oxidation agent. The gasifiers can be constructed to use air, but they can also use pure oxygen or steam in order to produce more energy rich gasses (Ciferno, J. P., & Marano, J. J. (2002)). There are various designs similar to the previously discussed combustion designs where the gasification process takes place. In the next section a short overview of these designs and a look at some more recent designs/processes that utilize 2 step approaches or co-gasification with coal.
**Fixed Bed design**

The most simple biomass gasifier is fixed bed design in which there is a single vessel without movements. There is the choice of using the oxidizing agent down or updraft:

![Fixed Bed Design Diagram](image)

The most traditional method is the updraft gasifier; in the bottom of the reactor the biomass is combusted at high temperatures and air, oxygen or steam passes through and moves upward while cooling down to have the gases coming out on top. The simplicity of the design makes it low cost and an established technology but according to EUBIA (2012) it is not a common design for new reactors (only 2.5% of companies offer this design). This is most likely due to the highly contaminated gas that it produces which requires a lot of cleaning up before it is market ready. (Ciferno, J. P., & Marano, J. J. (2002)).

Rather than having an updraft gasifier 75% of the companies in the EUBIA (2012) market research offer downdraft gasifiers. Here the principle is the same but the biomass and oxidizing agent are ignited on top and combust while going down, this delivers a very hot but also a lot cleaner gas. The remaining products (ash, char) go down through the grate at the bottom of the reactor allowing for mineral recovery. Due to the gas being so hot a secondary cooling system is required making this design more complex than updraft gasifiers but still simple however the process does not work well with very moist biomass.
Fluidized Bed design

The principle behind a gasification fluidized bed is the same as the fluidized bed discussed for combustion purposes. For gasification two types of fluidized beds are in use: circulating fluidized beds and bubbling fluidized beds. In a circulating fluidized bed the inert particles are travelling in a circular motion through the gas and biomass, the particles allow for good heat transport and break up the biomass yielding high conversion rates. Special attention needs to be paid though to the speed of the particles as too high speed of the gas and particles may lead to erosion damage of the vessel and less uniform heat spread through the link of the temperature gradient with the direction of the particles.

Bubbling fluidized beds are the second option, here the inert particles are bubbling in a boiling fashion within the fluidized bed. This system is capable of processing different biomass sizes and has the capability to keep an even temperature spread throughout the reactor. The gas it produces it very clean but can sometimes with large inert particle size leak through the bottom of the bed. (EUBIA, 2012)

Figure 10 - Schematic overview of fluid bed gasifiers (EUBIA, 2012)
Despite the developments of these systems biomass gasification installations are not very widespread and still too costly to operate. The EUBIA (2012) has this to say about gasification:

“After a long lasting development, which dates back to the 18th century, the commercial implementation of biomass gasification is still problematic. Very few processes have yet proved economically viable, although the technology has progressed steadily.”

Chapter Summary

There is a wide array of technologies available for converting biomass into bioenergy, ranging from traditional combustion to highly optimized high efficiency new combustion methods. This is supported by additional possibilities for wastes and more moist biomass to be digested and transformed into biogas which can be used to supply both heat and power either for own use in small scale installations or whole neighbourhoods in large plants.

Figure 11 – Energy flowchart (own work)
4.2 Bulk Chemicals

As a starting point for bulk chemicals there are several papers that have identified the possibilities. One report by the DOE (Werpy et al. 2004) is often used in literature; in this report the DOE has identified 12 chemical building blocks that can be made from sugars and syngas. Sugars are the main components of 1st generation biomass and after treatment also one of the main products from 2nd generation biomass. Currently often used for energy purposes, syngas can be produced from biomass through gasification and besides using it as an energy source it can be processed to create chemical building blocks as well. (Werpy et al., 2004, pp 1-2, )

Secondly there is the European Union funded BREW (Patel et al., 2006) project which has also identified 21 chemicals that show a lot of promise. The BREW report focused more on chemicals that can be used as end product as well as building block for the industry. There is some overlap between the two reports and when we group some of the brew chemicals together in the same way as the DOE report did than we get to the following table (Werpy et al. 2004) and (Patel et al., 2006):

<table>
<thead>
<tr>
<th>Brew project</th>
<th>DOE report</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xylose/arabinose and xylitol/arabinitol</td>
<td>levulinic acid</td>
</tr>
<tr>
<td></td>
<td>sorbitol</td>
</tr>
<tr>
<td></td>
<td>3-hydroxypropionic acid</td>
</tr>
<tr>
<td></td>
<td>1,4 diacids (succinic, fumaric and malic)</td>
</tr>
<tr>
<td></td>
<td>glycerol</td>
</tr>
<tr>
<td></td>
<td>aspartic acid</td>
</tr>
<tr>
<td>acrylic acid</td>
<td>2,5 furan dicarboxylic acid</td>
</tr>
<tr>
<td>lactic acid</td>
<td>glucaric acid</td>
</tr>
<tr>
<td>acetic Acid</td>
<td>glutamic acid</td>
</tr>
<tr>
<td>adipic acid</td>
<td>itaconic acid</td>
</tr>
<tr>
<td>fat and oil products*</td>
<td>3-hydroxybutyrolactone</td>
</tr>
<tr>
<td>Furfural</td>
<td></td>
</tr>
<tr>
<td>5-hydroxymethylfurfural</td>
<td></td>
</tr>
<tr>
<td>sucrose &amp; glucose*</td>
<td></td>
</tr>
<tr>
<td>1-butanol</td>
<td></td>
</tr>
<tr>
<td>1,4 butanediol</td>
<td></td>
</tr>
<tr>
<td>1,3 propanediol</td>
<td></td>
</tr>
<tr>
<td>Ethanol</td>
<td></td>
</tr>
</tbody>
</table>
Because this is still quite a long list without any way to see which chemical have more impact than the others. To resolve this I have done a very simple citation analysis meant to identify the chemicals that are currently most published in academic literature.

The main goal being a comparison of attention for specific keywords, the set up for the citation analysis was very simple. Each chemical served as search word in the Google scholar engine and the total results of all papers containing this word was used as quantitative data. Although this is a rather crude and simple method it does serve the purpose of referencing the chemical against each other for checking the amount of interest. Because of this most of the critiques on using Google scholar as input data for citation analysis are also irrelevant. (Falagas et al., 2007. pp 342)

Glucose/sucrose have been left out of this analysis as they will be discussed in the treatment section as they are an essential part for further processing of biomass. (Werpy et al., 2006, pp 1) Fat and oil products will receive more attention to their fuel possibilities later in this thesis while most of the attention will be on the chemical possibilities also fuel possibilities will shortly be discussed for e.g. Ethanol and Butanol.

This analysis has created the following chart:

<table>
<thead>
<tr>
<th>Keyword</th>
<th>Hits 2000-2010</th>
<th>Keyword</th>
<th>Hits 2000-2010</th>
</tr>
</thead>
<tbody>
<tr>
<td>1  Ethanol</td>
<td>1210000</td>
<td>12 1,3 propanediol</td>
<td>18100</td>
</tr>
<tr>
<td>2  acetic acid</td>
<td>587000</td>
<td>13 1,4 butanediol</td>
<td>18000</td>
</tr>
<tr>
<td>3  glycerol</td>
<td>433000</td>
<td>14 adipic acid</td>
<td>17500</td>
</tr>
<tr>
<td>4  lactic acid</td>
<td>356000</td>
<td>15 itaconic acid</td>
<td>16600</td>
</tr>
<tr>
<td>5  acrylic acid</td>
<td>290000</td>
<td>16 furfural</td>
<td>16300</td>
</tr>
<tr>
<td>6  glutamic acid</td>
<td>89900</td>
<td>17 2,5 furan dicarboxylic acid</td>
<td>8700</td>
</tr>
<tr>
<td>7  Xylose, arabinose, xylitol &amp; arabinitol</td>
<td>81390</td>
<td>18 levulinic acid</td>
<td>6250</td>
</tr>
<tr>
<td>8  1,4 diacids (succinic, fumaric and malic)</td>
<td>75200</td>
<td>19 glucaric acid</td>
<td>3800</td>
</tr>
<tr>
<td>9  aspartic acid</td>
<td>63200</td>
<td>20 5-hydroxymethylfurfural</td>
<td>2540</td>
</tr>
<tr>
<td>10 Sorbitol</td>
<td>60500</td>
<td>21 3-hydroxypropionic acid</td>
<td>1520</td>
</tr>
<tr>
<td>11 1-butanol</td>
<td>19900</td>
<td>22 3-hydroxybutyrolactone*</td>
<td>152</td>
</tr>
</tbody>
</table>
As can be seen in the chart there are 5 high interest chemicals:

- Ethanol
- Acetic acid
- Glycerol
- Lactic acid
- Acrylic acid

All the others are relatively close to each other in their interest level and do not show big changes in interest levels. Therefore in the following part a short summary of each chemical and the various ways in which it can be produced. For the top 5 interest level chemicals I will go more in depth and discuss them longer and look more in depth at new developments. Due to the simple search other uses of the chemicals might have a big impact on this order. If this is the case this will be shown in the following descriptions of the chemicals and possibilities for bulk use will be considered. The order in which the chemicals are presented is according to their interest level for the 2000-2010 period as was used for the chart creation.

* due to the low level of interest for 3-hydroxybutyrolactone this chemical has been excluded from further discussion as well.
1. Ethanol

![Ethanol molecular structure](http://www.chemspider.com/Chemical-Structure.682.html)

Although Ethanol is mostly known for its use as a biofuel there are other uses in the chemical industry that as of yet are primarily supplied by synthetic ethanol. Even more, ethanol can be dehydrated into ethylene which is one of the core platform chemicals. Ethylene production is ca. 120 million tons a year, almost a triple fold of total bioethanol production. With a value at the time of writing of $1350,- per metric ton and estimated production costs of $700,- ethylene can probably economically be made from renewable feedstock but will still be sensitive to feedstock prices and ethylene price developments. (Rass-Hansen et al., 2007, pp 329-332)

Still Christensen et al. (2008, pp 285) suggest that the process needs less pure ethanol than bio ethanol produced for fuel purposes allowing an even wider margin. Ethylene is one of the chemicals on the bio chemical value chain that has gotten below the cost of ethylene on the petrochemical value chain:

![Renewable vs Fossil chemical value chain](http://www.chemspider.com/Chemical-Structure.682.html)
Ethylene is used for a wide variety of products, some of the most well know examples are the polymerization products: Polyethylene or PE plastic and PolyEthelyneTerephthalate or PET plastic which is known for the plastic bottles we use today. But also glycols, acrylic acid and styrene belong to the possibilities. The list of possibilities is very long and would require up scaling bio ethanol production in order to replace the current fossil chemical industry by a renewable chemistry industry.

Other (chemical) products and derivatives for Ethanol are (Patel et al., 2006, pp 20 - 23):

- **Disinfectant**
  Ethanol has disinfecting abilities and is used for pharmaceutical and cleaning disinfectant products.
- **Solvent**
  Ethanol can dissolve various products (e.g. fat, oils, adhesives, varnish and more)
- **Preserving agent**
  Sometimes ethanol is used as a preserving agent to prevent decay and/or bacterial growth.
- **ETBE**
  An derivative from bioethanol that can be used as an anti-knock agent which is synthesized from Ethanol and Isobuten
- **Ethylesters**
  Due to the demand for green solvents Ethylester production has been commercialized and can potentially be produced from renewable building blocks only.

The other main product produced today is bioethanol, here the starch present in plants is processed through fermentation into Ethanol. Ethanol can be blended with gasolines or with engine modifications 100% Ethanol can be used as a fuel. This is one of the well-established renewable feedstock sectors, however it has also triggered the food vs. fuel discussion. Through this discussion and the better availability of lignocellulose it is expected that Ethanol as a fuel will be produced from lignocellulose (more in later sections).
2. Acetic acid

Due to the use of acetic acid as solvent for various chemical and pharmaceutical research it seems to have been overvalued in this simple citation analysis. Despite this it is still an important bio based product, as already indicated it used a lot as solvent and it part of several production processes. (Encyclopedia Brittanica, 2012)

At the moment acetic acid is produced through carbonylating methanol (ca. 6,8 million ta) and a smaller part through fermentation. The fermented acetic acids are mostly used for food purposes (wine vinegar) but it is also a more environmental friendly process making research in producing acetic acid from biomass a welcome new production process. Before this can be used though first the process needs to be optimized as current processes have a hard time reaching high solutions with high amount of acetic acid due to the high acidity. (Patel et al., 2006, pp 24-25)

Acetic acid is mainly used as ingredient for the production of acetic anhydride, Ethyl Acetate and Vinyl Acetate these serve mostly as intermediates for producing acetate ester, polymers and solvents. At the moment there is at least one commercial provider of biorefining processes that integrates the production of acetic acid in its production schemes. One of the methods described for acetic acid is through oxidizing ethanol with good economical possibilities as acetic acid is estimated to cost $1400,- per ton while its producing costs from ethanol are estimated at $650,- per ton. (Christensen et al., 2008, pp 285) (Rass-Hansen et al., 2007, pp 331) References about technologies and pilot projects are thin though and only one known pilot plant has been realized, still the same company is constructing several more plants in China. (Chempolis, 2012)

3. Glycerol

![Glycerol molecular structure](http://www.chemspider.com/Chemical-Structure.733.html)

Glycerol is one of the high interest products and has several interesting properties that explain this high interest. First of all unlike most of the chemical substances discussed in this section glycerol is not made from sugars but from fatty acids. Because of this there is already a large flow of glycerol produced today as a by-product from the splitting of natural fats. This process is mainly used in the growing biodiesel production industry and thus generating growing flows of glycerol. Furthermore there are petrochemical processes to synthetically produce glycerol but these are less important for this thesis or even in general nowadays. (Patel et al., 2006, pp 29-31)

Due to the already existing production of glycerol and the importance of giving value to glycerol as by-product from biodiesel production makes it one of the chemicals with more research than some of the other chemicals. Because glycerol is very versatile it can serve as a base for a wide variety of products and chemicals, this is shown by da Silva et. Al. (2009, pp 33-37) and Zheng et al. (2008, pp 5273-5274) in their overview of production possibilities from glycerol.

Zheng et al. (2008) have focused more on commodity chemicals and have made a figure analogue to petrochemical production figures to display the possibilities:
As one can see the possibilities are rich and some of the chemicals are also named by Patel et al. (2006) or Werpy et al. (2004) in their reports, see their respective reviews in the previous sections. The main message of Zheng et al.’s (2008, pp 5253, 5273) paper is that Glycerol has many possibilities to serve as commodity chemical family father, the different products in the family can be produced using a wide variety of processes and make glycerol a good substitute for commodity chemicals produced in petrochemical industry today.

Da Silva et al. (2009) have focused on some specific chemicals and products that go beyond just commodity chemicals. There is some overlap in chemicals, both da Silva et al. (2009) and Zheng et al.(2008) have identified 1,3 propandiol and dihydroxyacetone. But da Silva et al. (2009, show that it is also possible to use glycerol for the production of various building block mentioned by Patel et al. (2006) and Werpy et al. (2004):
succinic acid, Propionic Acid, Ethanol and Polyhydroxyalcanoate. Please see the respective sections in this thesis for more info on those building blocks. Furthermore Silva et al. (2009, pp 33-37) show some direct products that can be produced from Glycerol:

- **Pigments**
  There are 2 pigments that can be made from glycerol, prodigiosin can be used in the pharmaceutical industry as it is an immunosupressor and can help in cancer treatments. Furthermore Astaxanthin is used as a pigment for its colouring in the food industry; by using it as an food additive for salmon and trout it gives the fish a nicer colour and a bio based feedstock is preferred for food preparations instead of synthetic feedstock.

- **Bio surfactants**
Although not yet outside laboratory level there is some research in using glycerol to make bio surfactants which are more environmental friendly than current synthetic surfactants. More research is necessary before it can be up scaled to an industrial producing level though.

- **Citric acid**
Citric acid is currently produced by fermentation of molasses, a cheaper feedstock to use for production of this food and detergent additive would be welcome. Glycerol can be used to produce citric acid although optimization of yields and economic analysis is still necessary to confirm industrial possibilities of Citric acid production.

All in all glycerol is a very versatile feedstock that can be used for a wide variety of (chemical) products. There are still some weaknesses as recent companies have shown possibilities to produce biodiesel without glycerol as a by-product from biomass fat streams. This would however also lead to a drastic reduction of glycerol sources making it more expensive and still a feedstock for high value added products allowing for bio-glycerol with higher production costs. (Patel et al., 2006, pp 29-31) (Centi and Santen, 2005, pp 221)
4. Lactic acid

![Lactic acid molecular structure](http://www.chemspider.com/Chemical-Structure.592.html)

Lactic acid is one of the bio produced chemicals that is already existing on industrial scale, PURAC and Natureworks are both already producing (poly-) lactic acid on industrial scales using fermentation processes. Various forms of sugars can be fermented using several bacteria strains (providing different products and applicable to different circumstances). (Patel et al., 2006, 26-28)

One of the well know products that can be made by polymerization of lactic acid is PLA, this currently used a substitute for fossil based plastic (packaging) materials. This is and will probably be one of the main drivers of further growth in the future (market size 500,000+ tons/a (Wee et al., 2006, pp 164), however according to John et al. (2007, pp 529 – 532) there is more possible with lactic acid:

- Lactate esters can be produced through esterification with alcohols and can be used as green solvents. This makes it possible to create a completely biobased solvent to substitute current fossil based solvents. Processes for this are already commercialized and are expected to grow with decreasing costs.

- Use in the textile industry for acid dying purposes and leather tanning.

- Various pharmaceuticals that use lactic acid as ingredient in consumer products or medical applications. Due to the natural occurrence of lactic acid in human bodies it is good carrier for other substances.
- In the food industry as additive and disinfectant.

Furthermore lactic acid can serve as a building block for producing polyols (see 1,3 propanediol) and oxygenated chemicals like acrylic acid and propylene glycols.

Current developments for Lactic Acid are mostly focusing on using different feedstock (Laopaiboon et al., 2010, pp 1042), optimization of the bacteria that produce the lactic acid (Tanyıldızı, 2012, pp 8552) and on better fermentation technologies like simultaneous saccharification and lactic acid production (John et al., 2009, pp 1). These improved technologies should lead to reductions in costs for feedstock and production facilities combined with higher production rates and efficiencies while reducing the impact contaminations and making the process more environmental friendly. (Singh et al., 2006, pp 998) (Patel et al., 2006, 26-28)

Lactic acid is one of the best examples of an already existing bio based chemical that is used commercially as substitute for fossil materials. The continued developments and future possibilities of production from lignocellulose biomass combined with high efficiencies make this one of the key bio based chemicals that is currently already commercially produced. (Patel et al., 2006, 26-28) (Wee et al., 2006, pp 164)

![Figure 18 - PLA Pellets - Natureworks](image)
5. Acrylic acid

\[
\text{\text{H}_2\text{C} = \text{\text{C}} = \text{\text{O}}}\\
\text{\text{O}}
\]


Acrylic acid is a high quantity produced chemical (4.2 million t/a) the bio-based pathways are however limited the most important one coming from acid catalyzed dehydration of lactic acid. This process is still under development though and other processes do not yet show better performance and are economically more difficult to achieve. (Patel et al., 2006, 38) (Haveren et al., 2007, pp 51 - 52)

Acrylic acid is usually produced from fossil propylene feedstock and used (Kurland and Bryant, 1987, pp 203-207) “in the manufacture of plastics, in latex applications, in floor polish, in polymer solutions for coatings applications, emulsion polymers, paint formulations, leather finishes, and paper coatings”. For non-chemists this boils down to various paints, finishers and as a part of consumer health and medical products like shampoo, hair spray, artificial teeth and etc. (National Safety Council, 2012)

Despite the difficulties mentioned earlier it is expected that in 10 to 20 years bio-based acrylic acid production should be economically feasible in for example the Rotterdam port area (Haveren et al., 2007, pp 51 - 52). This is reinforced by more recent developments by big chemical corporations like Dow Chemical, Metabolix, Nippon Shokubai and Cargill. Unfortunately there is little information available in the academic literature, a pre-published commercial report indicates the following pathways that are currently under research or in pilot phase at the chemical corporations (Chemsystems, 2011, pp 4):
Academically there is one proposed plant design available from Pennsylvania University by Andrew Cie et al. (2012) which uses a bacteria strain capable of direct production of Acrylic Acid from sugars. This seems to be similar in design to the pilot run by Dow.
Chemical / OPX Biotech whom have also announced a pilot plant to start producing renewable acrylic acid. (Dow Chemical, 2011)

In short Acrylic acid is a bulk produced chemical which is not yet as far as Lactic Acid in its commercial phase but has received a lot of attention from chemical corporations and prediction in 2006 for commercial viability in ten to twenty years seem to be confirmed by the recent developments and tending rather to the ten than the twenty year prospects.

6. **Glutamic acid**

![Glutamic acid molecular structure](http://www.chemspider.com/Chemical-Structure.591.html)

Glutamic acid has been in the news for its uses in food products (Renton, 2006) but research done by Werpy et al. (2004, pp 39 – 41) has also identified glutamic acid as a possible bio based building block. This mainly for the possibility to produce it by fermentative routes and the derivatives have the potential to serve as monomers. These monomers can be polymerized to create various polymer products capable of substituting maleic anhydride.

Werpy et al. (2004, pp 39-41) expects this to be a midterm possibility for the bio based sector as there is still research needed to make it more price competitive before any possibilities can be realized. Recent research does not yet show any more ground breaking advances but has focused on the environmental impact of producing glutamic acid derivatives and has indicated that some process can be more harmful for the environment than today’s fossil processes (Lammens et al, 2011, pp 8521)
7. Xylose, arabinose, xylitol & arabinitol

Xylose and arabinose are high order sugars (C5) mostly present in the hemicellulose stream from lignocellulose biomass. Through further processing (fermentation, hydrolysis) xylitol, arabinitol and furfurals can be formed; xylitol has a direct use as a food additive (natural non-caloric sweetener). Through further processing of xylitol and arabinitol various derivative products are possible (similar to routes from sorbitol). Most important are the possibilities for the creation of polyesters, ethyl- and propylene glycols. This allows for large volume polymers made from biomass and direct uses of glycols in products like anti-freeze. (Patel et al., 2006, pp 53-55) (Patel et al., 2004, pp 61-64) Other possible (chemical) products that are further discussed in this thesis are lactic acid, glycerol, levulinic acid, furfurals and their derivatives.

The biggest problem for further usage of xylose & arabinose is separating them from other solubles in the hemicellulose stream(s) at a low price. With the variety of fermentation techniques to create commodity chemicals they do show a lot of promise however and can contribute to high usage and profitability of Lignocellulose biomass streams. (Patel et al., 2004, pp 61-64)
8. 1,4 diacids

Malic, Fumaric and Succinic acid are closely related acids that use very similar processes which is why they are grouped together. At the moment production is usually done by hydrogenating petrochemical feedstock but a biobased alternative is (mixed acid) fermentation of carbohydrates. At the moment the volume of production is still low, up to 16000 tons per year per acid. Although the processes for production are well developed there is still a need for further optimization and cost reductions to make the acids a competitive product. This will require optimized fermentation strains allowing for low cost carbohydrates as feedstock (e.g. lignocelluloses) and improved yields. (Werpy et al., 2004, pp 22-25) (Patel et al., 2006, pp )

When the production process for the acids can be made cost competitive there is wide variety of products and derivatives possible. Possibilities include solvents, deicers, polyamides, polyesters and derivatives capable of replacing 1,4 butanediol, Tetrahydrofuran and y-butyrolactone. The markets for those products are a lot bigger (150000 up to 500000 T/year) showing possibilities for growth of the 1,4 Diacids.

Currently there are pilot projects running for producing the 1,4 Diacids in the Suprablo program of the European union (Suprablo - E.C., 2012) and various private projects from chemical companies looking at establishing pilot industrial production facilities for example off succinic acid. (Most notably BASF, Bio-Amber, DSM and more) (Taylor, 2010).
9. Aspartic acid

Aspartic acid can be produced through both fermentative and enzymatic production process (synthetic more is possible but no discussed here), currently it is mainly in use as feedstock for aspartame production which is a sweetener additive in food (Patel et al., 2006, pp 47-49) When processes are optimized and allow low-cost fermentation and enzymatic treatment than more is possible such as the use of aspartic acid for polymers and solvents (Werpy et al., 2004, pp31 - 35) Since these studies there have not been major developments and aspartic acid is almost completely ignored in some recent publications, by for example Erickson et al. (2012) and Yu & Chen (2009), that have looked at the biobased chemicals. Only at Chalmers University there is on-going research in the use of aspartic acid as a bio-surfactant similar to the already mentioned bio-surfactant made from glycerol (Bordes, 2012).

10. Sorbitol

Sorbitol can be made by catalytic hydrogenation of glucose, after this it can serve as several (intermediate) products. Currently this process is already considered very mature and improvements can only be made in the speed of processing. Other research shows that it is possible to use fermentation techniques however these are not expected to be competitive anytime soon. The following (intermediate) products show promise to be made from Sorbitol:
• Vitamin C
• Surfactants/solubilizers
• Polyols and glycols to support production of PET

Especially the last option to allow the production of plastics from Sorbitol are very interesting, the polyesters made with sorbitol have special optical and heat properties allowing them already to be used as specialty chemical but possibly in the future also as a base for renewable bulk plastics (Patel et al., 2006, pp 75-76) (Werpy et al., 2004, pp 58-60). At the moment industrial scale processing should not prove problematic technology wise however the cost are still too high and improvements in the price are still needed before production can start. (Fenouillot et al., 2010, pp 1)

11. 1-Butanol


Butanol is already produced synthetically in a magnitude of ca. 2 million tons a year. However we already used to produce it biologically instead of synthetically earlier in the last century and only because the fossil fuels made it cheaper to produce it synthetically was the production replaced by synthetic production. It used to be produced using the ABE fermentation process in which Acetone, Butanol and Ethanol are produced (Patel et al., 2006, pp 49-51).

Butanol has various uses in the chemical industry but is also seen as the next “ethanol”, it has an higher energy content and is an more easy substitute for gasoline. Because it can already work in today’s engines without modification and can be transported in pipelines butanol is an option to be used instead of ethanol as renewable fuel. However the
fermentation process to produce butanol has not yet achieved high enough yields and is considered to be too expensive. However big companies like BP have invested heavily into more research in order to make the process commercially viable. Other chemical products that can be made from Butanol include (Patel et al., 2006, pp 49-51):

- Solvents
- Plasticizers
- Glycol & Acrylic esters

More recent several commercialization efforts have started, Green (2011, pp 2-5) has reviewed several investments in China to commercially produce biobutanol from corn starch. Furthermore an US based company (Gevo, 2012) has announced its ethanol to butanol plant conversion package implementation allowing ethanol plants to transform into a butanol plant which according to them allows them to commercially produce butanol. There is not much information available about the used process but they have developed a vision of the future of the butanol chain as they see it:

In order to review the developed process more information is necessary in the academic community which is not yet available but will hopefully develop in the coming years in order to see more improvements in the process from universities and institutions around the world.
12. 1,3 Propanediol

![1,3 Propanediol molecular structure](http://www.chemspider.com/Chemical-Structure.13839553.html)

1,3 Propanediol (PDO) is produced by a hydroformylation and hydrogenation process from fossil sources in the Shell process. Total world production is about 120,000 tons of which ca. 76,000 tons by the described synthetic process and the rest by the renewable process developed by Dupont. (Patel et al., 2006, pp 34 – 37) (Azom, 2012). The Dupont process uses a genetically engineered E. Coli K12 strain (microorganism) to produce PDO from glucose.

PDO its main use is as an ingredient for producing the polymer polytrimethylene terephthalate (PTT) this polymer has high potentials for substituting PET plastic and Nylons with further uses in engineering plastics, industrial fibers, resins and textiles. Other uses for PDO are solvents, laminates, adhesives and paints. (Patel et al, 2006, pp34 - 37)

Since the commercial process for PDO is already in place and supplying a large part of PDO supply the focus is now, according to Xiu and Zeng (2008, pp 917,925) on improving extraction methods in order to achieve better yields and a more cost-effective supply. On the other hand other researchers like Drożdżyńska et al. (2011, pp 98) find it more important to improve the microbial process and make the micro-organisms non-pathogenic. Saxena et al. (2009, pp 910) think that PDO show great promise and recommend policies for stimulating further development of bio-diesel with PDO production from its glycerol side product.
13. 1,4 Butanediol

1,4 Butanediol (BDO) was traditionally produced from fossil sources but has seen a quick move to biotechnological production. In 1995 there was a production level of about 500,000 tons per year which has grown to 1.3 million tons in 2005. There have been various developments in order to move towards biobased BDO. Several pathways have been developed of which the most important ones are the production of BDO from succinic acid and direct fermentation of BDO through a genetically engineered version of E. Coli. (Chemical week, 2006) (Patel et al., 2006, pp 52)

There are various companies working on production bio BDO, important names are DSM, Purac, Genomatics, BASF and BioAmber. Of these only Genomatics is using the direct fermentation route while the others hydrogenate succinic acid or have not yet disclosed their process. Although there is a variety of producers the price of BDO has been very volatile and ranged from 2000 dollars up to almost 3000 dollars in 2012 per ton. This combined with uncertain economic prospects due to the economic crisis make the outlook for BDO uncertain (Chemsystems, 2012) (Wang, 2012).

BDO is used for a variety of products, consulting and chemical knowledge firm Chemsystems (2012, pp 2) has created an overview of the possibilities:
Most of the growth for these markets is coming from Asia and specifically the Tetrahydrofuran (THF) and γ-Butyrolactone (GBL) are growing markets. As can be seen in the figure both serve mainly as an intermediate for other high value products such as fibres, solvents and intermediates for further product development (Chemsystems, 2012) (Wang, 2012).

Figure 30 - Butanediol possibilities - Chemsystems (2012)
14. Adipic acid

There is a large market for adipic acid, its estimated market size is 2.5 – 3.1 million tons. Adipic acid is used mainly for the production of polyamides but can also be used for the production of polymers. Traditionally it is produced from fossil sources and is usually made from cyclohexane which is hydrogenated from benzene. (Patel et al., 2006, pp 80 – 81) (Guzman, 2010, pp 22-23)

In the last couple of years there have been various developments in the bio route to adipic acid, several companies have opened bio adipic acid plants. The renewable production method uses microorganism like E. Coli to produce adipic acid from sugars. Rennovia (an industrial adipic acid producer) claims to be able to compete with fossil adipic acid as long as oil prices stay above $ 40,- per barrel. They use a 2-step catalyzed process to produce adipic acid from sugars. (Diamond, 2011) (Guzman, 2010, pp 22-23)

15. Itaconic acid

Itaconic acid is already produced in biotechnological way, by fermenting sugars (usually using Aspergillus terreus as the fungi) it is produced worldwide in small amounts. Its primary use is as a copolymer with butadiene, styrene and etc. It is on this list because the potential for Itaconica acid is much higher. Itaconic acid can potentially replace fossil
chemicals like acrylic acid. Because the current price lies around $3-4,- per kg it is too expensive to be used for these processes. The chances for itaconic acid lie in improving production and reducing costs. (Wilke and Vorlop, 2001, pp 289) (Werpy et al., 2004, pp 42 – 44)

According to industry it needs to lower costs to 1.5 dollars per kg to be competitive with polyacrylic acid. (Guzman, 2009) The expectation is that the development of Itaconinc acid into a platform chemical will be a long term perspective. (Werpy et al., 2004, pp 42 – 44)

16. Furfural

Furfural is just like Itaconic acid already produced from biomass, but it has a relatively small market of 200,000 – 300,000 tons per year. Production at the moment is too expensive and prevents using furfurals to their full capabilities. Currently it is produced from pentosan containing biomass which is hydrolysed by an acid treatment and then cyclohydrogenated to furfural (Patel et al., 2006, pp 58 - 60).

Furfural is now directly used as extractant or as fungicide but more is possible when further processing is applied. Several factories hydrogenate furfural to furfural alcohol which can be used for various processes like the creation of resins, solvents and help in other chemical production processes. When furfurals can be lowered in price one of the biggest markets is the Tetrahydrofuran market with an annual capacity of ca. 1.5 million tons (Patel et al., 2006, pp 58 - 60).
The possibilities for furfurals reside mainly in reducing current prices but also in adding value as it is an important waste product of several bio-refinery concepts. When value is added to furfural it can be a component that makes a bio refinery profitable instead of making losses (Patel et al., 2006, pp 58 - 60) (De Jong & Marcotullio, 2010, pp 20)

17. 2,5 Furan dicarboxylic acid

2,5-furandicarboxylic acid (FDCA) is built from oxidative dehydrated glucose; the product can be used as a substation for terephthalic acid which is used in polyesters like PET. This is already a big market (2 billion ton/year) but there is more possible through the combination with nylon fibres which has a total market size of 4.5 billion tones/year.

There are still some technical hurdles before further development can proceed for which more R&D is necessary to overcome problems in keeping FCDA reactivity under control and improve selective oxidation and dehydration technologies. It can also be used as a building material for succinic acid which is also one of the identified building blocks. (Werpy et al, 2004, pp 26-28)
18. Levulinic acid

![Levulinic acid molecular structure](http://www.chemspider.com/Chemical-Structure.11091.html)

Levulinic acid can be made in various ways; this can be done through enzymatic reactions or acid treatment(s). Usually cellulose or glucose is used as a feedstock but also ring cleaving furfurals will yield Levulinic Acid. In principal all carbohydrate sources can be transformed into Levulinic Acid. At the moment however world production is small (ca. 450T) and it is only used as a specialty chemical. When the production costs are reduced levulinic acid can serve as intermediate for several (chemical) products:

- Solvents
- Fuel oxygenates
- Herbicides
- Polymers
- Succinic & Acrylic acid

At the moment most of the proposed routes are still in a lab stage and need to be scaled up at economic viable levels through yield improvements and low price feedstock’s. Furthermore more research on the possible end products, especially the possible polymers is necessary to gain industrial interest (Patel et al., 2006, pp 56-58).

Ashby et al. (2012, pp 272, 277) have recently shown that by combining glycerine & levulinic acid the production of PHA, PHB and PHV is possible which can serve as a substitution for various petro chemically produced polyesters. This would increase the possibilities for biobased PHA production and offer novel pathway for utilizing levulinic acid.
19. Glucaric acid

Glucaric acid can be produced by oxidizing sugars, this process relies on nitric acid for the oxidation process. The production process still needs improvement and preferably needs to move away from using nitric acid. With the use of other inexpensive oxidation agents glucaric acid becomes a potential bulk chemical. Potential derivatives include solvents and polymer applications which can lead to polyamides produced from glucaric acid. More recent developments have focused on biotechnological pathways for producing glucaric acid but have not yet reached the necessary high yields to make it commercially interesting. (Werpy et al., 2004, pp 36 – 38) (Moon et al., 2008, pp 593 - 594)

Recently an start-up has started moving towards commercializing glucaric acid production targeting the detergent market using glucaric acid as a phosphate and citric acid alternative. The production method is still oxidation of sugars but the company claims to have found a method for better yields and nitric acid recycling. (Kolstad, 2009)

![Figure 36 - Glucaric acid molecular structure](http://www.chemspider.com/Chemical-Structure.30577.html)


![Figure 37 - Rivertop process for producing renewable chemicals and products including Glucaric Acid](http://www.rivertop.com)

Figure 37 - Rivertop process for producing renewable chemicals and products including Glucaric Acid (Kolstad, 2009)
5-hydroxymethylfurfural (HMF) is not yet produced larger than pilot scale but it is a very interesting chemical because of its many derivative possibilities:

- Polymerized to phenolic resins (various uses as a binder material)
- 2,5 bis(hydroxymethyl)furan (used in polyurethane foams)
- 2,5 dimethylfuran (fuel additive)
- FDCA
- Levulinic acid

However the biggest problem for utilizing HMF is its high price level, in 2006 this was already the case because of high fructose prices which were high enough to make the synthetic route cheaper (Patel et al., 2006, pp 76-79). Recently there have been various efforts to improve the situation leading to a preferred 2-step approach to produce fructose from biomass derived glucose and then in a second step produce HMF from fructose. This is necessary because the conditions required for the processes are very different. Despite the progresses made HMF production is still expensive because of its low yields, and unfavourable reaction conditions (Rosatella et al., 2011, pp 788 - 790).

Another concern with regard to HMF production is conflicting papers about its toxicity requiring more research into the consequences of HMF production and intake. Despite these hurdles HMF is still considered to be an important chemical because if it is produced environmentally friendly at a low prices it provides a lot of possibilities (Rosatella et al., 2011, pp 788 - 790) (Patel et al., 2006, pp 76-79).
21. 3-hydroxypropionic acid

Although both Werpy et al. (2004, pp 29-31) and Patel et al. (2006, pp 32-34) see promise in 3-Hydroxypropionic acid (3-HP), which is produced fermenting and subsequently dehydrating glucose or glycerol, there is also a lack in progress as both reports still show major difficulties despite the years in between. Both still think that there are a lot of possibilities for 3-HP, this mainly because there are various derivatives possible from 3-HP and theoretically high yields.

Despite the possibilities both Werpy and Patel show that little is known about production and it is indicated that this resides mostly within industry. Still more recently we can see an increased interest and more publications, almost half of all the publications indexed by scholar.google.com are from the last 8 years. Although this is not a thorough analysis it at least gives an indication of the interest. We can see this in recent reviews suggesting a wider variety in pathways but still showing the need for further research to optimize production (Xinglin et al., 2009, pp 1000-1001)

3-HP derivatives are acrylic acid and acrylamide which is already used nowadays from fossil source and has production levels of about 2*10^6 tons/year. Furthermore there are various derivatives that are not yet in use but could play a role in the future, most notably 1,3-Propanediol. (Patel et al., 2006, pp 32-34)

Innovations like the one by Zhang et al. (2004) which include the more direct usage of 3-Hp for the polymerization process allows 3-HP to be used as a plastic, considering their single vessel reactor and excellent mentioned properties these can be developments speeding up the usage of biobased materials.
5.3 Biobased Chemical production route(s)

There are various solutions to produce chemicals from biomass, the process is similar for most production processes though with mostly technological choices to be made. The main difference is usually which bacteria and/or enzyme is used to produce the chemicals as well as process parameters that influence them like PH levels and contaminants. These are usually determined for specific products and producing bacteria. The main focus here will be on the various technology choices that have to be made in the design phase for a lignocellulose bio refinery (see box for more information about lignocellulose). These can have a big impact but are also less specific than the biotechnological parameters.

(Mossier, 2005, pp 675, 682) (Fitzpatrick et al., 2010, pp 8915 – 8917)

The current future prospects are largely geared towards 2nd generation biomass in which the technology uses lignocellulose as a feedstock. Plants

LIGNOCELLULOSE EXPLANATIONs

The main input is lignocellulose, but what is lignocellulose? It is the structure of plant cells, they are made up from three main components, cellulose, hemicellulose and lignin. The cellulose is the basis while the lignin and hemicellulose ensure that it stay together. Cellulose and hemicellulose are made out of carbohydrate building blocks and lignin from phenolic blocks.

Figure 40 – Lignocellulose - Sannigrahi et al. (2010)
consist largely of cellulose, hemicellulose and lignin all these materials need to be valorised in a bio refinery to ensure high efficiencies and economic viability. Other possibilities are first generation biomass where the semi readily available sugar or fat contents of plants is used (which is not further discussed here since it is already in use but has various drawbacks). Also the so called third generation; algae can be an interesting option because of its high yields (Fitzpatrik et al., 2010, pp 8915 – 8917).

Less discussed and still requiring a lot of research is the possibility to directly use plant molecules to produce products. For this plants need to be specifically grown for a specific product (group). (Fischer et al., 2000) Algae receive a lot of attention but are not as near to commercial status as lignocellulose options, therefore the focus is on lignocellulose options and algae developments will be discussed shortly in a separate chapter. (Khan et al., 2009, pp 1) Direct use will probably be more and more interesting in the future but will not be discussed in this thesis as it is very specific chemical research and falls beyond the scope of this paper. (Fischer et al., 2004)

The various production process option discussed in this chapter will be followed and discussed by the route the biomass takes, so we start with how to use the biomass by fractionating the different compounds and the various process choices that can be made here. This is followed by the general explanation of the sugar/cellulose pathway processes and the various possibilities that serve as the basis for most of the chemical discussed in the previous chapter. While less detailed than the sugar pathway a short discussion will be done after this section for the possibilities of other types than cellulose biomass. These will include fatty acids but also the lignin compound of lignocellulose biomass which has not yet been discussed.
Processing - Fractionation

The main principle behind pretreating biomass is that a break down is necessary to separate lignin, cellulose and hemicellulose from each other combined with some rest products depending on the type of biomass used and possible contaminations that e.g. can be found in waste biomass streams. Secondly pretreatment can reduce cellulose its crystallinity which improves digestibility in the next step. See the following picture for a graphical display of this process:

Taherzadeh and Karimi (2008, pp 1622–1627) have identified seven optimal conditions that the pretreatment should perform:

1. “production of reactive cellulosic fiber for enzymatic attack”
2. “avoiding destruction of hemicelluloses and cellulose”
3. “avoiding formation of possible inhibitors for hydrolytic enzymes and fermenting microorganisms”
4. “minimizing the energy demand, (e) reducing the cost of size reduction for feedstocks”
5. “reducing the cost of material for construction of pretreatment reactors”
6. “producing less residues”
7. “consumption of little or no chemical and using a cheap chemical”
There is a lot of research on-going to try and reach those optimal conditions, as this pretreatment step has been identified by Zheng et al. (2009, pp 52–55) as one of the most costly process steps in the biomass to chemicals route. It is clear that this research is necessary and various new ways of processing have been developed or improved. In the following table an overview is given of the various options for pretreatment of biomass. Each option is accompanied by a summary of its advantages and disadvantages:

<table>
<thead>
<tr>
<th>Method</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mechanical comminution (e.g. milling)[1]</td>
<td>- Known process&lt;br&gt;- Reduces crystallinity</td>
<td>- (Very) high energy requirements increasing with smaller particle sizes.</td>
</tr>
<tr>
<td>Steam Explosion[1]</td>
<td>- Low capital investments&lt;br&gt;- Low environmental impact&lt;br&gt;- Energy efficient&lt;br&gt;- High yields (especially when catalyzed)</td>
<td>- Production of inhibitory compounds&lt;br&gt;- Less effective for lignin separation&lt;br&gt;- Partial destruction of xylan carbohydrates</td>
</tr>
<tr>
<td>Ammonia fiber explosion (AFEX)[1]</td>
<td>- High efficiency&lt;br&gt;- High yields (also improvements in subsequent hydrolysis)&lt;br&gt;- Suitable to variety of biomass&lt;br&gt;- No production of inhibitors</td>
<td>- Not suitable for high lignin content biomass</td>
</tr>
<tr>
<td>(supercritical) CO2 explosion[1,2,3]</td>
<td>- Small environmental impact&lt;br&gt;- Possibility for CO2 recycling/reducing CO2 impact&lt;br&gt;- No production of inhibitors</td>
<td>- Can be too expensive&lt;br&gt;- For separating Lignin &amp; Hemicellulose additional solvents (e.g. Ethanol) are necessary.&lt;br&gt;- Only high yield with additional solvents (or cellulose only with high pressure)</td>
</tr>
<tr>
<td>Ozonolysis[1]</td>
<td>- No toxic residues produced&lt;br&gt;- Removal of lignin</td>
<td>- Expensive&lt;br&gt;- Large amount of Ozone required</td>
</tr>
<tr>
<td>(dilute) Acid Hydrolysis (sulfuric acid)[1,3]</td>
<td>- Hydrolysis of hemicellulose to produce a sugar syrup.&lt;br&gt;- Removal of hemicellulose and (partial) lignin preparing cellulose for further processing.&lt;br&gt;- Solubilization of (heavy) metals.</td>
<td>- Corrosive effects requiring expensive equipment&lt;br&gt;- Requires a neutralization step before further processing of sugars.&lt;br&gt;- Gypsum solubility problems&lt;br&gt;- Formation of inhibitors&lt;br&gt;- Neutralization salts as waste product&lt;br&gt;- Requires already small particle sizes.</td>
</tr>
<tr>
<td>Method</td>
<td>Advantages</td>
<td>Disadvantages</td>
</tr>
<tr>
<td>---------------------</td>
<td>-----------------------------------------------------------------------------</td>
<td>-------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Alkali Hydrolysis</td>
<td>Removes hemicellulose and lignin</td>
<td>Needs to be combined with particle reducing pretreatment</td>
</tr>
<tr>
<td></td>
<td>High yields in subsequent enzymatic process.</td>
<td>Takes very long times compared to other methods (hours/days instead of minutes)</td>
</tr>
<tr>
<td></td>
<td>Possibility to easily recover ligning.</td>
<td>Formation of salts</td>
</tr>
<tr>
<td>Organsolv</td>
<td>High recovery of cellulose, hemicellulose and lignin</td>
<td>Expensive</td>
</tr>
<tr>
<td></td>
<td>Variety of possible solvents (Ethanol most common)</td>
<td>Solvent is an inhibitor and needs to be recovered adding a process step and high costs.</td>
</tr>
<tr>
<td></td>
<td>Possibility for 2-stage process further enhancing productivity.</td>
<td></td>
</tr>
<tr>
<td>Fungi</td>
<td>Mild environmental requirements</td>
<td>Still under research</td>
</tr>
<tr>
<td></td>
<td>Low energy requirements</td>
<td>Very long treatment times</td>
</tr>
<tr>
<td></td>
<td>No extra chemicals needed</td>
<td>Mainly leaving cellulose behind leaving little options for further usage of lignin and hemicellulose.</td>
</tr>
</tbody>
</table>

1- Balate (2011, pp 858 – 875)
2- Stavrinides et al. (2010 pp 234 – 240)
3- Taherzadeh and Karimi (2008, pp 1622–1627)

Summarizing the possibilities it is clear that there is not a single winner, some processes are better than others in specific areas but these should match with the intended purposes. It depends on location, biomass but also on possibilities for co-refining and producing multiple products on or off-site.

*Processing – Hydrolysing & Fermentation*

After fractionation the cellulose and hemicellulose is hydrolysed and fermented. First a short explanation of these steps and the organisms used. After that a look at recent process developments for designing the process.

Hydrolysis is the breaking up of a molecule usually in various steps with water as a reactant, so the bonds between the various molecules are broken with water being part of the reaction. The hydrolysis rates can be improved by utilizing catalysts like acid or base compounds which speed up the reaction process. It can also be done biochemically by
utilizing enzymes which take over some of the steps or produce different compounds. (Encyclopedia Britannica, 2012)

Fermentation is the enzyme catalysed production of various products using sugar as a base product from which production can start. Glucose is usually used but in the next section also an example will be given of long carbohydrate fermentation. Fermentation can yield energy and for industrial fermentation the pathways are usually very specifically defined in terms of feedstock, product and process. (Encyclopedia Britannica, 2012)

The hydrolysing and fermentation off biomass is done by specific organisms. For the fermentation part the organisms are specifically developed for producing the desired product and can vary widely in species and capabilities. For the hydrolysis part a group of organisms called Cellulasses are usually used, this is a group of organisms of that can effectively break down the cellulose. Commercial types have high efficiency but are expensive while the cheapest ones can be bought in most supermarkets (bakery yeast) but have lower efficiency. (Bhat, 2000, pp 355, 360,361 and 3777-378)

When the plants their three streams of cellulose, hemicellulose and lignin have been separated than there are various options for designing the processing:

- sequential hydrolysis and fermentation (SHF)
- simultaneous saccharification and fermentation (SSF)
- simultaneous saccharification and co-fermentation (SSCF)

The difference between these options is mainly in their process design; they all consist of a hydrolysis and fermentation step but there is a difference in how these are implemented. For the first option, SHF, the hydrolysis and fermentation step are done separately from each other in different reactors. This provides a high amount of control for both steps as their environmental parameters can all be optimized for their optimal levels (Ojeda et al., 2011, pp 195 -198).
However the accumulation of products in each phase inhibit the cellulase’s their activity (see box for cellulase & a short review of hydrolysis and fermentation information). To counter this the SSF process has been developed, here both the hydrolysis and fermentation step are done in one and the same reactor. This allows for less optimal environmental parameters as they are shared different organisms. Despite this production is higher because of the continued conversion of end products, first the cellulose is converted into sugars and directly the sugar is converted into an end product reducing the inhibiting effects of product accumulation (Ojeda et al., 2011, pp 195 -198).

Last but not least is the SSCF which is similar to the SSF process but uses organisms that are capable of not only transforming the glucose that was produced by the cellulases but also the longer carbohydrates that come from the hemicellulose and in smaller amount from the cellulases. This allows for performing all the reactions in just one reactor and maximizing the utilization of sugars present in the plants (Ojeda et al., 2011, pp 195 -198).

The choice between these various forms of hydrolysing and fermenting the biomass is dependent on the final chemical building block that is produced in the fermentation step. Depending on this choice organisms are used that can function in a combined step or cannot function and need very specific environmental parameters. (Cheng et al., 2011, pp A, H)

Final processing

When all the steps have been completed the mixture usually still needs to be purified allowing winning back of some reagents and at the same time purifying the final products. Some of the final products are end products (e.g. ethanol) but some can also be processed further e.g. through polymerization of monomers into polymers to create other specific chemical products (e.g. PLA). Because the final processing is very dependent on
the choices made in the previous sections it will only be discussed more in detail for specific cases in the case studies section. (Fitzpatrick et al., 2010, pp 8915 – 8917)

5.5 Lignin processing

One of the fractionated streams that has not yet been discussed is the processing of lignin, this already well known side product from paper mills used to be combusted for energy purposes. And even still today Sannigrahi et al. (2010, pp 384) indicate that academic literature on bio refineries usually utilize the lignin as an energy source and do not explore further possibilities. Yet there is more possible, most of the possibilities are still in research phase and not close to commercial operations, but the possibilities to further improve the value chain should not be underestimated as can be seen in the economic analysis made by Bergeron and Hingman (1990, pp 27-28) where lignin already provides value with oil prices above $28 per barrel. Due to the sometimes specialized chemical research status this section will be limited to a short discussion of the current and near future possibilities as identified by Gosselink (2011, pp 24 – 43)

Figure 42- Lignin possibilities & value (Gosselink, 2011)
This overview can be further reduced to the following groups from least developed to highest state of development:

- Macromolecules
- Aromatics
- Direct use
- Energy

The aromatic possibilities will be important in the future as it is one of the methods for drop in replacement of fossil oils. Lignin has the aromatic bonds and makes it possible to biologically produce the BTX chemical group which serves as the base for the petrochemical industry (Holladay, 2007, pp 26 – 30). For now a short overview of possibilities in each group. For the distant options just an overview of future possibilities will be provided while for the processes that can be used today or in the near future more detail will be provided and examples of possible products will be given.

*Lignin Macromolecules*

There is still a lot of R&D necessary before the macromolecules present in Lignin can be utilized directly. This comes from the difficulties in different Lignin kinds and associated processes. The chemical conversion and conditioning processes need further development before they can be deployed. Possible uses in the future according to Gosselink (2011, pp 24 – 43) and Holladay et al. (2007, p 22 - 30) can include but will not be limited to:

- Carbon fibres
  Lignin can be processed in carbon fibres which are currently made from petrochemical sources, when done correctly the reduction in price and higher availability makes it possible to replace part of the steel used for example in car manufacturing by carbon fibres boards.

- Polymer fillers
By adding lignin to polymer fillings it can provide enhanced capabilities to the polymer, so it is not only used as a low cost filling product but a high value additive that boosts certain properties. Possible applications are high strength polymers, anti-bacterial polymers, heat resistant polymers and more.

- Resins, adhesives & binders

Lignin can be used as a component of epoxy resins which is an ingredient commonly used for electronics. Other possibilities include the use of lignin as an adhesive or binder. Especially the substitution of formaldehyde which has proven to be toxic will offer opportunities to the use of lignin instead.

All these possibilities have in common that lignin purity and the use of different lignin feedstock are still problematic even in the test laboratory. When conditioning methods have been developed the next step will be to upscale and reduce costs to make the theoretical possibilities possible in practice. These problems make the macromolecule use of lignin a medium to distant future possibility. (Fachagentur Nachwachsende Rohstoffe, 2009, pp 5-9)

*Lignin Aromatics*

Lignin is the only renewable source of aromatics available in large quantities, this means that some of the most widely used commodity chemicals we know today – Benzen, Toluene and Xylenen – BTX can only be produced from lignin. As can be seen in the figure (on the next page), from these 3 commodity chemicals there is a wide range of possibilities. All using current chemical industry machinery making the complete substitution for oil a possibility (Gosselink 2011, pp 29)
Figure 43- Petroleum production routes (Gosselink, 2011)
Oil will still have to last quite some years to come as at current technology levels this is still impossible. There are still multiple barriers to be taken before lignin can actually be converted in BTX and serve as substitution product for input into today’s oil refineries. According to Holladay et al. (2007, p 22 – 30) the prospects are not bad and this should be easier achievable than the conversion of lignin into various lignin monomers for which lignin has to be depolymerized in specific ways.

The expected way to produce BTX is through aggressive catalytic reactions combined with some other treatments will make it possible to introduce it into current catalytic reforming chemistry processes. Besides this option there already is a process in place that used lignin from paper mills to produce vanillin by catalysis & selective oxidation. (Holladay et al., 2007, p 22 – 30)

Lignin Direct use

Since lignin has already been a long time side product from paper mills various uses for it have already been developed and been in use for some time. These sometimes involve chemistry and sometimes they use pure lignin to blend with other materials. For now a short overview of some of the possibilities (Ragauskas, 2012):

- Concrete additive
Low levels of lignin can be added to concrete mixture to provide added strength and better moisture and acid resistances.

- Thermal protection
Adding lignin provides thermal protection to various polymers and rubbers.

- Asphalt
Adding specific lignin mixture can have positive effects on asphalt production flows, handling and properties. These combined not only improve the product but also reduce costs.

- Binder
Lignin can already be used as a binder for wood boards, instead of using fossil glues lignin can be an renewable substitute (at the moment usually still in conjunction with fossil plastics). Another binding application is the use of lignin together with fertilizers which will also provide better soil water retention.

- Dust control

Specific lignin forms can together with water provide dust control, this can be especially useful in e.g. mines, coal transports but also for reducing nuclear particle spread after an nuclear explosion/meltdown.

- Batteries

Adding Lignin to batteries improves their function and capabilities and preverent formation of inhibitors. Milczarek et al. (2012, pp 1468 - 1471) recently have developed a renewable cathode based upon lignin capable of storing energy in a renewable battery.

**Energy & Lignin Fuels**

Lignin can be used for various energy generation purposes but also as an additive to fuels or pellets to enhance properties (Ragauskas, 2012). The most widely used way for it to generate energy is to simply use it as a fuel for combustion or gasification engines (see energy section). This makes sense as Lignin has one of the highest natural energy contents. It does however not add a lot of value. (Gosselink, 2011, pp 145-146)

More value is added by converting lignin into fuels for cars, currently there is a lot of research going on into making lignin a suitable feedstock for car fuels. Some of the research focuses on producing improved diesel (additives) from lignin with improved soothing capabilities (personal communication, M. Boot TU/e). There is also other research utilizing lignin as a high octane fuel additive (Shabtai et al., 1999) These processes are more complicated but also capable adding more value and are especially of interest due to legal changes in the European union limiting the use of 1st generation biomass making the production of diesel additives from 2nd generation biomass more likely to be taken up (Neslen, 2012).
5.6 Fatty acids & fuels

There are 2 important tracks for using fatty acids from plants in order to produce fuels. The first one is based upon first generation biomass in which plants with high oil contents are transformed in bio-diesel. The second option is the use of algae to almost directly produce an bio-oil stream or usable fatty acid stream. The first option has already been implemented on a commercial level while the for the algae option mostly pilot plants are in operation. Due to their higher yields algae are very promising. In this section first a short overview of the processes for transforming 1st generation plants in fatty acids and subsequently into usable fuels. Followed by a overview and comparison of the 1st generation vs. the algae option.

Fatty acid fuels

Fatty acids or the oil part of the plant can be used to produce various products. Currently the most well know product is bio-diesel which is made by trans esterification of vegetable oils. These are not necessarily from biomass they can also come from waste, e.g. used frying oil. The from biomass originating oils are produced from plants with a high oil content, one of the most used plants in Europe is Rapeseed but also plants like Jathropa, Palm and Soybean oil are often used. (Naik et al., 2010, pp 579 – 584) (Singh and Gu, 2010, pp 2597)

1st generation Ethanol
Besides biodiesel also ethanol can be produced from 1st generation biomass. For ethanol different plants with high starch/sugar contents are used instead of fatty acids. The processing is similar to the chemical production route but with 1st generation biomass as feedstock to directly supply sugars. Although there are differences between specific plants, most of the discussed negatives for bio-diesel can also be applied to ethanol production from 1st generation biomass. Because Ethanol is already widely discussed it is not receiving more attention here. (Naik et al., 2010, pp 579 – 584)
The oil fraction is usually imported in its liquid form to refineries in Europe (personal communication, Neste-Oil representatives) in these refineries the vegetable oils are transesterified into Bio-diesel with just one side stream: Glycerol. As can be seen in the chemical section there are various useful further processing paths for glycerol while the bio-diesel can be used directly in diesel engines (mixed with conventional diesel in low amounts (up to 5%)) or with adaptations when used in pure form (Escobar et al., 2009, pp 1277 – 1281)

*Algae vs. 1st generation biomass for fuel production*

Whereas both algae and 1st generation biomass can be used to produce biodiesels there are some differences between the 2 options:

<table>
<thead>
<tr>
<th>Algae</th>
<th>1st generation biomass</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aquatic (also brackish water)</td>
<td>Usually dry</td>
</tr>
<tr>
<td>Very high yields</td>
<td>Low to normal yields</td>
</tr>
<tr>
<td>Non arable land production possible</td>
<td>Competing with food crops</td>
</tr>
<tr>
<td>More expensive to produce</td>
<td>Cheaper to produce</td>
</tr>
<tr>
<td>Research stage</td>
<td>Industrial stage</td>
</tr>
<tr>
<td>Need for better harvesting methods</td>
<td>Conversion step necessary</td>
</tr>
<tr>
<td>Possibly direct production of biodiesel</td>
<td>CO2 Neutral</td>
</tr>
<tr>
<td>CO2 fixation</td>
<td></td>
</tr>
</tbody>
</table>

(Escobar et al., 2009, pp 1277 – 1281) . (Naik et al., 2010, pp 579 – 584) (Singh and Gu, 2010, pp 2597) (Khan et al., 2009)

Algae are typically grown in aquatic forms, there are various solutions present in current literature with the main difference on the level of encapsulation. The most common method is the production of Algae in an open e.g. the raceway pond, here the algae is produced outside and in big ponds with mixing machines for keeping an even mixture. This method is the cheapest but also has lower production and is less feasible for non-tropical climates. Furthermore there is the risk of contamination and lack of (bio) process control (Khan et al., 2009, pp 2369).
The other option is to produce the Algae in so called bioreactors, here the algae is encapsulated in tubes (various other forms and a variety of shapes are possible which will not be discussed here) allowing for optimization of processes and high amount of control but this also comes at high costs as closed bioreactor system can cost five to ten times more than open systems. Due to the higher production and better control the tendency is moving toward having the closed bioreactor as preferred method (Khan et al., 2009, pp 2369).

Algae their biggest problem is their high price; they are still expensive to produce and there is a lot of research going on in order to reduce this. One of the methods to reduce costs is by improving harvesting methods for algae, whereas this is well developed for normal crops for algae the process are due the aquatic nature very different and can still be optimized to prevent water & energy losses (Khan et al., 2009, pp 2371).

The biggest advantages for wanting to continue research in algae are their capabilities to directly produce high lipid contents but furthermore can also sequestrate CO2. They take more CO2 out of the environment than they produce. But probably the most important reason why algae are so interesting is their theoretically impressive higher yield than traditional crops. One of the highest yields for traditional crops are palm trees with yields up to 6000 L of oil per year whereas Algae can produce up to 10 – 20x more (Singh and Gu, 2010, pp 2597).

The combined positives of algae stimulate ideas to use algae as an improving refinery which produces biodiesel and other products and at the same time can provide energy and
sequestrate CO2. Before this is possible though there is still a lot of research necessary to improve species, reduce costs, energy and achieve economic feasibility for algae refineries. More research further goes into the use of algae for producing a wider variety of products. While some niche products are already produced today, bulk products are still far away and require a lot more research. Since still some basic processes for algae are not fully understood an discussion of these possible products falls outside the scope of this thesis. (Khan et al., 2009, pp 2371)

The production of biodiesel from 1st generation biomass has been well reviewed in academic literature and Escobar et al. (2009) or Naik et al. (2010) provide excellent reviews. It is a well-developed process but still has its drawbacks of which the indirect land use change factors are currently discussed in the European Union. Recently it has been decided that amount of 1st generation biomass to be used will be limited to 5% of the fuel supply, according to industry organisation this will severely hamper growth in this area (European Biodiesel Board, 2012). According to Escobar et al. (2009, 1279) for substituting 5% of the diesel supply by bio-diesel would already require 15% of available farmland in Europe. Algae have shown a lot higher production and could provide a solution providing fuels without using large amounts of farmlands but will need to reduce costs first. (Khan et al., 2009, pp 2366, 2371)

In short we have energy crops now which are capable of providing fuels and more but this comes at an (in)direct cost. Algae provide an good alternative but are more complex and still require more research before the alternative becomes feasible.
5. Model

Although it was possible to categorize and link all the possibilities in the model, this has not been done as it made it less understandable. Therefore the principle for the final model is simple: you move from the center outward to display the production chain. As this differs from whose standpoint you are looking it is possible to move back and forth to allow for intermediate products moving from one section to the other.

First a short discussion of the model contents, the model is available as a foldout on page 79.

6.2.1 Supply/Resources

For the supply of biomass materials there are 4 possibilities, here a short summary with description (for more information refer to the first chapter):

- Waste

For biobased production the organic waste can be utilized as a resource. According to the interviewees local laws and regulations make it harder to utilize waste as a resource. Despite regulations much of it is already used for specific purposes and research is ongoing to use more waste as a resource. (Pfaltzgraff et al., 2013, pp 1, Saakai et al, 2011, pp 87-90)

- 1st generation biomass

A lot of biomass is 1st generation; here the plants are grown for their biobased potential as a direct resource. Most plants that offer high contents of directly useable sugars or oil are grown in competition with plants grown for food and feed. (Havlik et al., 2011, pp 1) The biomass itself can still be imported or grown locally.

- 2nd generation biomass

2nd generation biomass offers potential for plants that can be used as a whole, every part of the plant is used. This lignocellulose process has been discussed in chapter 5.3. For
these streams agriculture offers waste flows and byproducts as a resource source. However these waste flows are often already used as a feed product. A lot of attention for 2nd generation biomass goes to plants that grow in quick cycles and on non-arable land. These could provide another source of biomass. These resource flows can still be grown locally or imported. (Havlik et al., 2011, pp 3-5)

- Algae
The previous options are all well known and have been used for long times. One of the newer resources - that still attracts vast amounts of R&D money – are algae. Algae are very tiny plants that usually grow in water. They can be grown on a molecular level (micro algae) or on a plant level (macro, algae). They have very high theoretical growth rates; this makes them a very interesting future resource for the biobased production. Despite the research algae are not yet suitable for commercial bulk production. There are some nice markets that gain attention but large quantity production still needs more research and development (Khan et al., 2009, pp 2366, 2371).

6.2.2 (Chemical & Mechanical) Pre-treatment
As identified by both the interviewees and the literature review generally biomass needs to be treated before it can be used for further production. The pre-treatment method is very dependent on the production which follows; still there sometimes is overlap and/or a wide variety of choices. Please refer to chapter 5.3 for an overview of pretreatment methods. Interviewees have indicated that cost is a major factor for choosing the pre-treatment method. This has lead to some methods being used more than others. On the other hand the chemical industry indicated that different methods are needed to produce resources more useable for the chemical industry.

6.2.3 Biobased Production
In the review the production possibilities have been shown, in the model they are summarized together. There are many possibilities and this should serve as a baseline where new possibilities can be added or obsolete entries can be removed. Please refer to the review for background information.
6.2.4 End user/consumer product examples

In order to show the complete link in the section some of the examples of end user products and/or intermediate products produced from biobased materials are shown here. Since the chemical industry produces long chains of various intermediate products the cycle from intermediate to end product is not completely shown as there will be relatively little change here. Some of the products produced directly from biomass do show their complete cycle if the amount of conversion steps is relatively low. (Erickson et al, 2012, pp 184-185)

The model is attached in a3 format to allow for easy viewing. Electronic reader can find it here: http://bit.ly/12baNEW
7. Placing the model into context: South-Holland

In this chapter the reviewed possibilities and pathways will be put into context. This has been done by doing qualitative interviews with various leading companies. A mix of companies from different industries has been selected. The selection was based on their size and possibility for interviews. In the following section the interviews will be analyzed providing the main thoughts in a summary format. This will be followed by an adjustment of the developed biobased utilization model to the industries and actors in South-Holland. This applied model will use the previously reviewed production possibilities, interview conclusions and statistical data.

7.1 Interview analysis

For this study various interviews have been done to identify which subjects are important for companies in the South-Holland (and surroundings) area are important for the further development of the Biobased Economy. From these interviews a fragmented vision comes forward from 2 distinct market groups: local & international companies. The only linkages were found in R&D projects and the Energy sector which is mostly locally focused but still buys biomass on international levels.

Because of this fragmentation the review of the interviews will be split in 2 sections, an international and a national one. In each section an overview of the main topics discussed during the interviews will be given and discussed along the lines of vision on the biobased economy and production possibilities. For some actors legal & policy issues were of major importance and have been discussed as well, the important parts of these discussions will be reviewed as well.
Locally focused actors

The actors with a strong focus on regional and national processes were

- van Vliet (waste management company)
- Delta Milieu (waste management company)
- LTO North (Agrarian association)
- Cosun (Sugarbeet processing cooperation)
- Eneco (Energy supplier)

Vision

Those actors all saw chances in the biobased economy; especially further valuation of residual and waste streams was deemed attractive. They judged closing the cycle with valorisation through the chain as important. Both the agrarians and the waste management companies see chances to create extra value in a biobased economy. The waste management companies are less determined and also see risks attached as they might lose various waste streams. They are now working more towards having a central role in the reverse logistics chain. Competition is becoming higher and higher because of the interest of energy plant operators as well as diminishing streams because of recycling at plant locations.

Other examples of increased competition can be seen on the supply side, agrarian parties see chances in utilizing their residual flows as feedstock for the chemical industry. The agrarians nor their corporations have the intent to start producing chemical products themselves, if the chemical industry needs specific agricultural products they expect to be asked for it. They also think that a large increase of biomass supply from the Netherlands is very difficult to achieve. We already have high yields and because of the rising food demands it is almost impossible to also grow for chemistry and energy purposes. This is only possible through the use of waste flows, 2nd harvests and cover crops that are grown to maintain soil quality. According to Eneco this makes the food vs. fuel discussion not
applicable in Holland, the increased revenues and valuation of waste streams is necessary to create extra income.

**Production**

Almost all the parties have installations to generate energy from biomass, differencing from Anaerobic Digestion installation using manure at farmers to the big bio energy plants are the energy suppliers. The energy supply from biomass however is very subsidy dependant, a lot of the small anaerobic digestion installations are going bankrupt because of lower electricity price (not taken into account in the subsidy program), lack of opportunities for (waste)digestate and high prices for streams that can be used as co-digestion substrate. For the bigger plants it is mostly the high price of pellets that can be used for co-combustion in coal plants.

One of the only companies already active in biobased production is Cosun, their products are made directly from their own waste streams. These waste streams which stay behind after they have made sugar from sugar beets can be converted into molasses which can serve as a feedstock for the chemical industry. But they have also started producing some products that can easily be made from their waste materials like plasticizers and micro fibres. The only problem they have is the high dependence on transport distance, at a long distance there is no margin left.

*International focused actors*

Interviewed actors with a more international focus are Sabic, British Petroleum (BP), Archer Daniels Midland (ADM), DSM and Neste Oil. All of these are multinationals with revenues in the scales of multiple billions a year. Because of this scale these parties have a lot more focus on the international levels. The same set up as for the local parties is used; a short discussion of their vision and thoughts on production in regard to the biobased economy.
Vision

From the multinationals especially the fuel producing companies have a lot more focus on legal issues, especially on the European Union level. The laws in regard to biofuels are very important. The chemical companies are less interested in the legal issues and are looking more for the impact and possibilities of the biobased economy on their business.

DSM and Sabic both see the biobased economy as a growth market, joining the developments is a necessity to survive in the future. Oil will run out and Sabic must have alternatives for their business. They both expect high growth for the lignocellulose developments but also much is expected from using molecules directly from plants without all the conversion steps. This is a lot more efficient than breaking everything up and reconstructing it in our existing infrastructure; this is more for the longer term though as developments go slow in this area. DSM sees itself as supplier of the processes necessary for the biomass treatment and conversion steps, their years of expertise with enzymes and microorganisms provide them with a good position in this market.

The fuel producing companies like Neste Oil, BP and ADM have big differences; BP is still mainly focused on producing fuels from petroleum and buys its biofuels on the market while Neste Oil and ADM are big biofuel producers. The drive for biofuels is coming very strongly from the European directives; biodiesel is still more expensive than regular diesel so only because of legal obligations is their business case feasible. Because ADM also has a strong position in the feed market and they see growth happening here as well they have their doubts about the 10% in 2020 target. The need for more feed will increase even harder because of the growing welfare in developing and industrial countries making it hard to also have competing biofuels.
Production

For the production of biofuels massive flows of feedstock are necessary, at the moment these mainly consist of vegetable oil streams. Neste Oil for example needs about 1 million ton of oil per year. Because of the size of these streams it is hard to buy these on the Dutch market and most of it is imported from abroad. The chemical companies do indicate that they are interested in the Dutch possibilities but it is hard to get a good price combined with consistent quality and delivery.

Some of the products that the companies have indicated as having their interest are:

- Grass
- Fatty acids
- Algae
- Succinic acid
- PLA
- Sugars
- Iso-butanol
- Polyamides

Besides this the expectation is that lignocellulose feedstock will be the resource of the future. But both Sabic and Cosun (local actor) have indicated that direct molecular farming is even better but a more long term pathway. Because of the low amount of residual flows often even still with high values these companies are not really interested in producing their own bio-energy. Price of the feedstock will remain the critical mechanism for buying, subsidies are not really important.
7.2 **South-Holland and the model**

Using the data gathered during the interviews current actors and processes can be placed into the model. There are actors present for all the different biomass flows. The different possibilities have all been placed in the model; please see the next page for the overview. Looking at the model the following is noticeable:

- **Resources**
  South-Holland has various options for acquiring biomass resources both locally and good importing qualities.

- **Mechanical (pre)treatment**
  This is done by various companies in South-Holland with a focus on waste focussed companies.

- **Chemical (pre)treatment**
  This seems to be an active sector in the region as the model is filled with various actors involved in chemical biomass treatment activities.

- **Biobased production**
  Here there are mostly the waste focused companies and an energy supplier with their combustion and biogas activities.

- **Products**
  Some of the previously identified products are produced in South-Holland, but less than 35% of the identified possibilities.

It can be seen that there is biobased activity in South-Holland but mostly centred around energy and R&D activities. Already the full chain from resource to product is present in the region allowing other developments to build on existing knowledge and infrastructure. (Interviews chapter 7)

8. Discussion & conclusion

The construction of this model and the review of production chains that went hand in hand has continued on some very good starting points made by Werpy et al. (2004) and Patel et al. (2006). Hopefully this research will be able to help set up the new supply routes of the future. Analogues to the transformation society underwent with the introduction of oil. (Murphy and Hall, 2010, pp 1)(Fouquet, 2010, pp 6595)

In this thesis a start was made by exploring pathways for production of fuels, energy and materials/products from biobased resources. The limits to the availability of those resources has been shortly discussed but was not a point of focus in this thesis. Future developments like algae have been discussed and show the possibility to develop high output bioreactors. The review of the several pathways has shown a large number of possibilities for producing not only energy but also (chemical) products we have gotten used to from biobased resources.

By constructing a graphical representation, a model, of the possibilities it is possible to map and expand our current state of progress. The model has been applied to one of the provinces in the Netherland, South Holland and has shown a province already in the biobased transformation.

As shown in the thesis there are several key components for the biobased production, one of them: Sugar can become the new oil. It has the potential to serve as a key resource for a wide variety of products. Counter to this development is the direct use of molecules in plants for products, this would be a less centralized development but would allow high efficiencies in the transformation of biomass to products and energy.
The developed biomass utilization model could be developed further, key focus points could be:

- Expanding the model
  This model is dependent on being as complete as possible, adding more information would be key for further usage.
- Adding a ranking system allowing for comparison of regions and etc.
  When the utilization is combined with a ranking system the model could be expanded to allow for ranking of regions, companies and countries.
- Developing a system for classifying actors in the model
  Currently the model is lacking a set of criteria to indicate actor placement, the qualitative interviews have provided actors but not yet a list of criteria that can be used more widely.

Critical notes can be put forward as this thesis is far from complete and more and more technologies and processes are developed to use biomass as a resource. I hope that by providing a continuation of previous work this model can serve as start for continued research. Furthermore the recent popularity of shale gas has not been taken into account in this thesis and research is needed to assess the long term impact shale gas can have. Overall more research in a systems approach towards the pathways of the future is necessary combined with a translation of research into product development. This would allow increasing our knowledge and at the same time serve as a boost in the development of new pathways.
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