CHALMERS

Renewable Ethylene

A Review of Options for Renewable Steam Cracker Feedstocks

Master of Science Thesis in the Master Degree Programme Innovative and Sustainable Chemical Engineering

SOFIE MARTON

Department of Chemical and Biological Engineering
Division of Chemical Engineering
CHALMERS UNIVERSITY OF TECHNOLOGY
Gothenburg, Sweden, 2013

Renewable Ethylene

A Review of Options for Renewable Steam Cracker Feedstocks

SOFIE MARTON

Department of Chemical and Biological Engineering

CHALMERS UNIVERSITY OF TECHNOLOGY

Gothenburg, Sweden 2013

Renewable Ethylene

A Review of Options for Renewable Steam Cracker Feedstocks

SOFIE MARTON

Department of Chemical and Biological Engineering
Chalmers University of Technology
SE-412 96 Göteborg
Sweden
Telephone + 46 (0)31-772 1000

Gothenburg, Sweden 2013

Abstract

As the environmental impact of fossil fuels increases it is more important than ever to find renewable alternatives. This thesis gives a literature review for the options for renewable ethylene. Ethylene is a chemical produced in large scale and there are a lot of steam cracker plants that produce it and a drop-in method is suggested. A drop-in method means that the ethylene plant already available should be used with changed feedstock. Pyrolysis of lignin with formic acid and methanol is suggested to fit with the existing infrastructure of the ethylene plants. This method gives 30-35% aliphatic hydrocarbons which makes the bio-oil similar to the naphtha used in steam cracker plants. The pyrolysis could be placed at an existing pulp mill with the hope of extracting methanol and formic acid from the existing process. Then the oil can be deoxygenated at a steam cracker plant where hydrogen gas is available.

Sammanfattning

Påverkan på miljön från fossila bränslen och material fortsätter att öka. Det är därför viktagre än någonsin att hitta förnybara alternativ. Det här examensarbetet ger en litterturöversikt över alternativen för förnybar eten. Eten är en kemikalie som tillverkas i stor skala över hela världen och det finns redan många krackeranläggningar. Därför föreslås en drop-in-process som lösning. Med drop-in menas att existerande utrustning används, men materialströmmen in i anläggningen ändras. Pyrolys av lignin med metansyra och metanol föreslås användas för att ge förnybar råvara till en existerande krackeranläggning. Metoden ger 30-35% alifatiska kolväten vilket gör bio-oljan lik naftan som används som råvara i krackeranläggningar idag. Pyrolysen kan placeras vid ett befintligt massabruk för att förhoppningsvis kunna använda metanol och metansyra från den existerande massaprocessen. Bio-oljan kan sedan hydrodeoxygeneras på krackeranläggningen där överskott av vätgas finns tillgänligt.

Preface

This master thesis is a part of a project to investigate options of renewable ethylene. The originator of this project is Borealis AB in Stenungsund and the work is conducted at the Chemical Engineering department at Lund University. This thesis studies the options for using renewable feedstock in an existing steam cracker plant, which Borealis has in Stenungsund. Borealis uses this ethylene to make polyethylene of both low and high density. Representing the forest industry, Holmen Paper AB, have been involved in the project as well. One of the aims is to find possible ways that can combine the forest industry and the petrochemical industry in the production of renewable ethylene.

A big thank you to the following people for helping me with my master thesis.

Fredric Bauer, Lund University
Christian Hulteberg, Lund University
Derek Creaser, Chalmers University of Technology
Lars Pettersson, Borealis AB
Jörg Brücher, Holmen AB

TABLE OF CONTENTS

1 INTRODUCTION

The worlds' oil demand keeps increasing and in 2014 the demand is expected to be 93 million barrels per day. Of these, about one third is in America and one third in Asia/Pacific. Europe is also a large consumer of oil with an expected oil demand of 14.8 million barrels per day. The increase in oil demand is calculated to continue although the oil efficiency is also increasing. (1)

The oil consumption is contributing to the global warming and therefore it is important to find options for fossil oil. Although the largest part of the oil is used for fuel, the chemical industry is a more difficult market to replace. Fuels used for energy can be replaced not only by biofuels but with renewable energy like wind, water and sun. Chemicals on the other hand, must be replaced by some kind of biomass.(2)

Ethylene is an intermediate chemical produced in large scale all over the world. It is important in the chemical industry since it is the base for many different products. However, 1 kg of ethylene gives 1-1.6 kg of CO_2.(3) It is therefore of great interest to find a renewable way to produce ethylene.

This thesis aims to investigate the options for renewable ethylene. Both what biomass that is suitable and how the biomass should be processed should be investigated. There are already large investments made in steam cracker plants. Therefore this thesis will focus on replacing the feedstocks of existing plants, instead of finding new process paths of ethylene production. This will lead to a suggested biomass process to further investigate for future production of ethylene.

The following sections will state the problem and limitation of this thesis. The method used will also be described.

1.1 PROBLEM

- What are the requirements for the feedstock for an existing thermal cracker plant for the production of ethylene?
- Which renewable feedstock is suitable for production of ethylene using existing infrastructure?
- How can they be integrated with the existing infrastructure?
- What pretreatment is required for the new feedstock?

1.2 LIMITATIONS

- The feedstock cannot be in direct competition with the food industry.
- Downstream effects of new bio-based raw materials on the plant should not be investigated in detail.
- Only a few raw material and process options should be selected to be investigated in detail

1.3 METHOD

The main method is a literature study. To find a suitable way to produce renewable ethylene a literature overview will be done. First an overview of the existing ethylene production will be made. The search will start wide, investigating possibilities with available literature of biomass processing. Some of the options will be selected to be studied and discussed to a greater extent. Both different kinds of biomass and processes should be considered.

2 CURRENT SITUATION

To be able to change the production of ethylene to a renewable process, the current production must be investigated. This chapter describes the current use and production of ethylene.

2.1 PRODUCTION OF ETHYLENE

Ethylene is a chemical produced in large scale all over the world. In 2008 the production capacity of ethylene was about 120 million tonnes per year with 29.9% produced in the North America and 29% in Europe. Other regions with large production are the Far East with 25.1% and the Middle East with 8.7%. In the Middle East and in China the production of ethylene is growing fast. (4)

It is a reactive intermediate chemical used as a building block for different chemicals, commonly production of plastic. The plastic is mostly polyethylene of both low and high density which is made from polymerization of ethylene. Polymerization of ethylene is an exothermic reaction done under high pressure and with the use of different catalysts. Other uses of ethylene are for production of 1,2-dichloroethane, styrene and acetaldehyde. The uses of ethylene are listed in Table 1.(3–5)

Table 1 Table of the most common uses of ethylene (5)

Uses of ethylene	
High density polyethylene	26 %
Low density polyethylene	18 %
Linear low density polyethylene	14 %
Ethylene dichloride	14 %
Ethylene oxide/ Ethylene glycol	12 %
Others	16 %

2.2 THERMAL CRACKING

The most common way to produce ethylene today is by thermal cracking from petroleum-based feedstock, but there are many pathways of producing ethylene (3). Other than thermal cracking, catalytic cracking is also an industrial method. However, the main product of catalytic cracking is propylene with ethylene as a minor product.(4) There are exceptions from petroleum-based ethylene. A plant in Brazil, which produces renewable ethylene via ethanol, was the first to produce green polyethylene in 2007(6). However, that path requires a totally new plant and cannot use the existing infrastructures of the existing cracker plants.

The process of thermal steam cracking to produce ethylene has the same principles as when it was developed in the 1960's. The raw material is heated to high temperatures, first to 500-650˚C and then to 750-875˚C. It is heated in two steps and the first heating step can use energy from the flue gas. The hydrocarbons are then cracked to ethylene and other smaller molecules. The decomposition of the molecules is an endothermic reaction, which requires a lot of heat. It is important that the stream of hydrocarbons is cooled rapidly to avoid unwanted side reactions, and the residence time is usually 0.1-0.5s. The stream is also mixed with steam since the lowering of the partial pressures for the hydrocarbons also lowers the reactivity. Thermal cracking is performed in fired tubular reactors in most plants.(3,4)

2.2.1 FEEDSTOCK IN THERMAL CRACKERS

The raw materials used in thermal crackers are hydrocarbons of different kinds. Both lighter feedstock like ethane, propane and butane and heavier like naphtha. The ethylene yield is higher for n-alkanes but branched alkanes, olefins, aromatics and napthenes can also be used. Hydrocarbons with an even number of carbon atoms give a higher yield of ethylene than odd-numbered. Which type of feedstock is used varies with price and availability over time and geographically. About 20 ppm of sulfur is added to the feed. This is to prevent coke gasification on the tube walls. (3)

Lighter feedstocks typically used in thermal crackers are ethane, propane and butane. Ethane gives the highest yield of ethylene but a low yield of propylene which is also a desirable olefin. It is a stable molecule that requires high cracking temperatures and the conversion is usually 60-75%. This is lower than for other feedstocks and a lot of ethane is recycled. For propane the conversion is 90-93% and for butane 94-96%. However, the yield of ethylene is lower for these feedstocks than for ethane. There is also a significant difference between n-butane and iso-butane in yield. The yield of ethylene for iso-butane is about 15% and for n-butane 40%.(3,4)

Another common feedstock is naphtha which has a lower yield of ethylene than the lighter feedstocks. Naphtha is a mixture of paraffins, olefins, napthenes and aromatics. It is a heavier feedstock with hydrocarbons of a boiling point in the range of 35-180°C. Naphtha can be divided into light naphtha (35-90°C), heavy naphtha (90-180°C) and full range naphtha. Full range naphtha is used in a large extent in Europe and Asia. The aromatic content of naphtha varies and a normal value could be between 3-15%. The quality of the naphtha increases with higher ratio of paraffins and lower ratio of aromatics. This is because the yield of ethylene decreases with the amount of aromatics, and straight hydrocarbons gives the highest ethylene yield. Why the ethylene yield is lower for aromatic structures is explained in section 2.2.2. (3–5)

Some of the specifications of the feedstock searched for in this thesis are presented in Table 1.

Table 1 Table of preferred content of feedstock.

Substance	Preferred quantity
H/C-ratio	High
O	None
S	Small amounts allowed (~20 ppm)
Other inorganics	None
Metals	None
Aliphatic/aromatic hydrocarbons	Aliphatic hydrocarbons preferred

2.2.2 CRACKING REACTIONS

The main reactions in the furnaces involve breakings of carbon-carbon bonds and carbon-hydrogen bonds. The simplest case is the reaction of ethane to ethylene, which is shown in

Figure 1. When the feedstocks become more complex, so do the reactions. There are several reactions and different products occurring in the cracker furnaces.(4)

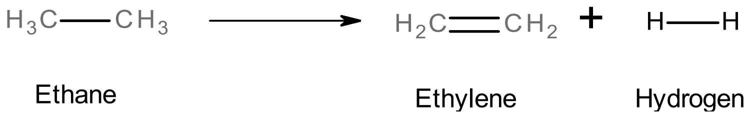

Figure 1Cracking of ethane to ethylene

Since the bonds that are broken in cracking are strong, the temperature needs to be high to be able to break them. However, at those high temperatures the elements are the favored product. That meaning that the free energy of the substances is positive. Therefore it is important to break the reaction as soon as possible with a rapid cooling, a so called quenching. This is since equilibrium is not favorable for this reaction. For ethane cracking the temperature needs to be at least 1000K. At 1000K the free energies for ethane and ethylene cross, and ethylene becomes more preferred. The same considerations need to be accounted for in cracking of different raw materials. That is why different raw materials are cracked in different furnaces. That way the conditions can be optimized for the specific feedstock.(4)

For larger carbon chains of paraffinic molecules, any of the carbon bounds can be broken. This means that for example, hexane can be cracked to C_1 and C_5, C_2 and C_4 or two C_3 molecules. There is a possibility that the carbon chain breaks more than one time, which increases the ethylene yield. However, aromatics are hard to break and benzene is more stable than ethylene. Which leads to that aromatic content lowers the ethylene production and increases the production of benzene. If there is an aromatic molecule with an alkyl group, the carbon bond to the group is likely to break, as well as the carbon bounds within the group. (4)

2.2.3 ETHYLENE PLANT OVERVIEW

After the furnaces, the stream is rapidly cooled. After that follows a long series of separation processes and different reactions to get as high content of ethylene as possible in the product. For the ethylene to be able to polymerize, the ethylene content must be at least 99.9%. An overview of some of the major process steps in an ethylene plant is shown in Figure 2. (3–5)

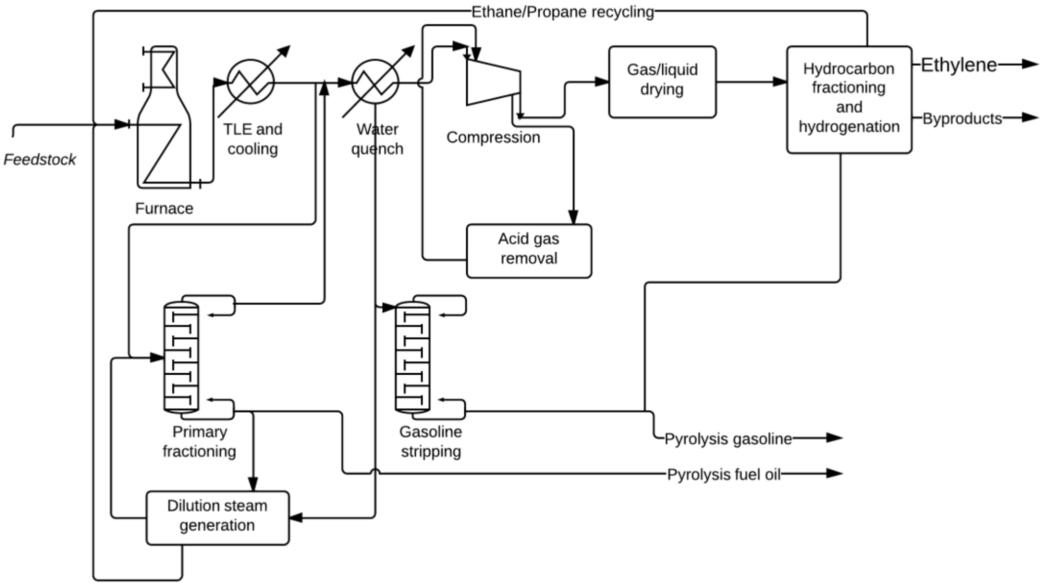

Figure 2 Overview of a typical ethylene steam cracker plant. (3)(4)

The production of ethylene generates 1-1.6 kg carbon dioxide for every kg of ethylene produced, with the amount of carbon dioxide varying for different raw materials. (3) It is therefore of great interest to find other feedstocks to produce ethylene with green carbon dioxide emissions. A transition is necessary not only because of the environmental effects of fossil fuels but also because it is a limited resource. It is hard to predict for how long it will be available and how the price of oil will develop.

3 OVERVIEW OF RENEWABLE ETHYLENE OPTIONS

There are many different pathways possible to investigate for production of renewable ethylene. It is important to look at several options since there are several factors that are not clear. Many processes are in research stage and which will be most successful is hard to predict. Also, the future market of biomass is uncertain since the demand of biomass likely will increase with increasing oil prices.

First of all there are several options considering the biomass. It should preferably be cheap, easily processed and available in large quantities. However, it is difficult to find a biomass that fulfills all these criteria and a compromise has to be made. Due to the ethical point of view the raw material should not be in competition with the food industry.

For every available biomass there are several options for processing the biomass. This vastly increases the total number of options. However, every kind of biomass and process brings new challenges since they differ from the current feedstock used in cracker plants. Naphtha from fossil fuels is very clean compared to biomass which consists of more complex chemical structures. Therefore a lot of the methods of converting biomass can be easily rejected due to impurities.

In this project, an overview of options for renewable ethylene is made. As stated above the theoretical options for producing renewable ethylene are many. However, there are only a limited number of ways available at this point. Of these options, many are only in research phase and not commercially available yet. In this project those options are also interesting since it looks at a long term picture of producing renewable ethylene.

3.1 VEGETABLE OIL CRACKING

Since the current steam cracker feedstock consists of mostly straight hydrocarbon chains a natural substitute would be vegetable oils.(7) Fatty acids consist of a straight hydrocarbon chains which are very similar to the feedstocks from crude oil. The main difference is that fatty acids have a carboxyl group that binds to a glycerol molecule. Three fatty acids and one glycerol molecule makes one fat molecule. The aim of the method is to thermally crack the oils to make it more suitable for chemical and fuel production which shows promising results.(7,8)

Although vegetable oil cracking shows great benefits, this method is not an option for this project. That is because it is in competition with the food industry. Because of the ethical point of view one of the limitations of this project is that the biomass used should not be in direct competition with the food industry.

3.2 BIO-SYNFIED NAPHTHA CRACKING

The idea of making ethylene from bio-synfied naphta is to use waste fats. The fatty acids are catalytically converted to renewable naphtha and high quality diesel or jet fuel. The renewable naphtha contains high amounts of paraffins, 92.6wt%. It consists both of iso-paraffins and n-paraffins. The rest of the bio-oil is naphthenics, olefinics and a small amount of aromatics. It is a feedstock similar and in line with the current cracker feedstock. One of the most positive factors of this naphtha is the low content of oxygen which is wanted in the cracker plants. Studies show that this feedstock gives high yields of olefin, when used in a thermal cracker plant. (9,10)

Although this method shows great results the problem lies in the raw material. Fats of different kinds are in competition with the food industry and not included in the scope of this project. This is because of ethical reasons. The method is an option only if waste fats are used and if they are available in large amounts.

3.3 TALL OIL CRACKING

Tall oil of different kinds are already commercially available and are already used for different products like bio-diesel. It comes from the extractives from wood and is a by-product from pulping process. Tall oil fatty acids and distilled tall oil can both be used to obtain cracker feedstock. To remove as much oxygen as possible they need to be hydrodeoxygenated first.(11)

Cracking of hydrodeoxygenated tall oil have been studied in pilot scale with successful results. They give high yields of ethylene and propylene and can be used in existing steam cracker plants. It ought to be cracked in a separate furnace rather than to be co-cracked with naphtha. This is to be able to optimize each process separately and not need to compromise on operating conditions. Because of the different carbon range of tall oil and naphtha the optimal operating conditions vary considerably. (11)

Hydrodeoxygenated tall oil shows promising technical possibilities for working as a cracker feedstock. The problem lies in the demand of tall oil and the volumes available. There are only limited amounts of tall oil on the market and there are already different uses for the oil.

3.4 PYROLYSIS OIL UPGRADING

Pyrolysis is an old and well developed method. In the recent years, interest for renewable materials and fuels has made it an eagerly researched method. Fast pyrolysis can be applied to almost any kind of biomass. It is a thermal decomposition of the biomass without the presence of oxygen. It gives three phases; gas liquid and charcoal. The amounts of the different phases vary a lot with process conditions and types of biomass. Since it can be used for so many different kinds of biomass it can be applied to biomass that is considered waste. Studies have been made and shown high conversions to bio-oil from for example saw dust, agricultural waste, wood and lignin. (12–17)

3.5 GLYCEROL TO OLEFIN

Glycerol is an alcohol also known as propantriol. The amount of glycerol produced in the world is increasing. It is therefore an interesting raw material to investigate for conversion of higher value products. Conversion of glycerol to olefins has not been studied thoroughly. However, the process of converting other alcohols like methanol and ethanol to olefins has been studied in more detail. Those methods could give a basic understanding of the possible reaction pathways for glycerol, since the reactions ought to be similar.(18)

There are two possible pathways to make olefins from glycerol. The first is to first convert the glycerol to syngas and then to olefins. The second option is a catalytic transformation directly to olefins.(18) The use of glycerol conversion to olefins is until now unclear, and very little research has been made on the method. It is outside of the scope of this project since it is a totally new process, which does not use the existing cracker plant.

3.6 METHANOL TO OLEFIN

Methanol to olefins is a process of great interest. Since the possibilities of methane from decomposed biomass are increasing, the possibilities of methanol increase as well. Methanol can be obtained from methane conversion via syngas. The methanol can then be reacted to dimethyl-ether (DME). The dimethyl-ether can be converted to light olefins in a fluidized or fixed bed reactor. (19–23)

This method offers a possibility of producing renewable ethylene because of the increasing interest in methanol. It is nonetheless not in the scope of this project since it require a new process and not renewable feedstock to an existing process.

4 RENEWABLE MATERIALS FROM FOREST RESIDUES

This chapter is used to describe wood as a potential raw material, how wood is used today and to explain the different biomolecules present in wood.

4.1 WOOD AS A RAW MATERIAL

Today wood is used for several different purposes. If new forest is planted to replace the harvested wood, it could be considered a carbon dioxide neutral raw material. The main use is as fuel in developing countries but a large part is also used for industrial wood. The industrial use of wood is more common in developed countries. Of the industrial wood several product chains can be described. Those include wood products, paper, energy and wood based chemicals. The chain of wood products includes furniture, sawn lumber and house elements. Pulp production and recycling of paper is included in the paper product chain. The energy chain contains lignin and wood waste. With wood-based chemicals means ethanol, lignin products, cellulose products and more.(24)

The forest industry in Sweden is a large part of the economy. It contributes to 15% of the total Swedish export. In a European perspective the forest industry is also important. Of the total manufacturing industry in Europe, the pulp and paper accounts for 8% of the total value.(24) Since it is a large part of the both Swedish and European industry it is important that it follows the development of new materials and the industry has several challenges for the future. One of these challenges is to find green chemicals, green energy and biofuels.(24) A collaboration with the petrochemical industry is one way of developing green chemicals.

4.2 WOOD CHEMISTRY

Wood has a complex structure of different fibers and varies among species. The most abundant biomolecules in wood are cellulose, hemicellulose and lignin. Wood also contains other chemicals like extractives and other carbohydrates. Generally, wood can be divided into two kinds of trees; softwood or hardwood trees. Softwoods are mainly pine and spruce. In Scandinavia there are great amounts of softwood trees like Norway Spruce. The properties of different trees are shown in Table 2.(24,25)

Table 2 The table shows the properties of some common species of trees in wt%.(24)

	Cellulose	**Hemicellulose**	**Lignin**	**Extractives**
Hardwoods				
Birch	41.0	29.8	22.0	3.2
Beech	39.4	29.1	24.8	1.2
Softwoods				
Norway Spruce	41.7	24.9	27.4	1.7
Scots Pine	40.0	24.9	27.7	3.5

One of the biggest differences between softwood and hardwood is the fibers in the stem. In softwood, the fibers are longer than in hardwood. Therefore, softwood gives higher pulp quality. Also, in hardwood pulp there are often a lot of different species mixed which lowers the pulp quality. Hardwood trees are more common in tropical and sub-tropical countries whereas softwood trees are more common in Scandinavia.(24,25)

As stated above, the most abundant biomolecules in wood are cellulose, hemicellulose and lignin. Cellulose is a large, linear chain of β-glucopyranoside monomers with the formula $(C_6H_{10}O_5)_n$. The main function of cellulose is as a mechanical fiber in the cell wall of the tree cells. It is also the main raw material in paper. Hemicellulose is a branched polymer built up by different monomers. The most common types of hemicellulose are xylan, glucomannan and galactans. Xylan is the most abundant hemicellulose in hardwood and glucomannan is most abundant in softwood.(24–26)

Lignin is a very complex bio-molecule polymer, and the oxygen content is lower than in cellulose and hemicellulose. It is branched and has a three dimensional, web like structure. The monomers are different kinds of phenylpropanes. The basic phenylpropane structure is shown in Figure 3, where the groups Q and Q* varies. The main use of lignin is for energy in pulp mills since lignin is unwanted in the pulp. The energy is used to regenerate the cooking chemicals amongst other uses.(24) Recently several ways to extract lignin from the black liquor have been developed. (27)

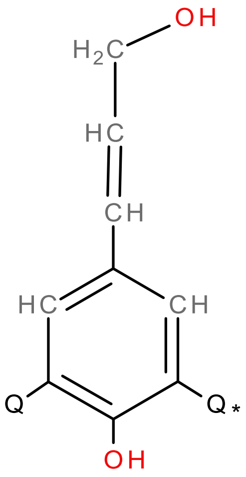

Figure 3. Shows the basic building blocks of lignin.(24–26)

5 CRACKER FEEDSTOCK BY PYROLYSIS

To convert biomass to cracker feedstock, the biomass must be processed in several steps. How these are done varies for different kinds of biomass but it can generally be divided into three parts. This is shown in Figure 4. The figure shows the process of treating biomass in three major steps. These steps vary of course for different processes and all three are not always necessary.

Figure 4. The figure shows the process of treating biomass in three major steps.

The first step is the pretreatment of the biomass. The pretreatment is the breakdown of the biomass to smaller particles. The size of the particles is important because of factors like heat transfer and reaction rate in the process. This first step might not be mechanical breakdown but could also involve separation of a desired product. For example it could be an existing waste stream at a process plant or separation of a specific molecule.

Secondly the larger, complex molecules present in biomass must be broken down into smaller molecules. Biomass contains large quantities of cellulose, hemicellulose and lignin which are too large to work as a cracker feedstock in an existing cracker plant. This could be done in different ways depending on the biomass, and depending on how many different biomolecules that are present. This step is not always necessary either, since some extractive chemicals already are in the right size.

In the third step the material needs to be purified. This is necessary prevent harm to the existing infrastructure and to avoid unwanted byproducts. The atomic composition of the ideal feedstock contains nothing more than carbon and hydrogen. For example oxygen is often present to a much larger extent than in existing cracker feedstock and must be removed. If there is a high concentration of aromatics, they might need to be modified to straight carbon chains to some degree.

One option for processing biomass is pyrolysis. It can be applied to most kinds of biomass which makes it a very flexible method. It has already been studied for over 100 kinds of biomass. This makes the pretreatment step very different depending on the kind of biomass. Since the product varies and can be adjusted, the finishing also varies considerably. The pyrolysis itself would work as step two shown in Figure 4. Pyrolysis is a well-known process that has been used for several years and it can be varied to give different products. Even though it has been used to make charcoal for several thousand years it is not until the last 30 years it has been done commercially. This is because it can now be done at reasonable operation conditions regarding time and temperature.(16)

5.1 FAST PYROLYSIS OF BIOMASS

The basic idea of pyrolysis is that the biomass is heated without the presence of oxygen for a short time. This makes the biomass' organic matrix thermally decompose. The process is very fast and it is important to stop at the right time to favor the desired products. Pyrolysis gives three different phases; charcoal, bio-oil and gas. In this case the interesting product is bio-oil. The process can be varied to give different amounts of the phases. Fast pyrolysis favors the liquid product the most and can give a yield of 75% liquid product. The liquid product contains both bio-oil and a water soluble part. For production of bio-oil a short residence time of about one second is preferred. A longer residence time favors the production of charcoal.(16,26,28)

The principles of fast pyrolysis reactions are very similar to the reaction of steam cracking. This is because cracking is a kind of pyrolysis. The goal is to break the carbon-carbon bounds to break down the large and complex biomolecules. This is done by increasing the temperature and making the molecules free energy positive.

How far the reaction is going is dependent on the temperature, residence time and the cooling rate.(16)

Fast pyrolysis of biomass gives different products depending on the biomass used but there are similarities in the products. The gas phase usually contains different amounts of carbon dioxide, carbon monoxide, methane, hydrogen, ethane and ethylene. Depending on the temperature and biomass the charcoal characteristics varies and it consists of different amounts of inorganic ashes. It also contains unchanged biomass and carbonaceous residues. The liquid product consists of two phases, one water phase and one organic phase. The organic is mostly a mixture of acids, aldehydes, alcohols, ketones, esters, phenolic compounds and heterocyclic derives. The different products and the fast pyrolysis process are shown schematically in Figure 5. (26)

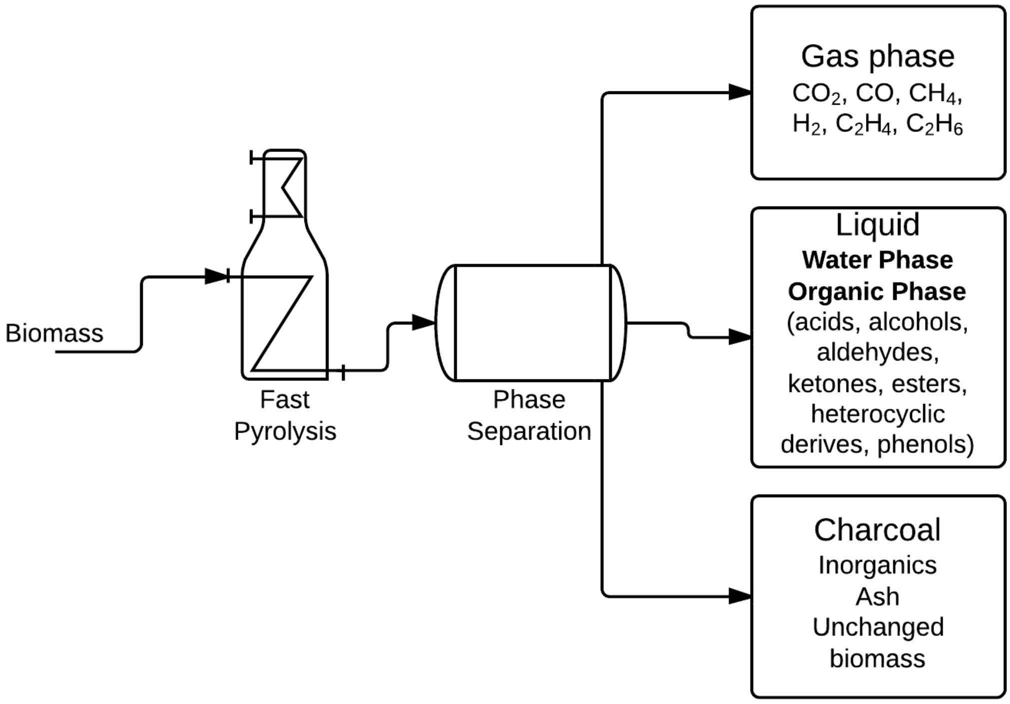

Figure 5 The figure shows the basic process blocks of fast pyrolysis

The bio-oil needs to be processed further to be adjusted to a suitable cracker feedstock. This is primarily to remove oxygen and to break down the high amount of aromatics. However, the need for a finishing process also varies. This is because the content of the bio-oil varies with both the pyrolysis process and the biomass used.

As stated above, pyrolysis has been studied to various degrees for different kinds of biomass. In this chapter, pyrolysis of raw material in the scope of the project will be explained. This meaning that the raw material does not compete with the food industry and is available in abundant quantities.

5.2 FAST PYROLYSIS OF LIGNIN

Studies of fast pyrolysis of lignin have been done for different kind of lignin. Both for lignin obtained by lignoboost and by CO_2 precipitated lignin from the pulp. (29–31) The results for the lignin from the lignoboost process show yields of more than 30 % bio-oil on dry weight basis. The composistion of the bio-oil from this process are shown in Table 2. It contains a lot of aromatics and a high amount of oxygen. For it to work as a cracker feedstock, the oxygen needs to be removed and the amount of aromatic structures needs to be lowered. Most of the aromatics are methoxyphenols.(29)

Table 2 Shows the composition of bio-oil from fast pyrolysis of lignin(29)

Bio-oil composition (wt%)	
Acids	2.71
Nonaromatic aldehydes	0.05
Nonaromatic ketones	0.19
Sugars	1.70
Benzenes	0.33
Cathecols	0.61
Lignin derived phenols	0.82
Methoxyphenols	25.64
Total	**32.15**

5.3 FAST PYROLYSIS OF AGRICULTURAL AND INDUSTRIAL WASTE

Since it is possible to use many different raw materials for fast pyrolysis, it is interesting to study biomass otherwise considered as waste. Fast pyrolysis of potato skin has shown to give bio-oil yields of more than 40% (32). Other waste that has been studied as raw material for fast pyrolysis is waste saw dust. It can come from different kinds of industries like saw mills and furniture industry. It gives high yields of liquid of up to 60%. This is however including the aqueous phase which is about 40-60% of the liquid. The organic part of the liquid, the bio-oil, contains a lot of different compounds and the oxygen content is high. The most abundant molecule in the bio-oil is acetic acid.(17,33,34)

5.4 PYROLYSIS OF LIGNIN WITH FORMIC ACID AND ALCOHOL

Since lignin only is used for energy in pulp mills it is a good raw material for witch to find other uses. Fast pyrolysis of lignin gives a product with lot of aromatics, high oxygen content and almost no aliphatic hydrocarbons. To lower the oxygen content hydrogen needs to be added somehow. If formic acid and an alcohol are added, it gives many benefits and formic acid works as both a reaction medium and hydrogen donor. The oxygen content is thereby decreased. Other benefits is that the amount of aliphatic hydrocarbons increases drastically and the amount of char is only 5%. This kind of process with pyrolysis of a solid substance in a reactive solution can be called solvolysis, liquefaction or alternative pyrolysis.(35–40)

The bio-oil produced from this process seems very promising because of its high conversion of oil and high content of aliphatic hydrocarbons. It gives 30-35% aliphatic hydrocarbons which is high considering the original structure of lignin.(39) These aliphatic hydrocarbons is in a large extant 2-methyl-heptane and 2-methyl-nonane.(35) 2-methyl-heptane has a boiling temperature of 118˚C and 2-methyl-nonane has a boiling temperature of 167˚C.(41) The other part of the bio-oil consists of phenols of different kinds. The main kinds of products from the process are shown in Figure 6. Another advantage of this process is that most of inorganics are in the water of the liquid phase. This makes the content of inorganics in the bio-oil very low.(35)

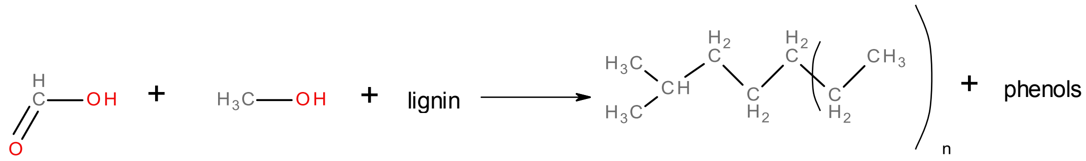

Figure 6 The figure shows the main kind of products produced in the solvolysis

Why this process differs from pyrolysis without lignin is not yet well researched. However, there are theories supported by some research. Since no formic acid is found in the product, all formic acid must react in the pyrolysis process. The degradation of formic acid can go two ways, either to H_2 and CO_2 or to H_2O and

CO. The most likely is that it goes both ways considering all gases are found in the gaseous product. It is the hydrogen content, in combination with the relatively high temperature, which is believed to prevent the lignin from re-polymerizing. It is also believed to be the reason for the low oxygen content of the bio-oil. The alcohol is also an important solvent and a variation of the alcohol used can be seen in the alkyl groups of the phenols, suggesting that the alcohol has a role as a reactant.(37)

For this process, different kinds of alcohol can be used. C_1-C_4 alcohols work for this process, although most studies are done with ethanol. This is because it is designed to fit in a total biorefinery concept where all parts of the wood is converted to fuel and ethanol is produced in the same plant.(35) However, this might not be the case for this study since lignin from an existing pulp mill is a promising option.

6 DISCUSSION AND CONCLUSION

Large scale production of ethylene is done all over the world from fossil raw materials. The long term future for this production is a challenge in a world with decreasing oil resources. Since fossil fuels affects the environment in a negative way and it is just a matter of time before the oil resources are exhausted, the transaction towards renewables needs to start. In the latest report from IPCC, they state that there is no time to wait.(42) If the use of renewables does not replace fossil fuels soon there will be no turning back climate change. This challenge is even bigger for production of fine chemicals than fuels and energy. For energy and fuels the options are more extensive, like energy from sun, water and wind.

There are already a lot of cracker plants adjusted for fossil feedstock which have large investment already made in them. They are often parts of large infrastructures of plants using the produced ethylene for production. Therefore it would be desirable to find a sustainable alternative that can be used in the existing plants. The feedstock should be as similar as possible to the existing ones but based on a renewable raw material. The current feedstocks used in ethylene production are naphtha, LPG, butane, propane and ethane. These feedstocks contain no, or very low, amount of inorganics except for sulfur. To not harm equipment in the existing steam cracker plants it is important that the new feedstocks have the same characteristics.

6.1 RENEWABLE MATERIAL

What biomass that should be used and how it should be processed is far from obvious. There are a lot of factors that are hard to predict, like oil price variations, demand of biofuels and global warming taxes. Regarding the technical aspects of renewable ethylene, there is no obvious answer what to use. This is because a lot of the processes are in a developing state and it is hard to predict which process will be successful. If the competition of certain renewable raw materials becomes tougher than others, those raw material prices will increase significantly. Also, which technical difficulties that will be solved in an energy efficient and cheap way, can only be estimated but never be certain.

The forest industry in Scandinavia is also in the need of change. They need to start to make more high value products to be able to compete with their products. It is also important to take advantage of all parts of the tree as renewable materials become more valuable. Lignin is a material often combusted for energy in pulp mills. Since the need for energy in the pulp mills is less then what the lignin gives, some of it might be used somewhere else. If needed, bark can also be combusted for energy instead of lignin.

Since lignin is an abundant part of trees and treated as a waste in pulp mills it is a promising starting raw material for a bio-oil. In recent years several methods to extract lignin have been developed. The need for renewable raw materials will increase and since lignin is available in large amounts it is a raw material worth further investigation. One important benefit of using forest residues as a raw material is that it does not compete with the food industry.

6.2 CHOICE OF PROCESS

Lignin is a very complex molecule but since pyrolysis is such a flexible method, pyrolysis is an option to convert lignin to more valuable products. Pyrolysis is flexible because it can work for different kinds of biomass and can handle variations of the lignin raw material. It is also a process that can break down large and complex molecules and is a well investigated method. Although pyrolysis is a well-known process, the knowledge of its use on biomass varies a lot for different biomasses and a lot of research is in process.

Fast pyrolysis of lignin without a solvent gives about 20-40% bio-oil and char up to 60% as pyrolysis product. The pyrolysis oil mostly consists of different aromatic rings.(27,29) These aromatics are not similar to current cracker feedstock and would need further processing to be able to be used as cracker feed. The oxygen content is also quite high and oxygen needs to be removed since it is not wanted in the steam cracker plant.

However, if you add formic acid and an alcohol to the pyrolysis, the result improves a lot. The char is only 5% and it gives a high amount of pyrolysis oil. Of the bio-oil, there are high amounts of aliphatic hydrocarbons. The total conversion gives 30-35% aliphatic hydrocarbons on a wet weight basis. Other benefits of this method include a low oxygen content and lower reaction temperature than other fast pyrolysis processes. Some downsides are that the residence time is quite long and the experiments are mostly done in batches. Nevertheless, continues experiments have been done, which gives a positive prospect of the development of the process.

The bio-oil obtained from the solvolysis should be made as similar to naphtha as possible. This is to make it possible to crack in existing cracker furnaces at steam cracker plants, without making any changes to the plant. If most of the phenols are separated from the bio-oil, a bio-oil containing mostly iso-paraffins is obtained. A small amount of phenols could be allowed since the naphtha used today contains some aromatics. The bio-oil also needs to be washed to make sure that no inorganics and other impurities are present. Finally any remaining oxygen needs to be removed. If this is possible, the bio-oil is very similar to heavy naphtha.

The main products in the final bio-oil product would have boiling temperatures of 118˚C to 167˚C, which is in the range of heavy naphtha. Cracking of heavy naphtha is well-known and the bio-oil should give similar cracking results. Since the naphtha already has some variation of its specifications, this bio-oil should give equally good results. The reactions of aliphatic hydrocarbons in the furnaces are breaking of carbon-carbon bounds and carbon-hydrogen bounds. Those reactions should be the same for the bio-oil but an optimization of residence time and temperature ought to be made. The products obtained should be both ethylene and propylene since the carbon bounds are as likely to break anywhere in the carbon chain. Although since the aliphatic hydrocarbons in the experiments have an equal number of carbon atoms, the ethylene yield ought to be high. The alkyl-phenols that might be left in the finished product are should not be a problem in smaller fractions, if they are first hydrodeoxygenated. It is likely that the alkyl groups will break from the aromatic ring in the cracking and benzene will also be a product.

6.3 SUGGESTED PROCESS

The proposed process to obtain this bio-oil consists of five different parts. The first one is the pyrolysis with formic acid and alcohol. Then there are several steps to separate chemicals and make the bio-oil clean enough to be suitable as cracker feedstock. The goal is to get bio-oil with very low oxygen content and straight hydrocarbon chains. The suggested process design is shown in Figure 7.

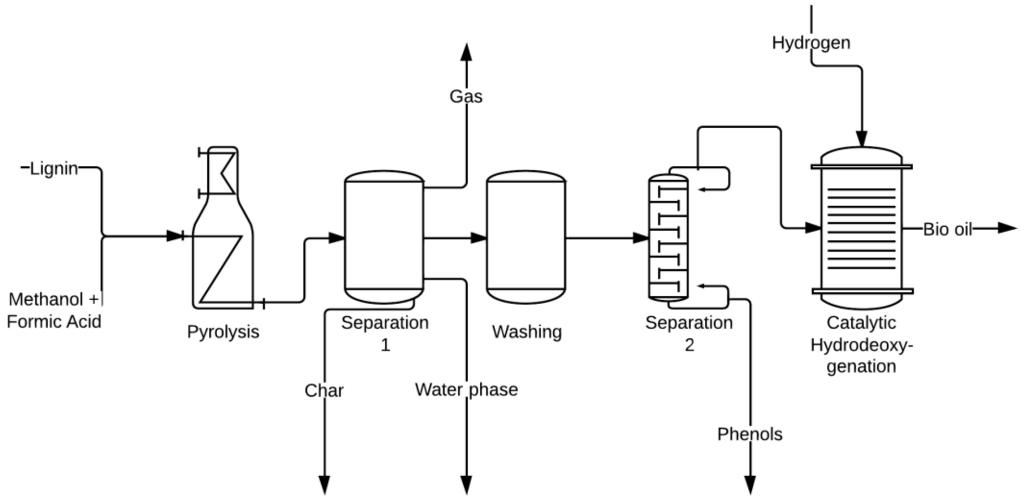

Figure 7 overview of the suggested process design

The solvolysis process is suggested to be placed at a current pulp mill where lignin can be separated from the process. Methanol and formic acid can hopefully be extracted from the existing pulp process, although it needs further investigation. The pulp contains about 10kg of methanol hydroxide for every ton of pulp and the black liquor contains about 10-20% formic acid salts depending on the wood used.[1]The idea is that the char and other waste streams can be used for energy in the pulp process and for heat in the solvolysis. The separation of different phases should be placed directly after the solvolysis, including separation of the aqueous and oil phase. To ensure that the inorganic content in the bio-oil is low a washing step is included in the process design.

Depending on the interest in phenols, the second separation step can be placed either at the pulp mill or at the cracker plant. If none of the plants are interested in the phenols, they can be combusted for energy at the pulp mill. To ensure that the oxygen content is as close to zero as possible, a catalytic hydrodeoxygenation step might be needed. This step is more convenient to have at the cracker plant because of the excess of hydrogen gas from the existing process. It is a process removing oxygen, by converting it to water with high pressure hydrogen. The pressure is usually up to 20 MPa and the temperature is up to 400˚C. (16)

---

[1] Jörg Brücher, Holmen AB

The oxygen content of the bio-oil mainly comes from the aromatic content of the oil. That leads to that the hydrogen gas needed is dependent on the aromatic content of the finished bio-oil product. If the bio-oil should be similar to existing naphtha feedstock used in cracker plant, an aromatic content of about 10% could be allowed. Calculations show that it theoretically would require about 1 kg of hydrogen gas to react with the oxygen to water, for every ton of bio-oil. However, in reality an excess of hydrogen would be needed. The calculations are shown in Appendix 1.

Since this solvolysis process only has been studied in laboratory scale it is not certain that the process will be the same in industrial scale. Factors like mass and heat transfer can play a larger part in the reactions. Also, it would be more feasible to have a continuous process, rather than batch. Some successful experiments on continues process have been made, which is positive for the future progress of this process.

6.4 CONCLUSION

To summarize the conclusion, the suggested process is the one that corresponds the most to the requirements of the project. The oxygen content of the bio-oil is low, although it needs to be lowered further, and the impurities in the bio-oil are considered low. There have been found no other processes that have the possibilities to give the same amount of aliphatic hydrocarbons as the solvolysis of lignin. Even though this process only is in research phase it seems very promising. Lignin is a good biomass to use since it is often considered waste in pulp mills and is only used for energy. It is beneficial for both the forest industry and the petrochemical industry to find this new use for lignin as a higher value product.

7 FUTURE WORK

There are a lot of possibilities for future work to continue this study. Some suggestions on future work are listed below.

- Do solvolysis experiments in larger scale. The method seems promising but needs to be tested and developed further. Size, residence time and possibilities of a continuous process could be further investigated.
- A deeper study on the process steps in the suggested process ought to be studied. Experiments of the entire process are a possible future work as well as further literature studies.
- A cost approximation to investigate the feasibility of the process. This should be done to see if it is worthwhile to continue the work at the present time. Although it is difficult to predict prices of biomass and fossil fuel, several outcomes can be studied.
- The cracking characteristics of the bio-oil can be simulated in Spyro Suit.

8 REFERENCES

1. IEA. Medium-Term Oil & gas Markets. Int. Energy Agency. Paris; 2011.

2. Vennestrøm PNR, Osmundsen CM, Christensen CH, Taarning E. Beyond petrochemicals: the renewable chemicals industry. Angew. Chem. Int. Ed. Engl. 2011 Nov 4;50(45):10502–9.

3. Zimmermann H, Walzl R. Ethylene. Ullmann's Encycl. Ind. Chem. Weinheim: Wiley-VCH Verlag GmbH & Co. KGaA; 2009. p. 465–529.

4. Seddon D. Petrochemical economics: Technology selection in a carbon constrained world. 8th ed. Hutchings GJ, editor. London: World Scientific; 2010.

5. Sundaram KM, Shreehan MM, Olszewski EF. Ethylene. Kirk-Othmer Encycl. Chem. Technol. New York: John Wiley & Sons, Inc.; 2010. p. 1–39.

6. Lundgren A, Hjertberg T. Ethylene from Renewable Resources. In: Kjellin M, Johansson I, editors. Surfactants from Renew. Resour. Chichester: John Wiley & Sons, Ltd; 2010. p. 111–26.

7. Zámostný P, Bělohlav Z, Šmidrkal J. Production of olefins via steam cracking of vegetable oils. Resour. Conserv. Recycl. 2012 Feb;59:47–51.

8. Sadrameli SM, Green AES. Systematics of renewable olefins from thermal cracking of canola oil. J. Anal. Appl. Pyrolysis. 2007 Mar;78(2):445–51.

9. Pyl SP, Schietekat CM, Reyniers M-F, Abhari R, Marin GB, Van Geem KM. Biomass to olefins: Cracking of renewable naphtha. Chem. Eng. J. 2011 Dec;176-177:178–87.

10. Van Geem KM, Abhari R, Pyl SP, Reyniers M-F, Marin GB. From Biomass to Ethylene: Steam Cracking of bio-synfined Naphtha. AIChE Ethyl. Prod. Conf. Proc. New York: American Institute of Chemical Engineers; 2010. p. 509–39.

11. Pyl SP, Dijkmans T, Antonykutty JM, Reyniers M-F, Harlin A, Van Geem KM, et al. Wood-derived olefins by steam cracking of hydrodeoxygenated tall oils. Bioresour. Technol. Elsevier Ltd; 2012 Dec;126:48–55.

12. Gayubo AG, Valle B, Aguayo AT, Olazar M, Bilbao J. Olefin Production by Catalytic Transformation of Crude Bio-Oil in a Two-Step Process. Ind. Eng. Chem. Res. 2010 Jan 6;49(1):123–31.

13. Gong F, Yang Z, Hong C, Huang W, Ning S, Zhang Z, et al. Selective conversion of bio-oil to light olefins: controlling catalytic cracking for maximum olefins. Bioresour. Technol. Elsevier Ltd; 2011 Oct;102(19):9247–54.

14. Mercader FDM, Groeneveld MJ, Kersten SR a., Venderbosch RH, Hogendoorn J a. Pyrolysis oil upgrading by high pressure thermal treatment. Fuel. Elsevier Ltd; 2010 Oct;89(10):2829–37.

15. Vispute TP, Zhang H, Sanna A, Xiao R, Huber GW. Renewable chemical commodity feedstocks from integrated catalytic processing of pyrolysis oils. Science (80-.). 2010 Nov 26;330(6008):1222–7.

16. Bridgwater AV. Review of fast pyrolysis of biomass and product upgrading. Biomass and Bioenergy. 2012 Mar;38:68–94.

17. Carlson TR, Cheng Y-T, Jae J, Huber GW. Production of green aromatics and olefins by catalytic fast pyrolysis of wood sawdust. Energy Environ. Sci. 2011;4(1):145.

18. Zakaria ZY, Amin NAS, Linnekoski J. A perspective on catalytic conversion of glycerol to olefins. Biomass and Bioenergy. Elsevier Ltd; 2013 Mar;In press.

19. Chang CD. Methanol Conversion to Light Olefins. Catal. Rev. Taylor & Francis; 1984 Aug;26(3-4):323–45.

20. Liu Z, Liang J. Methanol to olefin conversion catalysts. Curr. Opin. Solid State Mater. Sci. 1999 Feb;4(1):80–4.

21. Keil FJ. Methanol-to-hydrocarbons: process technology. Microporous Mesoporous Mater. 1999 Jun;29(1-2):49–66.

22. Mariano AP, Harlin A, Manninen J, Chambost V, Stuart P. Techno-economic analysis of process alternatives for the production of ethylene-propylene rubber from forest-based feedstocks. Tappi J. 2013;12(1):19–32.

23. Ren T, Patel M, Blok K. Steam cracking and methane to olefins: Energy use, CO2 emissions and production costs. Energy. 2008 Feb 11;33:817–33.

24. Ek M, Gellerstedt G, Henriksson G. Pulp and Paper Chemistry and Technology 1 - Wood Chemistry and Wood Biotechnology. 1st ed. Berlin: Walter de Gruyter & Co.; 2009.

25. Rowell RM. Handbook of Wood Chemistry and Wood Composites. 2nd ed. CRC Press; 2013.

26. Yaman S. Pyrolysis of biomass to produce fuels and chemical feedstocks. Energy Convers. Manag. 2004 Mar;45(5):651–71.

27. Beis S, Mukkamala S, Hill N, Joseph J. Fast pyrolysis of lignins. Bioresources. 2010;5(3):1408–24.

28. Yanik J, Kornmayer C, Saglam M, Yüksel M. Fast pyrolysis of agricultural wastes: Characterization of pyrolysis products. Fuel Process. Technol. 2007 Oct;88(10):942–7.

29. Choi HS, Meier D. Fast pyrolysis of Kraft lignin—Vapor cracking over various fixed-bed catalysts. J. Anal. Appl. Pyrolysis. Elsevier B.V.; 2013 Mar;100:207–12.

30. Nagy M, Kosa M, Theliander H, Ragauskas AJ. Characterization of CO2 precipitated Kraft lignin to promote its utilization. Green Chem. 2010;12(1):31.

31. Kosa M, Ben H, Theliander H, Ragauskas AJ. Pyrolysis oils from CO2 precipitated Kraft lignin. Green Chem. 2011;13(11):3196.

32. Önal EP, Uzun BB, Pütün AE. Steam pyrolysis of an industrial waste for bio-oil production. Fuel Process. Technol. Elsevier B.V.; 2011 May;92(5):879–85.

33. Guo X, Wang S, Guo Z, Liu Q, Luo Z, Cen K. Pyrolysis characteristics of bio-oil fractions separated by molecular distillation. Appl. Energy. Elsevier Ltd; 2010 Sep;87(9):2892–8.

34. Heo HS, Park HJ, Park Y-K, Ryu C, Suh DJ, Suh Y-W, et al. Bio-oil production from fast pyrolysis of waste furniture sawdust in a fluidized bed. Bioresour. Technol. Elsevier Ltd; 2010 Jan;101 Suppl(1):S91–6.

35. Kleinert M, Barth T. Towards a Lignincellulosic Biorefinery : Direct One-Step Conversion of Lignin to Hydrogen-Enriched Biofuel. Energy & Fuels. 2008;46(7):1371–9.

36. Gasson JR, Forchheim D, Sutter T, Hornung U, Kruse A, Barth T. Modeling the Lignin Degradation Kinetics in an Ethanol/Formic Acid Solvolysis Approach. Part 1. Kinetic Model Development. Ind. Eng. Chem. Res. 2012 Aug 15;51(32):10595–606.

37. Holmelid B, Kleinert M, Barth T. Reactivity and reaction pathways in thermochemical treatment of selected lignin-like model compounds under hydrogen rich conditions. J. Anal. Appl. Pyrolysis. Elsevier B.V.; 2012 Nov;98:37–44.

38. Forchheim D, Gasson JR, Hornung U, Kruse A, Barth T. Modeling the Lignin Degradation Kinetics in a Ethanol/Formic Acid Solvolysis Approach. Part 2. Validation and Transfer to Variable Conditions. Ind. Eng. Chem. Res. 2012 Nov 21;51(46):15053–63.

39. Gellerstedt G, Li J, Eide I, Kleinert M, Barth T. Chemical Structures Present in Biofuel Obtained from Lignin. Energy & Fuels. 2008 Nov 19;22(6):4240–4.

40. Kleinert M, Gasson JR, Barth T. Optimizing solvolysis conditions for integrated depolymerisation and hydrodeoxygenation of lignin to produce liquid biofuel. J. Anal. Appl. Pyrolysis. 2009 May;85(1-2):108–17.

41. NIST Chemistry Webbook [Internet]. 2013. Available from: http://webbook.nist.gov/chemistry/

42. IPCC. Working Group I Contribution to the IPCC Fifth Assesment Report Climate Change 2013 : The Physical Science Basis. 2013.

9 APPENDIX 1

This appendix describes the calculations for the hydrogen needed in the hydrodeoxygenation step of the process described in Chapter 6. The calculation is only to get an estimation, not to get any exact numbers. The following assumptions were made.

- 10wt% of the bio-oil is aromatics
- All of the aromatics are diethyl-phenol, $C_{10}H_{14}O$
- There is no oxygen in the aliphatic quantity of the bio-oil
- All hydrogen will react with oxygen to water
- The atomic weights are H=1g/mole, C=12g/mole, O=16g/mole

For every 1000kg of bio-oil, $0{,}1 * 1000 = 100kg$ will be aromatics.

The oxygen ratio of diethyl-phenol is $\frac{16}{12*10+1*14+16} = 0{,}1$.

That makes the total oxygen content of 1000kg of bio-oil $0{,}1 * 100 = 10kg$.

For 10kg of oxygen $10 * \frac{2}{16} = 1{,}3kg$ of hydrogen is needed.