Production of four selected renewable aromatic chemicals

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Abstract

Today, there is a higher awareness for a sustainable society, a growing concern about greenhouse gas effects, the fact that petroleum is a limited resource implies a business opportunity and an increased market interest for renewable raw materials, and for companies their long term survival. While biomass has potential to replace a large fraction of imported petroleum based products, the main obstacle to the more widespread utilization of our low-cost biomass resources is the absence of low-cost processing technologies. This report has evaluated the lignin and hemicellulose pathway to green aromatic compounds (Benzene, Toluene, Ethyl benzene and Xylenes). Lignin has a more complex structure then hemicellulose. The literature studies that were made were divided in to two sections, Lignin and cellulose/hemicellulose. The purpose with the study was to find a way to make green BTeX. The lignin pathway were not fully evaluated, the lignin that were studied were in solid form and it behave different then a lignin in soluble form. The literature study showed that there is ways to make green aromatic compound but it was not further evaluated, for this project hemicellulose were chosen. Furans from the hemicellulose have a got potential to produce green aromatic compounds. Two experiments were made to evaluate the route that the literature studies have found. A setup of a catalytic continuous flow bed reactor where made to study Diels-Alder reactions. Reactions has been performed with 2-methylfuran (2MF) and propylene over a ZSM-5 catalyst and furfural without propylene over ZSM-5. It has been shown that the green aromatic compounds, BTeX, is possible to produce using this methodology. The yield for reaction between propylene and 2MF was 62 % BTeX. Toluene dominated the composition. Transformation of 2MF without propene also produced BTeX with a yield of 21%. Further, furfural transformations without propene also produced BTeX with a yield of 31%. Both catalytic Diels-Alder reactions and cracking reactions were seen during the experiments. The observation that furfural is transformed to BTeX without Diels-Alders reactions suggests that cracking mechanisms are important. This opens up for the use of less specific/purified substrates in future development.

Sammanfattning

I dag så strävar vi efter ett mer hållbart samhälle. Den olja som finns i dag vet vi alla att den är ändlig och kommer i framtiden att behöva ersättas. Men detta måste göras på villkor att den nya produkten håller samma kostnadsnivå som oljan annars är det inte lönsamt att byta den samt att det finns en förnyelsebar källa som kan ersätta oljan. En av de största förnyelsebara källorna vi har är skog och grödor. Denna rapport omfattar en litteraturstudie om hur man kan använda lignin och hemicellulosa för att tillverka gröna aromatiska kolväten och de ämnen som är i focus är bensen, toluen, etylbensen och xylener (BTeX). Litteraturstudien var indelat i två delar, en lignin del och en hemicellulosa del. Syftet var att finna reaktions vägar till gröna aromater (BTeX). I litteratur studien utvärderades inte lignin helt för att i litteratur studien tar bara hänsyn till lignin i fast form och lignin i upplöst form har inte utväderas. Det litteratur studien har visat är att lignin har potential att skapa gröna aromater men i detta projekt valdes hemicellulosavägen. Hemicellulosa och dess derivat är mer i tiden för att det är enklare molekyler att arbeta med för att skapa gröna aromater. Experiment utfördes för att utvärdera den, enligt litteraturstudien, mest lovande reaktionsvägen till gröna aromater.

En katalytisk kontinuerlig bädd reaktor sattes ihop för att dessa experiment skulle kunna genomföras. Ett av försöken var att reagera 2-metylfuran med 10 % propen blandning över an ZSM-5 katalysator. Det visade sig att man kan tillverka grön BTeX genom att använda denna metoduppställning. Ur 2MF med 10 % propen blandning var utbytet 62 % BTeX där toluen var den mest dominanta av dem. Det genomfördes även experiment utan propen med 2MF och BTeX utbytet var då 21 %. Furfural är en grundsubstans som 2MF framställs ur. BTeX utbytet från reaktion med furfural var 31 %, enbart med katalysator. Både katakytiska Diels-Alder reaktioner och kracking reaktioner kunde observeras under experimenten. Observationen att furfural transformeras till BTeX utan Diels-Alder mekanisker tyder på att krackingsmekanismerna är viktiga. Detta öppnar för att mindre specifika startsubstanser eller mer orena startsubstrat skulle kunna användas för framtida utveckling.

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Table of content

1 Scope

The scope of this thesis is to perform a literature survey, and experiments, in field of production of some selected renewable aromatic hydrocarbons. Specifically the substances of interest are BTeX (benzene, toluene, ethylbenzene and xylenes) and phenol.

The information that is collected for the report is based on articles and books from different data bases like SciFinder, Google Scholar, and course literature. The literature study will contain some base information on lignin, pyrolysis, pentoses and isomerization of xylenes.

1.1 Delimitations

This report will focus on BTeX and phenol as chemical, and their downstream derivatives are not included. The methods that have been studied are pyrolysis, cracking (catalytic cracking and hydrocracking), briefly introduction of isomerization of xylenes and of hydrolysis. Biochemical pathways are only to minor extent discussed. This sentence reaction ways will be discussed later in the report.

2 Introduction

Why renewable raw materials? Today, there is a higher awareness for a sustainable society, a growing concern about greenhouse gas effects, the fact that petroleum is a limited resource implies a business opportunity and an increased market interest for renewable raw materials, and for companies their long term survival. While biomass has potential to replace a large fraction of imported petroleum based products, the main obstacle to the more widespread utilization of our low-cost biomass resources is the absence of low-cost processing technologies. The objective of current research in this area should be to develop highly efficient and low-cost catalytic processes, catalytic materials and reactors for biomass conversion to chemicals, polymer materials, and also fuels.

2.1 Aromatics – use today

Aromatic compounds are the basis for a wide variety of products used by consumers and industry. Fossil oil and its downstream products (naphta) is the main source for these hydrocarbons[3]. BTX (Benzene, Toluene and Xylene) is mainly produced by catalytic reforming, typically using hydrogen and catalysts under high temperature (500 °C) and high pressure (10-50 Bar). Production of benzene can also be performed using steam cracking or toluene disproportionation/dehydroalkylation. Benzene is a part of gasoline fuel but it is also a starting material for production of ethylbenzene, cumene, cyclohexane, aniline and chlorobenzenes (fig 1, fig 2). The yearly production is about 21 million tons[1].

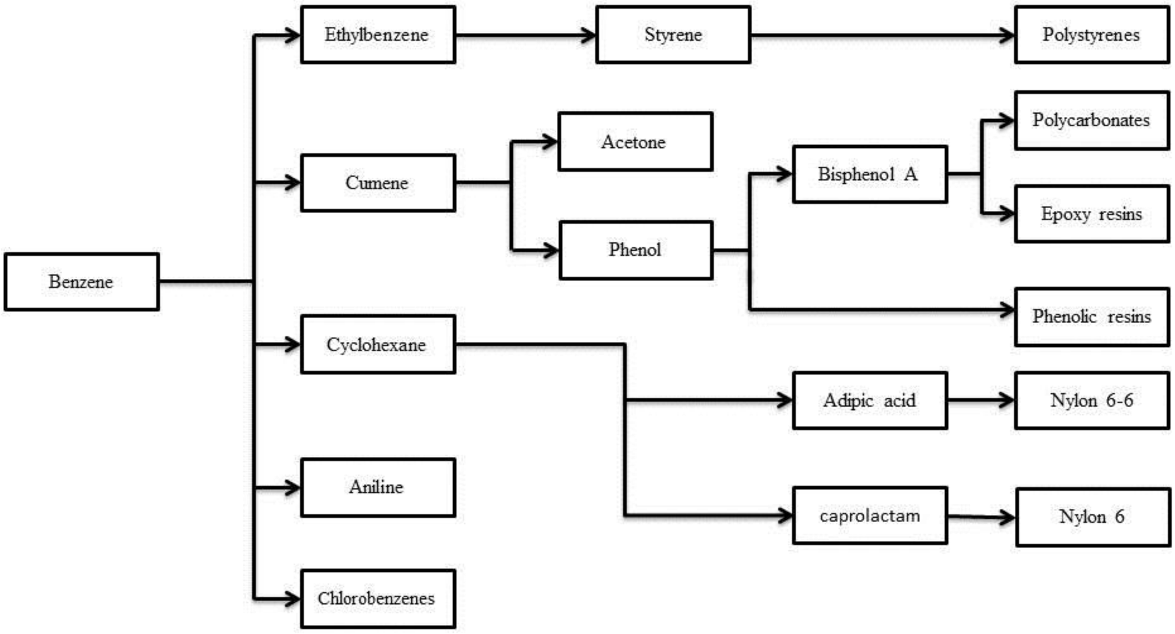


Figure 1 Products of the start compound benzene[2]

Most of the benzene production is transformed to etylbenzene by reaction with ethylene. The ethylbenzene is then dehydrogenated to styrene and hydrogen for supply of monomers to polystyrene resins (fig 1, fig 2). The yearly production of ethylbenzene is about 20 million tons[1]. Some of the benzene is alkylated with propene roughly for the production of isopropylbenzene (cumene). This reaction is the basis in the cumene process, where the cumene is further oxidized with air to yield acetone and phenol. These two chemicals are therefore linked to each other and are mainly used for production of polymethylmetacrylate (from acetone) and polycarbonates/epoxy resins (from phenol). In 2004 the total production of phenol was about 3.4 million ton[3] .

During catalytic reforming of petroleum naphtha, toluene is also formed when the aliphatic hydrocarbons cyclizes. The use is diverse, but the main uses are as solvent and as a reactant for production of isocyanates. From isocyanates and a polyol, polyurethanes of different kinds can be made (fig 2)[1].

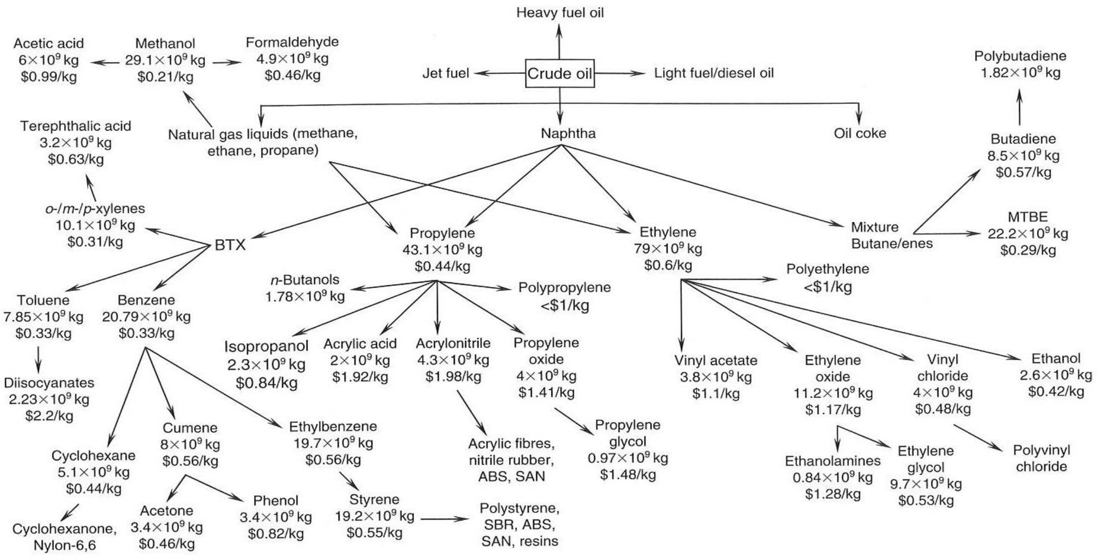


Figure 2 products that can be produced from crude oil[1]

The most used and desired group from the naphta reformate is the xylenes. para-Xylenes has the largest production of the isomers (ortho-, meta- and para-xylene). Around 98% of the p-xylene is consumed in the polyester chain, in production of fibers, films of polyethylene terephthalate (PET)[4]. The two intermediates of p-xylenes are terephtalic acid (TA) and dimethyl terephthalate (DMT). The residual 2% is used as solvent. The second largest isomer is the ortho-xylene, most of the o-xylene is consumed for the production of making phthalic anhydride (PA), which then can be used for production of alkyd resins and paints. It is also used for production of phthalate plasticizers for PVC. m-Xylene uses are mainly as the polyester precursor, isophthalic acid. The demand of ortho- and para-xylene and the raising oil price have made the price of these chemical become more expensive, the price over time is showed in figure 3[5].

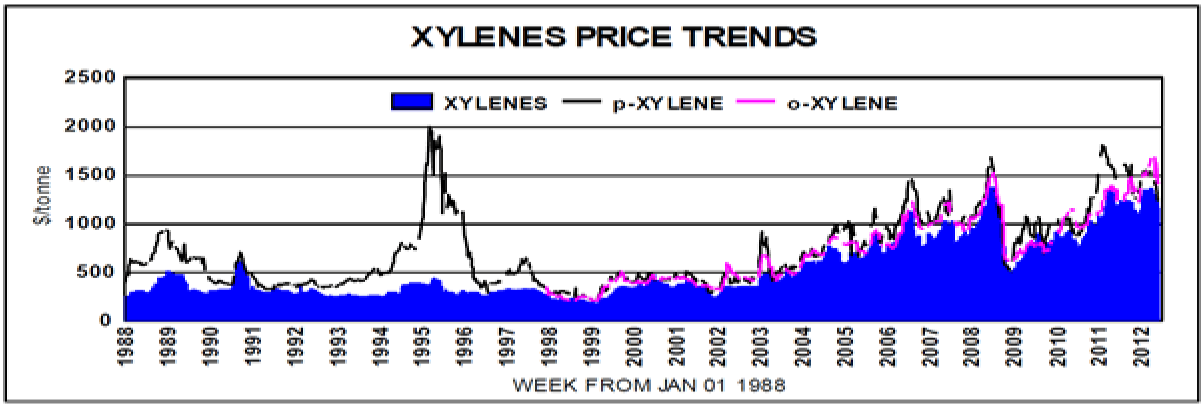


Figure 3 shows the xylenes price over time[5]

The aromatic compounds overall have increases in price and according to SunSirs-China Commodity Data Group[6], however the price has become cheaper during the current economic crises. BTeX-Phenol prices are shown in figure 4.

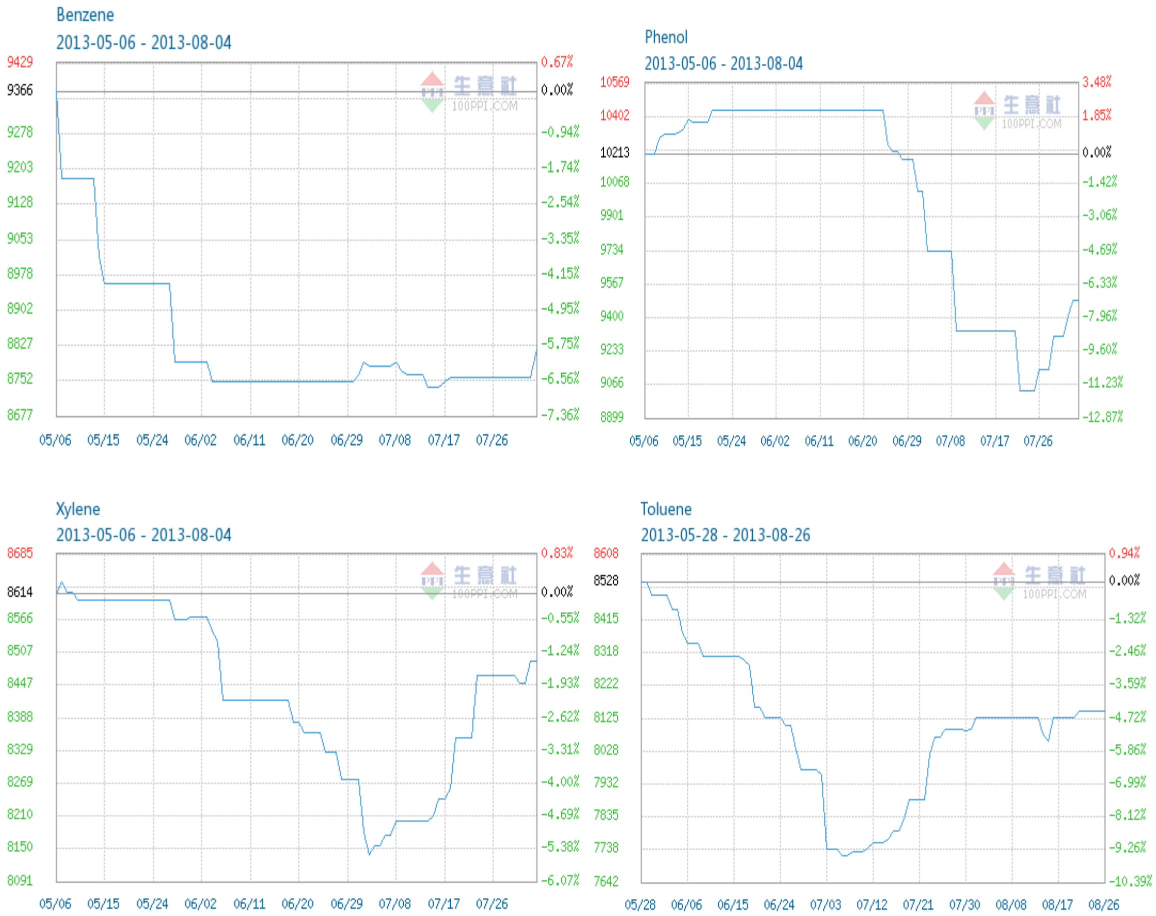


Figure 4 shows price over time on the BTeX-phenol over time, On the left side is the price in RMB and on the right is percent if the chemical is going up or down[6].

The price of phenol has been raising in the last five years, a report from ICIS shows that in one year the price in China has doubled (see figure 5). As figure 4 shows the prices of BTeX-Phenol have dropped in price the last month but in a longer perceptive the prices have increase and the prices for BTeX-Phenol are link together because they all come from the same naphtha source.

Figure 5 shows the Phenol price over time[5]

The xylene, especially p-xylene is driven by a big market, i.e. the plastic industry. In 2011 the total plastic production was 47 million tons in Europe and PET was 6, 5 % of this total (see figure 6)[7].

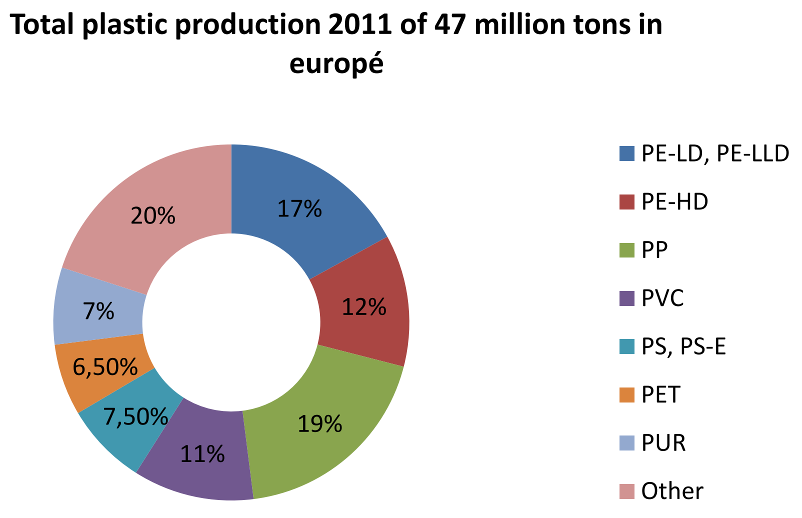


Figure 6 The total production of plastics in Europe 2011[7]

As stated in the introduction, one of the main driving forces of finding renewable alternatives is the oil price. As can be seen in Figure 7, the oil price has been steadily increasing the last couple of years.

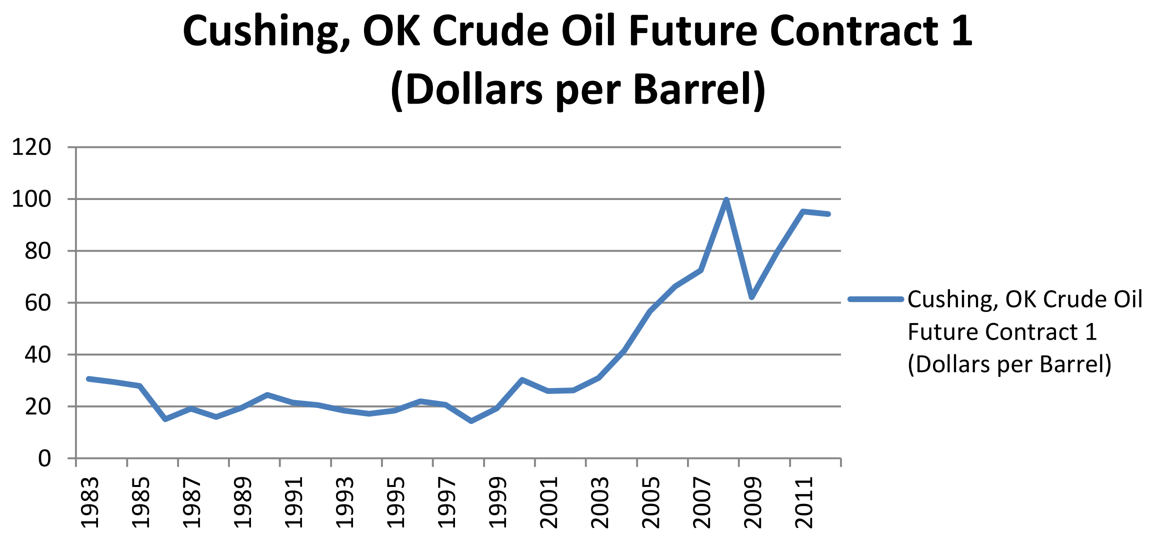


Figure 7 showed the crude oil over time from 1983 to 2013[8]

2.2 Green demand –

In later years countries over the world seek to find more renewable resources and processes. This is due to the rising oil price and decommissioning of oil dependency coupled to the CO_2 issue. Companies are trying to replace as much of petroleum crude oil as possible in to a more and more renewable sources. To find these sustainable ways, it requires that several factors are fulfilled. One of the most common strategy is the "triple bottom line" in figure 8 below.

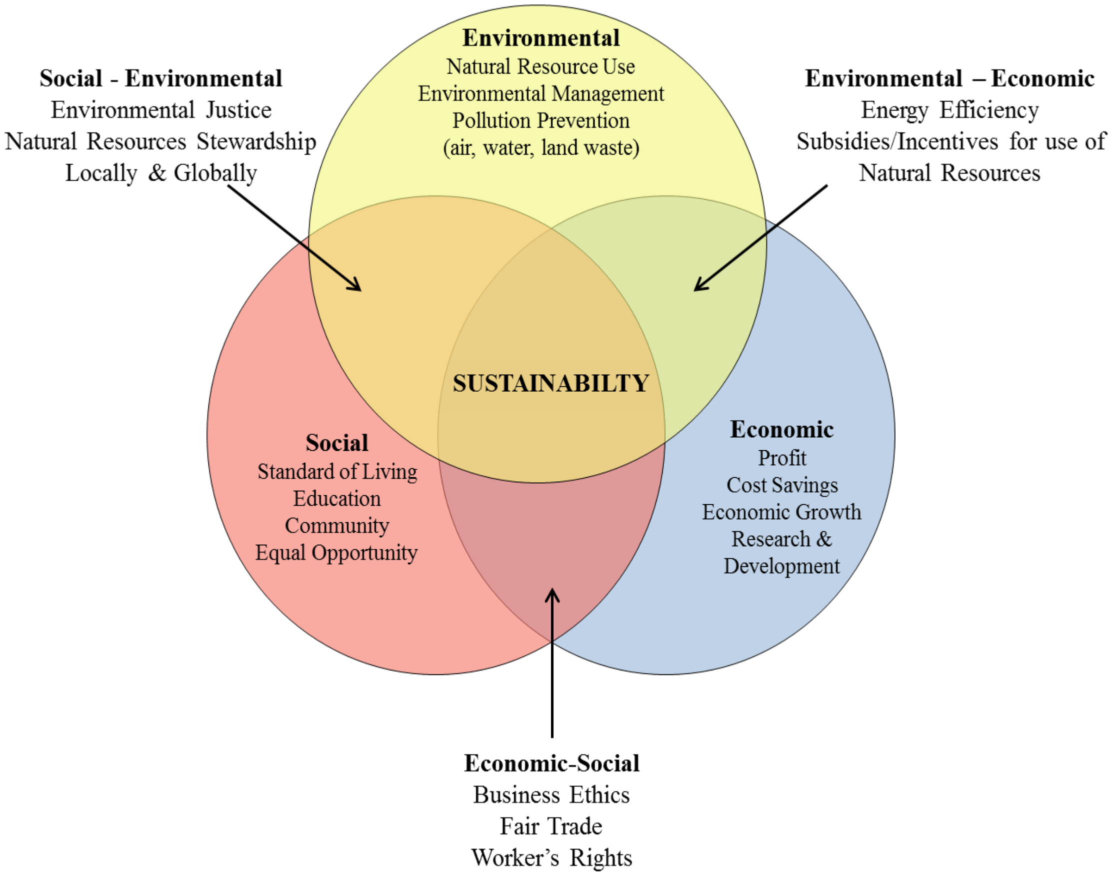


Figure 8 the triple bottom line.

The definition of the term sustainability, according to the Report of the World Commission on Environment and
”Our Common Future. “Sustainable development is development that meets the needs of the present without compromising the ability of future generations to meet their own needs. It contains two key concepts:

- the concept of 'needs', in particular the essential needs of the world's poor, to which overriding priority should be given; and

- the idea of limitations imposed by the state of technology and social organization on the environment's ability to meet present and future needs.”

As shown in figure 8, sustainability is in the middle where the economic social- and environmental needs are overlapping. When we speak about the renewable resources, generally the technologies are new, and thus not yet fully commercialized. However, there are many ongoing research projects with aim to make renewable resources economically viable. In order to switch to sources other than petroleum it has to be for a price that the customer is willing to pay. Companies in general are both talking about drop-in chemicals (drop-in chemicals is a chemical that would replace the current process chemical with a new one without changing the process) that would replace the petroleum based chemical, and completely new chemical solutions.

2.3 Biomass as a renewable source

Sustainable routes to aromatic hydrocarbons usually involve biomass of some kind. The reasons being it is carbon richness and large amount of availability[8]. Biomass is a renewable source which containing carbon, oxygen, and hydrogen [9] and can be an inexpensive. The biomass from plant and tree is composed of natural polymers with complex compositions. The typical lignocellulose biomass contains 40-45 wt% cellulose, 25-36wt% hemicellulose, 15-30wt% lignin and up to 10wt% extractive [10]. The two main types of wood is softwood and hardwood, in Scandinavia hardwood is leaf tree as birch, and softwood is like spruce. The chemical composition is different in hard- and softwood, Table 1 shows the differences.

	Softwood (wt%)	Hardwood(wt%)
Cellulose	43.7 ± 2.6	45.4 ± 3.5
Hemicellulose	25-36	25-36
Glucomannan (%)	15	2 to 5
Glucuronoxylan (%)	8	15 to 30
Lignin	25 to 35	18 to 25

Table 1 Composition of soft- and hardwood[11]

Lignin is one of the components in biomass and is the second most abundant biopolymer on earth. The use of lignin as a renewable carbon source would solve some of problem that the world is facing. This is due to the fact that 95% of lignin is combusted to generate energy and recover chemicals [12]. The interesting part of lignin is that it can be broken down in to several building blocks and from reduction of them the primal substances as phenol, and xylene can be produced.

The aim of this report is to describe the status of current research in the field of renewable aromatic chemicals, and also identify potential renewable sources for the production of specific chemicals such as phenol and xylene, i.e. answer questions like: what chemical reactions can be utilized on what renewable substrates?

3 Theory

3.1 Renewable sources

Renewable resources include solar energy, wind, falling water, plant materials (biomass), waves, ocean currents, temperature differences in the ocean and energy of the tides[6]. The renewable resource is converted in to energy in different form as electricity and motive power, in other cases they are converted in to different substances[6].

This report is biomass most interesting to make BTeX of the renewable resource from tree and plants.

3.1.1 Lignin

Lignin is an heterogeneous polymer with a three-dimensional structure (see Figure 9)[13]. The natural state of lignin is found in plants where the lignin fills the gap between hemicellulose and cellulose, i.e. lignin is the structural element that holds the lignocellulose matrix together [13]. Softwood has the most wt% lignin. Today, lignosulfonate is the most used lignin application worldwide. Lignosulfonate is used as additive in concrete.

It is also used as an industrial cleaning applications where the lignosulfonates is added to boiler and cooling tower to prevent scaling[14]. They can also prevent certain insoluble heat-coagulable particles[14].

Lignosulfonate is the reagent to produce vanillin. Borregaard is one of the companies that produce vanillin.

The biosynthetic lignin involves three primary monomers: p-coumary, coniferyl and sinapyl alcohols (see Figure 9)[13].

The depolymerization of natural lignin uses techniques that target the linkages that are most easy to break, one of the most dominant linkage is the β-O-4, some other linkages in lignin that can be broken are: 5-5, β-5, 4-O-5, β-1 and β-β[13].

p-coumary-, coniferyl-, and sinapyl alcohols can be used as building block to form many different chemical compounds.

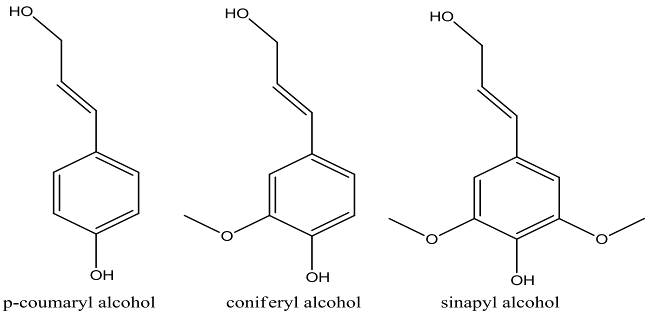


Figure 9 the structure of the alcohols from lignin

3.2.1 Methods for breaking down Lignin

There are different ways to harvesting lignin that are coupled to the paper industry in which lignin are used as a fuel. The different processes lead to different lignin qualities depending on the chemistry used. The major processes are:

Kraft lignin process, sulfide process, and Organosolv process (not a commercial process)

3.2.1.1 Kraft lignin process (LignoBoost)

The lignoBoost is a more effective process comparing to the traditional Kraft lignin process. There are four steps in LignoBoost, precipitation, dewatering, resuspension, and final washing[6]. A stream of black liquor is obtain from the black liquor evaporation plant. In the first step the lignin is precipitated by acidification with CO_2 and filtered. The filter cake from the dewatering step is redispersed and acidified with H_2SO_4. The pH decrease is dependent on the ionic strength, of more phenolic parts of the lignin gets protonated the more the pH will drop. In the final washing some of the slurry is recycled to the black liquor evaporation plant and the rest is processed in the final step[6]. By using this process the primary bonds in lignin are broken, however, the 5-5 bond is not easily broken in the Kraft pulping process. The product is washed lignin. The good part of this process is that it can produce high quality lignin at a low cost[6].

3.2.1.2Lignosulfonate process

In sulfite pulping process, the wood is reacting with hydrogensulfite or sulfite ions. the counter ion can be magnesium, calcium, sodium or ammonium ions. In the process there are three major reactions; including sulfonation, hydrolysis, and condensation. Typical reaction times are 3-7 h, and the reaction temperature is between 125 to 150°C[15]. The β-O-4 bonds are stable under acidic conditions but if the process uses another substance, an operator like sodium or ammonia as base, β-O-4 bonds will cleave[15].

3.2.1.3 Organosolv Pulping Lignins

In the kraft and lignosulfonate processes the content of sulfur. In order to get a low sulfur content in the lignin, the orgonosolv process can be used. Hardwood chips are cooked at different temperature and pH in an ethanol/methanol mixture.[13-15] The advantages of this separation is that cellulose, hemicellulose and lignin are in three separate streams[13]. A disadvantage is that there is a high cost of recovery of the solvent[13]. Then the lignin is separated and dried, it results in a brown powder with low sulfur content. In Canada at Repap Alcell pilot plant, a modified pretreatment technique has been developed to produce organosolv lignin with high purity and potentially high value[13].

3.2.2 Cellulose and hemicelluloses

carbohydrates is one of the major components in biomass (see figure 10). It can be divided into cellulose and hemicellulose. These are polymers and cellulose is based on the six carbon sugar glucose and hemicellulose on several different monomers such as xylose, mannose, galactose and arabinose. Most of the hemicellulose monomers are five/six carbon sugars. Cellulose is used mainly for papermaking but also for textiles, binders and other derivatives. Cellulose and hemicellulose, can be hydrolyzed and fermented to ethanol using common yeast. Hemicellulose and its five carbon sugar monomers are available as raw material for further processing[16].

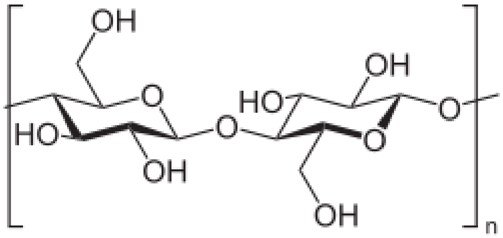


Figure 10 Cellulose structure[16]

3.2.2.1 Furans from cellulose

Hemicellulose is easily separated from the cellulose and lignin using hydrolysis. A two-step acidic hydrolysis is often used, first a mild treatment where the hemicellulose is preferentially hydrolyzed. In the second stage, the cellulose is converted to glucose using more acid and harsher conditions. The complete hydrolysis of cellulose is however difficult[16]. Two important reactions take place during the acidic hydrolysis. Namely the hydrolysis of the polymer to monomers and secondly the de-watering of the sugar monomers, via anhydrosugars, to furans. These furans have attracted large attention, especially when reacted with olefins to form toluene and xylenes.

One of the furans that is commercially available in large quantities is furfuryl alcohol, linking foundry sand and used for lubrication oil extraction[17]. Another important chemical is furfural. The latest research has shown that furfural has a potential to react further to xylenes. The largest production of furfural is in China where the production is 280 kton/yr[17]. Other large-scale plants are located in the Dominican Republic and South Africa.

The furfural can undergo hydrogenation to form Furfurayl alcohol and dehydrogenation to form 2-MF (see figure 11)[18].

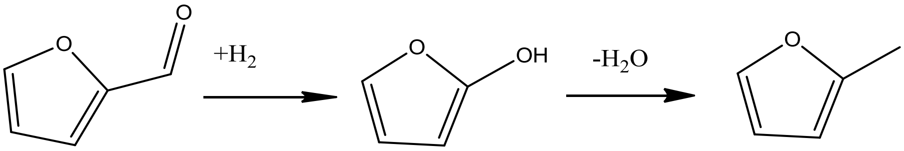


Figure 11 The reaction from furfural to 2-metylfuran

From the 6-carbon sugar cellulose 5-HMF can be produced and further reacted with propylene by a Diels-Alder reaction to form p-xylene (see figure 12)[19].

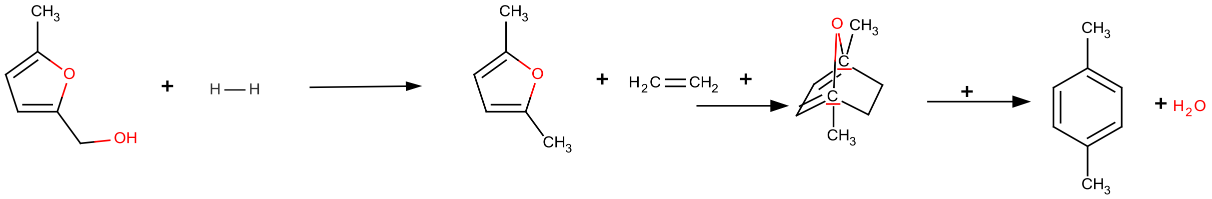


Figure 12 Reaction of 5-HMF from celloluse to p-xylene

3.3 Processes / Transformations

3.3.1 Lignin depolymerization

Lignin has many different types of linkages, and depending on type of process chosen to degrade the lignin, different linkage will break [13].

3.3.1.1 β-O-4 Linkage

The β-O-4 linkage is the most abundant in lignin[13]. Under acid condition these linkages undertake solvolytic cleavage primarily forming secondary alcohols that are converted in to carbonyl, ethylene, and carboxyl structures [14]. During alkaline pulping (Kraft pulping) the β-O-4 bonds cleaves and the lignin is depolymerized in to a water-soluble compounds containing phenolic hydroxyl groups [13]. The β-O-4 linkage is important because when it undergoes depolymerization the cleaved product is forming simpler compounds resembling the p-coumaryl, coniferyl, and sinapyl alcohol building blocks[13].

3.3.1.2 Carbon-carbon linkage

The carbon-carbon linkage is the most difficult bond to break, it survive the pulping process[13]. Carbon-carbon linkage is found in native lignin and can also be formed during the digestion of wood chips in the kraft process.

3.3.2 Pyrolysis

Pyrolysis is a thermal decomposition occurring in absence of oxygen. Low process temperature and longer vapour residence time favour the charcoal production[20]. If lignocellulose is pyrolysed at high temperature and long residence time it will be converted into gas. If the settings were moderate temperature and short residence time the process will produce a liquid instead. The product formed is called bio-oil or pyrolysis oil and the method is called fast pyrolysis[20]. The pyrolysis oil is a dark red-brown to almost black solution. The colour depends on the chemical composition[21]. Typical properties of pyrolysis oil are shown in table 2.

Physical property	Typical Value
Moisture content	25 %
pH	2,5
Element analysis	
C	56 %
H	6 %
O	38 %
N	0,01 %
Ash	0,20 %
Heat value [MJ/kg]	17

Table 2 Composition of pyrolysis oil[20,22]

3.3.3 Cracking

Cracking is most common in the petroleum industry, the principle behind cracking is that it cleaves C-C bonds. It convert high-boiling hydrocarbon into low-boiling hydrocarbon products[13]. The mechanisms of cracking and hydrocracking (see section 3.2.3.2) are shown below (see figure 13).

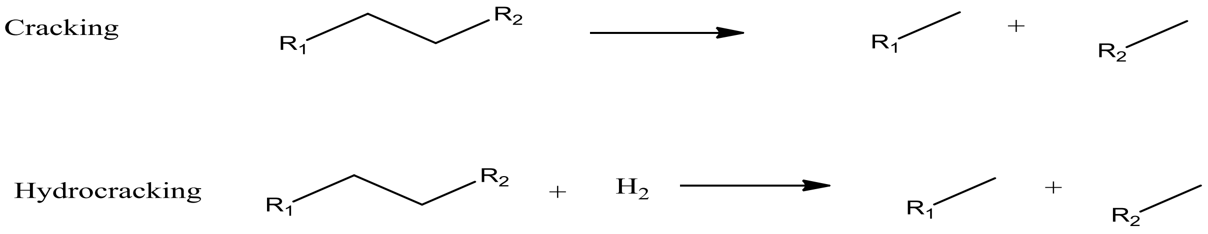


Figure 13 Principle mechanism of cracking and hydrocracking

3.3.3.1 Fluid catalytic cracking (FCC)

The catalytic cracking is based on an acid zeolite catalyst, this method has a high acidity, low tendency towards coke formation and high thermal stability [2]. The zeolite (catalyst) is the key ingredient of the FCC catalyst [23]. Zeolite is like a molecular sieve [23]. The zeolite is shaped like a pyramid with oxygen bases (4 oxygen) and at the top there is an alumina or a silica atom, all those atoms form a tetrahedral pyramid (see figure 14)[23].

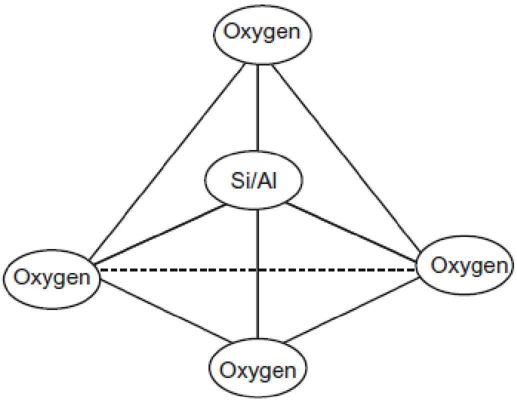


Figure 14 Tetrahedral silica-aluminia structue of a zeolite[23,24]

The zeolite builds up a network of small pores. There are 3 different types of zeolite commonly used in FFC, Type X, Type Y and ZSM-5. Type X and Y have the same crystalline structure but the X zeolite has a lower silica-alumina ratio than the Y zeolite[23]. ZSM-5 is a multilateral zeolite, which has a pore size of 5.1 – 5.6 Å [23]. The shape of the ZSM-5 is designed to be optimized for cracking long-chain carbons, low-octane normal paraffin and olefins[23]. The aromatic content increases with the usage of a ZSM-5 catalyst. Zeolites are a better choice since they are 1000 times more active than the old amorphous silica-alumina catalyst[23].

The purpose of the catalytic cracking is twofold, cracking gas oil molecules and rearrangement and recracking of cracked products.

The cracking take place in the reactor with presence of the zeolite, in order to make them operate at full potential, a catalytic site is required. There are two different types of catalytic acid sites, Brønsted and Lewis type[23]. A Brønsted-type acid (e.g hydrochloric and sulfuric) is capable to donating a proton[23]. A Lewis-type accepts a pair of electrons. Lewis acids do not have hydrogen in them; a classic example of a Lewis acid is aluminum chloride[23].

In the mechanism of catalytic cracking of propane ($CH_3CH_2CH_3$) two different carbon ions are formed. The first is the carbonium ion, which is formed by adding a proton from the zeolite to the paraffin molecule, $CH_3CH_3{+}CH_3$[23]. The second and more stable carbon ion is the carbenium (carbocation) ion, $CH_3CH{+}CH_3$. It is formed by adding hydrogen or by removing two electrons. Carbenium is the most active species in the cracking process [23]. Secondary carbenium ions are more stable than primary. Therefore, the chain scissoring occurs at the more stable carbon atom[23].

It is also possible to use the catalytic reactions for isomerization. Instead of cracking it the catalyst can rearrange the carbenium ion to form a tertiary ion. Which are more stable than the second and primary ions [23].

In olefins hydrogen transfer reactions can occur. In the reaction two olefins adsorb close together on an active site[23]. One of the olefin becomes a paraffin and the other one becomes a cyclo-olefin. The hydrogen has to move from one olefin to one other[23]. Typical catalysts for hydrogen transfer reactions are rare earth-exchanged zeolites ($CeCl_3$, $NdCl_3$, $SmCl_3$, $EuCl_3$ and $YbCl_3$)[25]. From an aromatic perspective, the cycloolefin can further undergo hydrogen transfer and yield a cyclodiolefin that can arrange to form an aromatic hydrocarbon[23].

3.3.3.2 Hydrocracking

Hydrocracking is a thermal process (>350°C) where hydrogen is participate in the cracking reactions. The process works under high pressure between 0.7 to 14 MPa. Hydrocracking can be combined with catalytic cracking. All the catalytic reactions take place, however in presence of hydrogen, some secondary reaction are stopped due to hydrogen inhibition. Methyl groups attached to secondary carbon are easily removed. Aromatic hydrocarbons are resistant under mild hydrocracking but under more severe conditions the main reaction in hydrocracking convert aromatic rings to naphthenic rings, the naphthenic may also be converted into paraffin[26].

3.3.4 Supercritical water reactions

The super critical point for water is 374°C and the pressure is 22.1 MPa[10]. Supercritical water has some advantages as a solvent, it accelerates the decomposition of polymers to produce more valuable monomers by a shorter reaction time. Supercritical water is completely miscible with light gases, hydrocarbons, and aromatics[10].

3.3.5 Isomerization

A molecule under right conditions can rearrange its structure like m-xylene can rearrange to p-xylene (See figure 15).

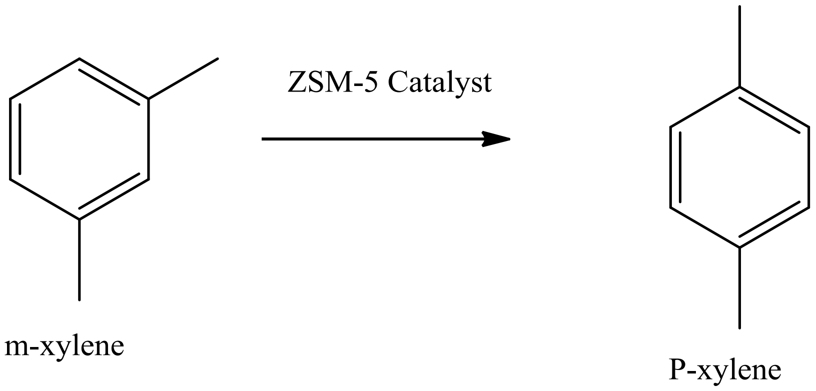


Figure 15 Isomerization of m-xylene to p-xylene

Xylene isomerization is a known reaction; it is preformed over a catalyst. The common reaction is transalkylation (transalkylation is a chemical reaction where a alkyl group is transferred from an organic compound to another) to isomerize xylenes[27]. It has been shown that when xylenes is isomerized toluene, benzene and trimethylbenzene has been identified along with the xylenes through transalkylation[27]. Isomerization of xylenes have shown that meta-xylene give the most yield. There are this two documented. Ways to preformed isomerization one the transalkylation, the other way is the disproportionation [27].

3.3.6 Hydrolysis

Hydrolysis is a used method in the pulping industry to break the aryl ether linkages between the phenylpropane units in the lignin structure[16]. The reaction increases the hydrophilicity of the lignin and facilitate its water-solubility. Hydrolysis is a slow reaction rate compared to the sulphonation, but when lignin is under acid sulphite pulping the hydrolysis is fast compare to the sulphonation[16].

3.3.7 Diels-Alder reactions

Diels-Alder is a cycloaddition reaction, sometimes it is describe as a [4+2]-π-electron cycloaddition. The simplest reaction is butadiene reacting with ethylene in the presence of thermal energy. The mechanism (see figure 13) is that the ethylene is the dienophile (electron poor) and the butadiene (electron rich) is the diene. The butadienes π-election is connected with the ethylene and at the same time the ethylenes π-electon bonds with the butadiene to form an aromatic compound (see figure 16). If the reactant is in trans-state it won't react, it has to be in cis-state for the Diels-Alder reaction. If the reactants are reacted in the present of a Lewis acid (ex $AlCl_3$, Et_2AlCl, BF_3, $B(OAc)_3$, $ZnCl_2$, $SnCl_4$ and $TiCl_4$) a faster reaction rate is occuring.

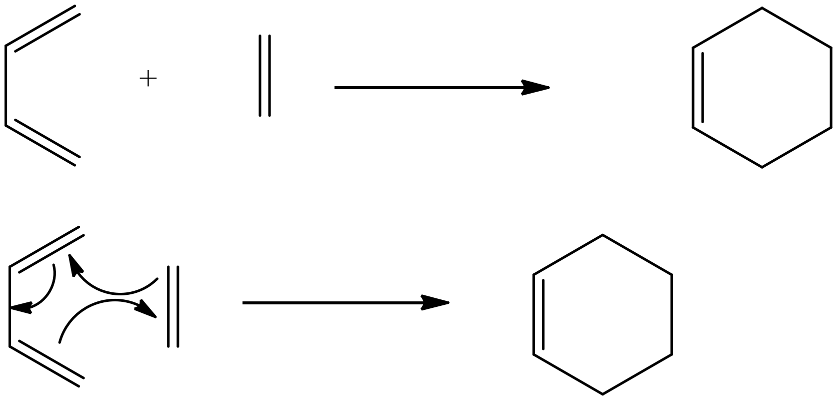


Figure 16 The Diels-Alder mechanism

4 Lignin analysis

The lignin molecule has a complex structure and several studies have shown the complicity of decomposing the molecule([12,27-31]). Lignin is a renewable resource that has a great potential for be used as both a raw material for fuel and chemical. Lignin has so far been classified as a low value product. In 2010 2% (1 million tons) of all the pulp and paper industry was commercially sold as low value product[28]. The rest of the 49 million tons lignin was burned as a low level fuel[28]. The lignin business represent around 300 million dollars worldwide[28]. In order to break down the lignin in to chemical blocks, different types of methods need to be developed.

Pyrolysis of lignin is an easy way to break down lignin into smaller molecules. Researchers in the field have found that different types of lignin gave different yield of chemical compounds. The pyrolysis itself can generate many different compounds but it is often connected to a catalytic setup to increase the yield of the targeting chemicals, including BTeX-phenol. From the literature study is has been presented that the catalyst ZSM-5 is the most effective one. Thus, giving the highest yield ([13,29-33]).

The zeolite cracking is related to fluid catalytic cracking FFC. The reactions that occur in the zeolite cracking are decarboxylation, decarbonylation, hydrocracking, hydrogenation, hydrogeoxygenation and cracking. The main reaction is cracking (see figure 12). The cracking reaction increases with higher temperature[22]. In zeolite cracking BTeX and phenol are products. Different types of zeolite are used over pyrolysis oil. The different types of catalyst that have been study are HZSM-5 (instead of ammonium form that is the most common one this have hydrogen on the Si/Al), Y-zeolite, silicatite, H-Beta and so on.The catalyst that gave the highest aromatic yield is the HZSM-5. On pure lignin the yield of aromatic compounds is 8 wt% and BTeX is around 5.80 wt% (benzene 1.33, toluene 1.83, ethyl benzene 0.17, p-xylene 0.96, o-xylene 0.39)[33].

Reported experiments were not only with the presence of catalyst, but also without it in order to distinguish any differences. The catalysts that were used were HZSM-5 and CoO/MoO_3 and they were compered against each other. The lignin that was used was:

- “Asian” lignin (pure liginin in solid form)
- Lignin from Lignol innovations, inc (pure liginin in solid form)
- Pretreatment of sugarcane bagasse form ethanol production in brazil (solid form)

Sample containing both cellulose and lignin from SEKAB Sweden (solid form)As the pyrolysis oils were pyrolysed without catalyst, the chromatograms showed a small amount of recovered BTeX (the wt% was around 0.1% total). The yield of BTeX increased when a catalyst was added, where HZSM-5 showed the highest yield. Benzene in the different types of lignin was around 1 wt%, toluene around 1.9wt%, ethyl benzene around 0.3 wt%, para-xylene around 1.8 wt% and ortho-xylene around 0.2wt%. It shows that from the pyrolysis oil over a HZSM-5 around 6wt% of BTeX is formed. The remaining 94% constitutes higher molecules or molecules with complex structures. Pyrolysis as a method to make pyrolysis oil is a good way to go, however it comes to making single chemical compounds it would not be the best way because the products after the pyrolysis oil over a catalyst are many. The separation of the chemicals from this method would thus be demanding

Instead of using pyrolysis some researchers use hydrothermal conditions for the decomposition of lignin([34],[10]). Guaiacol was used as a model compound of lignin in this experiment. The experiment is done in a batch reactor, it is feed with guaiacol and water, argon was purge before the reactor war closed. After the experiment was performed the products were analyzed with GC-MS, HPLC and MALDI. Two different temperatures were tested 390°C and 400°C. When the reactants are in water they undergo hydrolysis when the water reaches its supercritical state, the bond between the heteroatoms and carbon atom cleaves. The targeting bonds are the ether and methylene bridges connecting the structure. The products in this experiment were phenol, o-cresol, guaiacol and catechol (see figure 17). Yield of the compounds after the reaction were, catechol 24.26 wt%, phenol 5.13 wt% and o-cresol 1.18 wt% at 390°C and catechol 26.26 wt%, phenol 8.23 wt% and o-cresol 2.63 wt% at 400°C. The highest yield was observed after 120min, 400°C at and high density of water.

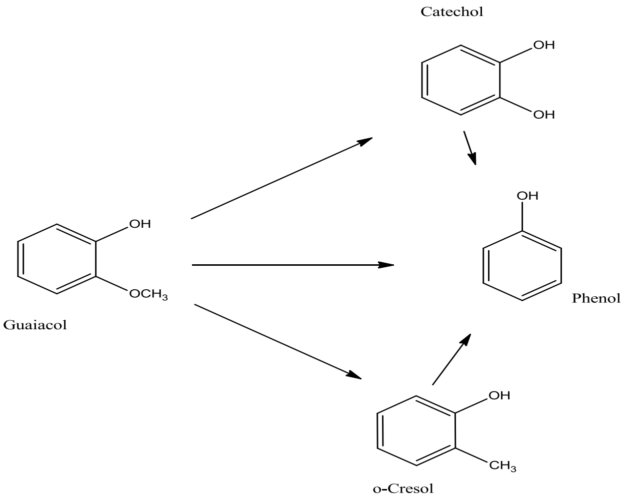


Figure 17 reaction pathway of guaiacol in near critical and supercritical water

The same research team used catechol instead of guaiacol for further studies. Experiment as these were carried out in a batch reactor, where catechol reacted with supercritical water. The result shows that phenol was one of the compounds that were found. The pathway of catechol to phenol is shown in Figure 18.

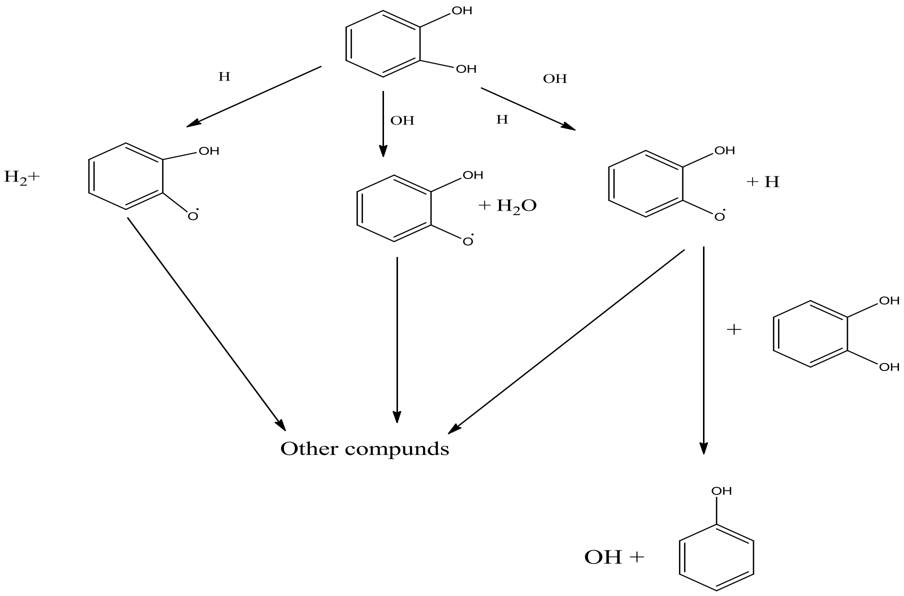


Figure 18 reaction pathway for catechol in near- and supercritical water

Another method that has been used in research is the hydrodeoxygenation.

In hydrodeoxygenation (HDO) the most dominant reaction is hydrodeoxygenation (see figure 19) the other reactions that can occur are cracking, decarboxylation, decarbonylation, hydrocracking and hydrogenation[22].

Hydrodeoxygenation $R{-}OH + H_2 \longrightarrow R{-}H + H_2O$

Figure 19 Mechanism of hydrodeoxxygenation

The principle of hydrodeoxygenation is that the hydrogen reacts with an oxygenated hydrocarbon to form water and an olefin. The separation is easy to make because the process has a water phase and an organic phase[22]. HDO of pyrolysis oils have shown to deoxygenate functionalities such as ketones, carboxylic acids, phenols and furans. The reactions are temperature dependent, usually between 250 °C and 450 °C depending on type of group and catalyst used. Yields were usually high, pyrolysis oil reactants can be deoxygenated up to 70%[35]. More complex bonds and sterically hindered oxygen requires higher temperature for the process to proceed (furans). If furans are the reacting compounds more hydrogen is required for the deoxygenation to be the dominate reaction. A problem with the catalyst is the deactivation, which can occur through poisoning by nitrogen species or water[22]. The method of HDO is nowadays adapted in the biodiesel production (Neste, Preem). The equipment used is similar to the more common HDS (hydrodesulphurization) equipment.

5 Cellulose analysis

The chemical similarities between the polysaccharides in lignocellulose and the aromatic hydrocarbons aimed at in this thesis are small. The process approaches that has been used for lignin are mainly based on degradation of the large and complex aromatic lignin structure to produce smaller aromatic compounds, followed by further transformations. The transformation of polysaccharides to BTeX-Phenol seems to follow partially other routes with more selective reactions.

Zeolite cracking- Diels-Alder

Most of the work performed has focused on zeolite cracking or zeolite-cracking coupled to Diels-Alder reactions ([19,36,37]). Cracking processes are used when the source is complex, such as woodchips (treated with fast pyrolysis) or other lignocellulosic materials [31]. Diels-Alder reactions over zeolite catalysts has been used when the raw material is less complex e.g pure compounds[19].

One of the reported method in the zeolite cracking-Diels-Alder field is fast pyrolysis over a ZSM-5 catalyst[19]. The method involves reaction of DMF and ethylene over the ZSM-5 catalyst. Other compounds that were tested were furfural, furan, furfurlic alcohols and 2-methylfuran (2MF) with different co-stream of ethylene and propylene in a 2% gas composition. The experiment setup with 2MF and 2% propylene has the highest yields of xylenes than the rest of the different experiments setups. The ZSM-5 has the ability for isomerization of the xylenes[37]. This favours the p-xylene over the other xylenes. The whole experiment was carried out at different temperatures. If p-xylene is the wanted product. A temperature of 450°C favoraizes p-xylene[19]. The different reaction pathway is shown in Figure 20.

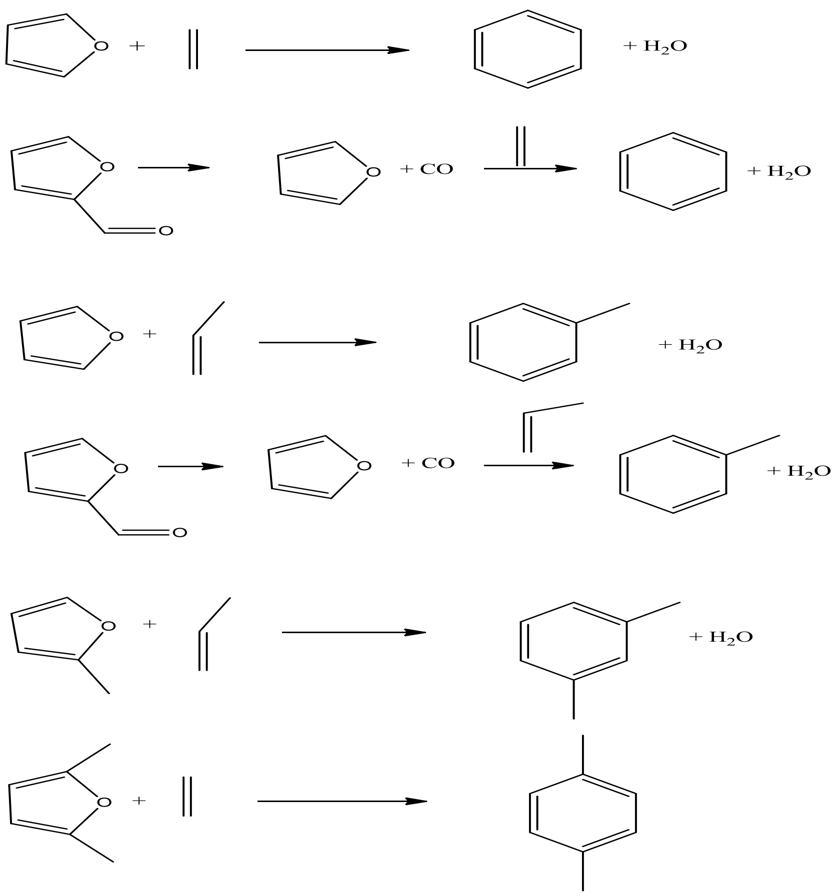


Figure 20 Examples of cycloaddition in the experiment

A Diels-Ander reaction with a different approach with furans and furfurals is to produce p-xylene from 2.5-Dimethylfuran and acrolein[36]. The method was based on a 5 step concept strategy to explore the reaction from biomass to final PET polymer. From biomass are celloluse and glycerides extract, they react further in two different steps, cellulose become HMF and glycerides become glycerol by transesterification. HMF and the glycerides is exposed to hydrogenation to form 2,5-dimethylfuran and acrolein. This is the first step of the reaction, the second step the Diels-Alder reaction of 2,5-dimethylfuran and acrolein to form an intermediate that are further reacted to form p-xylene (step 3) , the study they made was focusing on step 2 and 3. The experiment were performed at -55°C, using a $Sc(OTf)_3$ (OTf = trifluro methanesulfonate) catalyst. The intermediary state was further reacted with an aqueous solution NaH_2PO_4/CH_3CN mixture at -55°C this mixture was heated to 0°C when H_2O_2 and $NaClO_2$ was added and it oxidated for 5h. The 7-oaxbicyclo[2,2,3]hept-2-ene is mixture with concentrated H_2SO_4 to form compound 3, compound 3 is reacted with a Cu_2O catalyst in 210°C for 4 h and p-xylene is formed. The yield of the experiment from DMF and acrolein to p-xylene was 34%.

Other researchers have found different ways. Paul J. Dauenhauer's[38] team have find a way to convert dimethylfuran to p-xylene using a Y zeolite. Dimethylfuran and ethylene are the reactants used in this experiment. DMF and ethylene are reacted with a zeolite catalyst over 200-300°C . The reaction that occur over the catalyst is a Diels-Alder reaction.

Current actors on the market

The chemical market is looking for a chemical compounds that are easy to separate, comes from renewable resources, and has a competitive price. Celloulse is expensive in comparison to lignin and hemicellulose . Furans from the hemicelloluse comes for a good price especially furfural, It is not as cheap as lignin but it's a product to a fair price. In June 2011 the DalimYebo Trading and

Development (Pty) Ltd, shipped furfuran for 2000$ per ton. In the latest 7 years DalimYebo has seen a raising price on the furfural. The furfural is a 6 carbon molecule and it has a reactive double bond (see figure 21). The researchers have later years seen the potential of furfural and studies have been made on furfural. One of the main reasons is that furfural can further react to form xylenes, where the most important one is p-xylene to produce PET (Polyethylene terephthalate).

Figure 21 shown the price over time of the furfural[39]

There are three operators that are trying to find different ways to replace crude oil based product and make them in to greener products. Each of the companies has developed their own method to produce greener products. The companies are Virent, Inc; Gevo, Inc.; and Anellotech, Inc.

Virent have a BioForming platform based on a combination of Aqueous Phase Reforming (APR). The process is using sugar sources and a wide variety of cellulosic biomass. It is possible to run this process on C5/C6 sugar derived as furfurals and other products from biomass. The reaction steps of the APR process are:

1. Reforming to generate hydrogen
2. Dehydrogenation of alcohols/hydrogenation of carbonyls
3. Deoxygenation reactions
4. Hydrogenolysis
5. Cyclization

The products from these reaction steps, alcohols, ketons, acids, furans, paraffins and other oxygenated hydrocarbons. The product can react over a modified ZSM-5 to produce high octane gasoline, Virent call that stream for BioFoirmate.

Gevo is one of the leading companies of renewable chemicals and biofuels. They have a method to make PET from isobutanol (the process is described in section 2.9). They call it a “drop-in” product that can replace petroleum based compounds. In 2011 Gevo had an agreement with Coca-Cola Company to create renewable p-xylene from plant-based isobutanol. With this technique Coca-Cola can develop their second-generation PlantBottle.

Anellotech has developed a clean technology platform to find substitute for petrochemicals from biomass. The core of this development is the CFP catalytic fast pyrolysis that Professor George Huber has developed. Anellotech have registered trademark called BTA, biomass to aromatics and with this they can produce green BTX, i.e benzene, toluene and xylenes.

The para-xylene that is produced today is coming from naphtha and a plant capacity of 1000 kta on a USGC basis, Anellotech's has a plant capacity 250 kta USGC basis on their demonstration plant. Gevo also have a capacity of 250 kta and Virent also.

The Conversion of renewable isobutanol to p-xylene

There is a recent patent describing a method where they have find a way to convert isobutanol to p-xylene[40]. The company that owns to patent is GEVO Inc. The method will be described in more detail below and an overview of the reaction steps I shown in figure 22.

In the method an Escherichia coli bacteria is modified to produce isobutanol[40]. The isobutanol is dehydrated with an γ-alumina dehydration catalyst (BASF AL-3996)[40]. The reactor temperature is 325°C and it operating in atmospheric pressure. The products in this process are isobutylene and water, and they are separated through a gas-liquid separator at 20°C. The yield of isobutylene was 95% isobutylene and the yields of 2-butene and 1-butene were 3.5% and 1.5% respectively[40].

The product stream is dried over molecular sieves, isobutylene is cooled to 20°C and condensed to liquid, and pumped through a fixed-bed oligomerization reactor packed with a ZSM-5 catalyst (CBV 2314)[40] . The reactor temperature is at 175°C and operating pressure is 5.1MPa. The product stream is around 30% unreacted butenes, around 69% isooctenes and 1% trimers.

Isooctane was distilled to remove trimers and tetramers, and then the stream is fed with nitrogen diluent gas to a fixed bed reactor containing a chromium oxide doped alumina catalyst (BASF D-1145E 1/8"). The reactor is operating under atmospheric pressure and a temperature of 550°C. p-Xylene is produce in the last step of this process.

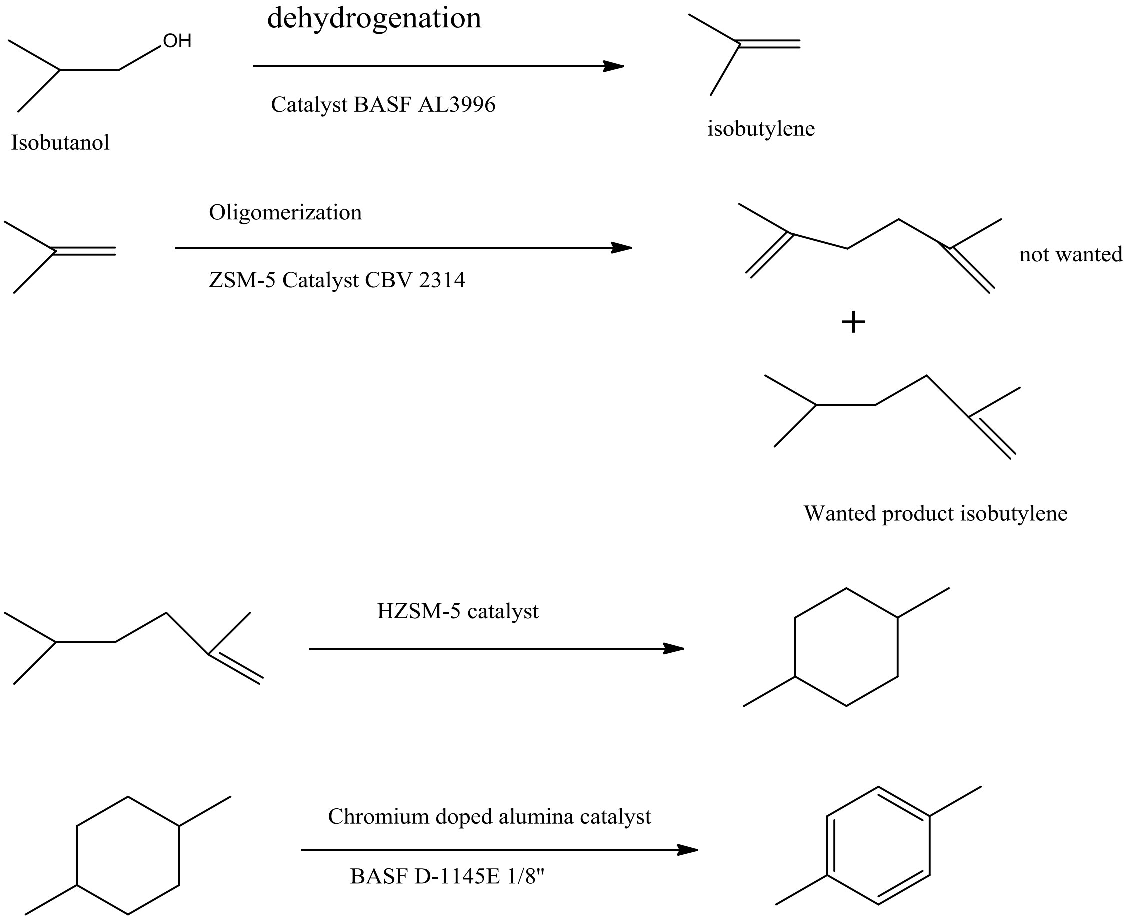


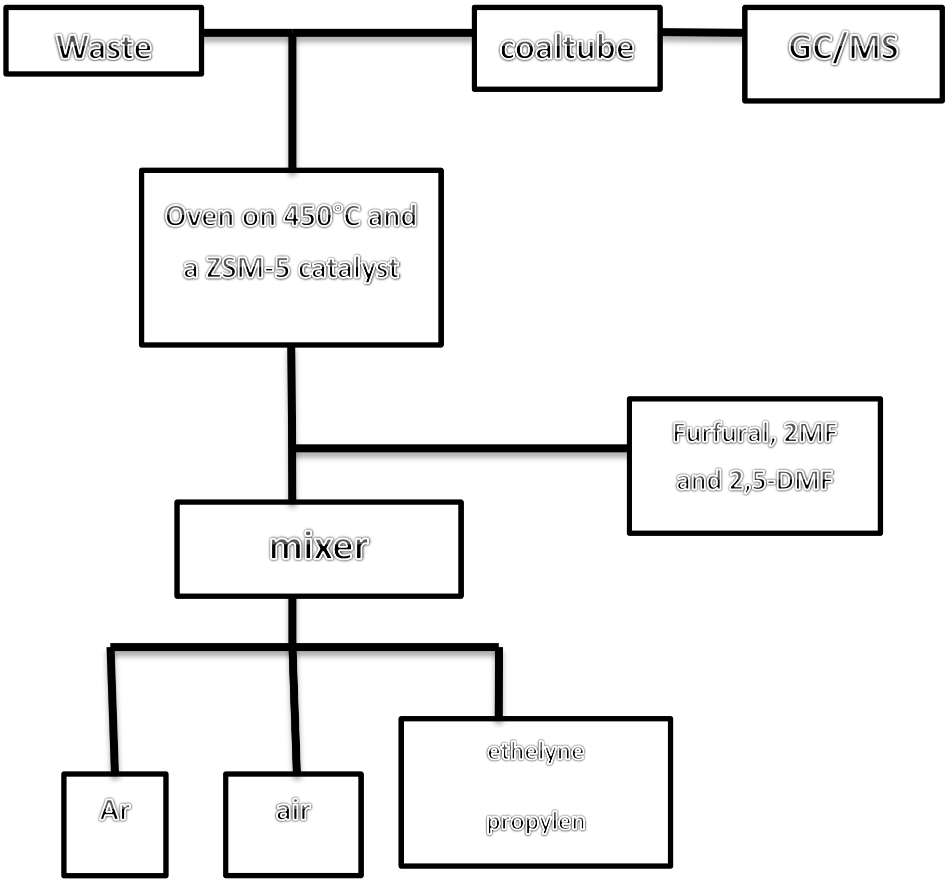
Figure 22 shows the interpreted way of the patent pathway from isobutanol to p-xylene

6 Experimental conversions of furans and olefins to aromatics

One of the more interesting pathways to renewable aromatic compounds is from hemicellulose via furans to form products. The intentions with these experiments were to verify literature results and gain insight into this kind of conversion. The reaction studied was the Diels-alder reaction between propene and 2-methylfuran.

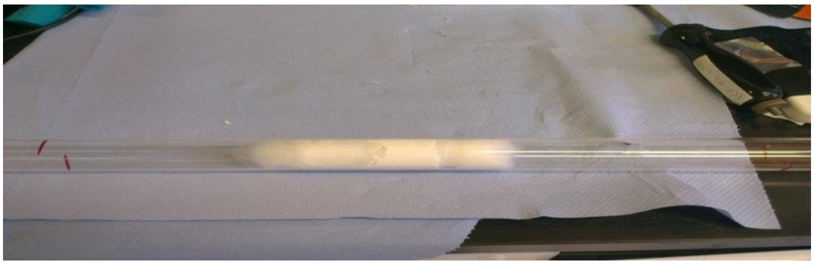
6.1 Experimental setup

The reactor for the experiment is a continuous flow fixed bed reactor with a ZSM-5 zeolite catalyst from Alfa Aeser. An overview of the system is shown in picture 1.



Picture 1, shows an overview of the whole system.

The reactor is tube-oven from Heraeus fitted with a quarts tube filled with the catalyst. (see picture 2)

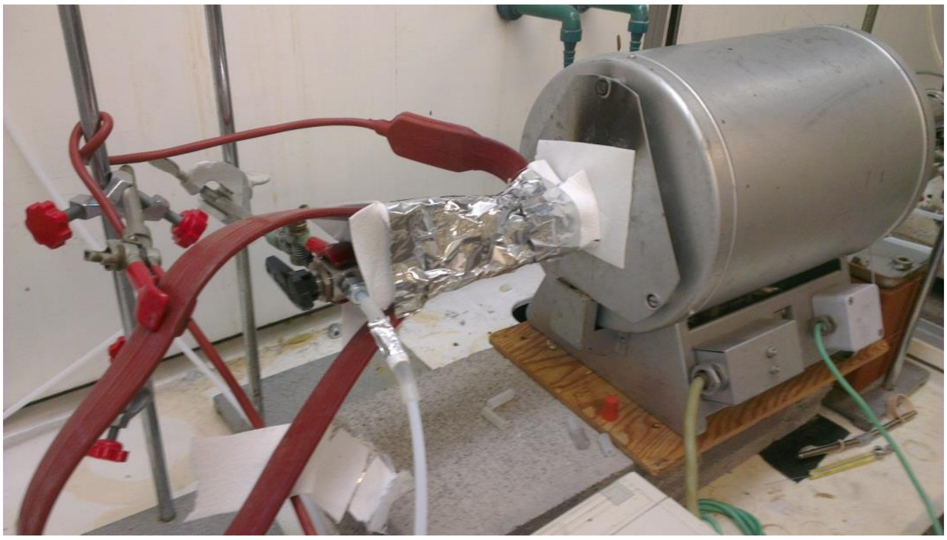


Picture 2, the zsm-5 catalyst is held in place with quartzwool inside a quartzglass tube.

The gases used in the experiments were propene, argon and air. The propene and argon were both supplied by Air Liquide. The propylene gas mixture is 10% propene diluted with argon. The argon and propene are connected to mass-flow regulators and the gas flow was controlled by computer, and the air is connected the mass-flow regulators that is manually controlled. Nitrogen is used as a safety gas to be flushed if the tube cracks. All gases and liquids are supplied via a special stainless steel manifolds fitted to the quarts tube (picture 3).

Picture 3 shows how the gases are connected, air on the top, the connection with the red strap is the argon and propylene inlet, the last one is the nitrogen.

The chemicals used in the experiment were 2-Methylfuran (Sigma-Aldrich) and furfural (Sigma-Aldrich). They were pumped in the reactor with a syringe pump with its outlet over the boiling point of the chemicals. When the reactants have passed the catalyst, the outgoing gas is coupled to adsorbent tubes (charcoal) intended to trap the reactions product for analysis. The quarts tube's outlet valve was heated to 80 °C to prevent condensation of formed products (see picture 4).



Picture 4 showes how the gas is trapped in the coaltube

The rector gas flow was 44ml/min and the furans were pumped at 16 µl/min. This yields a 1:1 stoichiometric relation between the furans and propene. The catalyst temperature was 450°C. To activate the zeolites, delivered in an ammonium form, calcination was performed. The purpose was to evaporate ammonia and establish the acid form of zeolite. This was made by heating the catalysts for 30 minutes with airflow. The catalysts were regenerated (from coke) after each reaction using air at 450 °C. See a schematic picture of the system below.

A recovery test was run on the system, in which 70mg m-xylene was injected in the system and the gas was only argon. The catalyst will isomerize the m-xylene so the calculation is done in total amount of xylenes. 40mg xylenes were found and that shows that the system works. No further optimize test runs was made. The results are thereby multiplied by a factor 1,75 (the injected compound/the outlet compound) to correct for the low recovery. The unit of the results are reported in ortho-xylene units.

6.2 Chemical analysis

The adsorbent tubes fitted on the outlet of the reactor were analyzed to quantify the content of products. Charcoal tubes were used to be able to trap the desired molecular range (benzene- xylene). The tubes were fitted with two serial layers of coal, both were analyzed separately using ultrasonic extraction in dichlormethane (5 min), followed by centrifugation (10 min). To the extracts were added an internal standard (chlorobenzene) and this was injected into a GC/MS system. The separation was performed using a DB5-MS 25m×250µm×0,25µm column and detection using a quadrupole MS with EI- ionization. Calibration of the GC/MS system was performed with o-xylene in the range (1.2-12 ml/ml) figure 22. The response factors of the other xylene isomers were identical, verified with reference mixtures (BTeX mixture from Sigma-Aldrich 2000ppm each in methanol). Toluene and other products are quantified in o-xylene units. Unknown substances were identified using the NIST MS library.

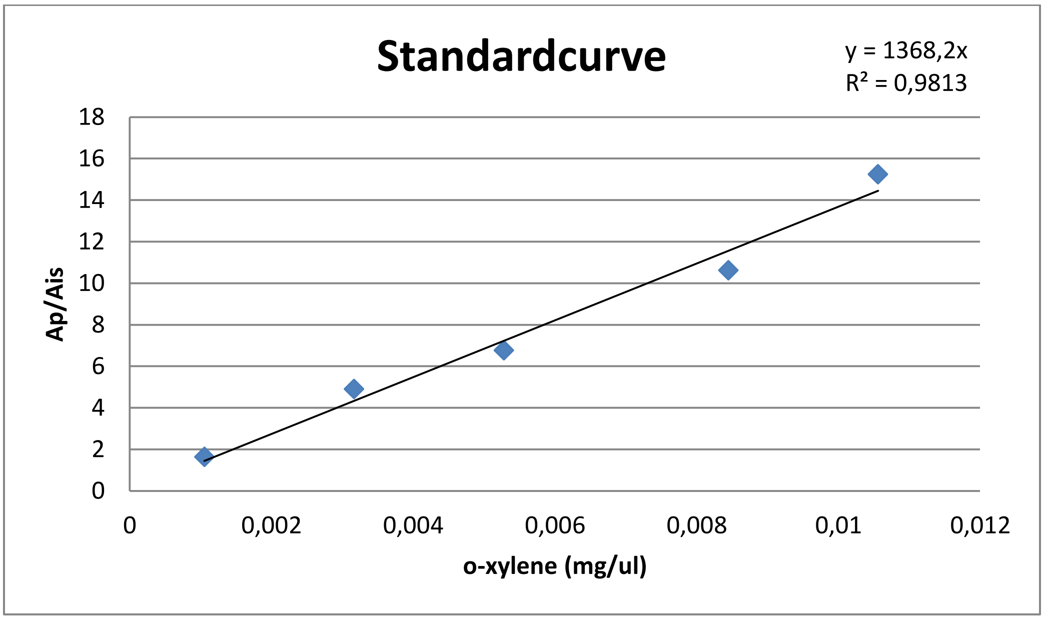


Figure 23 Standardcurve of o-Xylene that were used in the calculation of this experiment

To characterize the amount of coke formed during the experiments the outlet gas from the calcinations were sampled into gas sampling bags and further analyzed with a GC/TDC to quantify the CO and CO_2.

6.2.1 List of experiments

Reactant 1	Reactant 2	Gas flow (ml/min)	Liquid flow (ul/min)	Catalyst
Argon	-	44	-	No
Propene	-	44	-	Yes
Argon	2-Methyl furan	44	16	Yes
Argon	2-Methyl furan	44	16	No
Propene	2-Methyl furan	44	16	Yes (pellets)
Propene	2-Methyl furan	22	16	Yes (pellets)
Propene	2-Methyl furan	88	16	Yes (pellets)
Argon	2-Methyl furan	44	16	Yes (powder)
Propene	2-Methyl furan	44	16	Yes (powder)
Argon	Furfural	44	16	Yes (powder)
Argon	Iso xylene	44	16	Yes (powder)
Propene	2-Methyl furan	44	44	Yes (powder)

The last experiment with blue strip is an over-time experiment to see when the catalyst breaks.

6.2.2 Results

It was showed when the 2-MF was injected through the system without catalyst the result was that 2-MF hade not forms any BTeX. The chromatogram shows only 2-MF was detected (see figure 24).

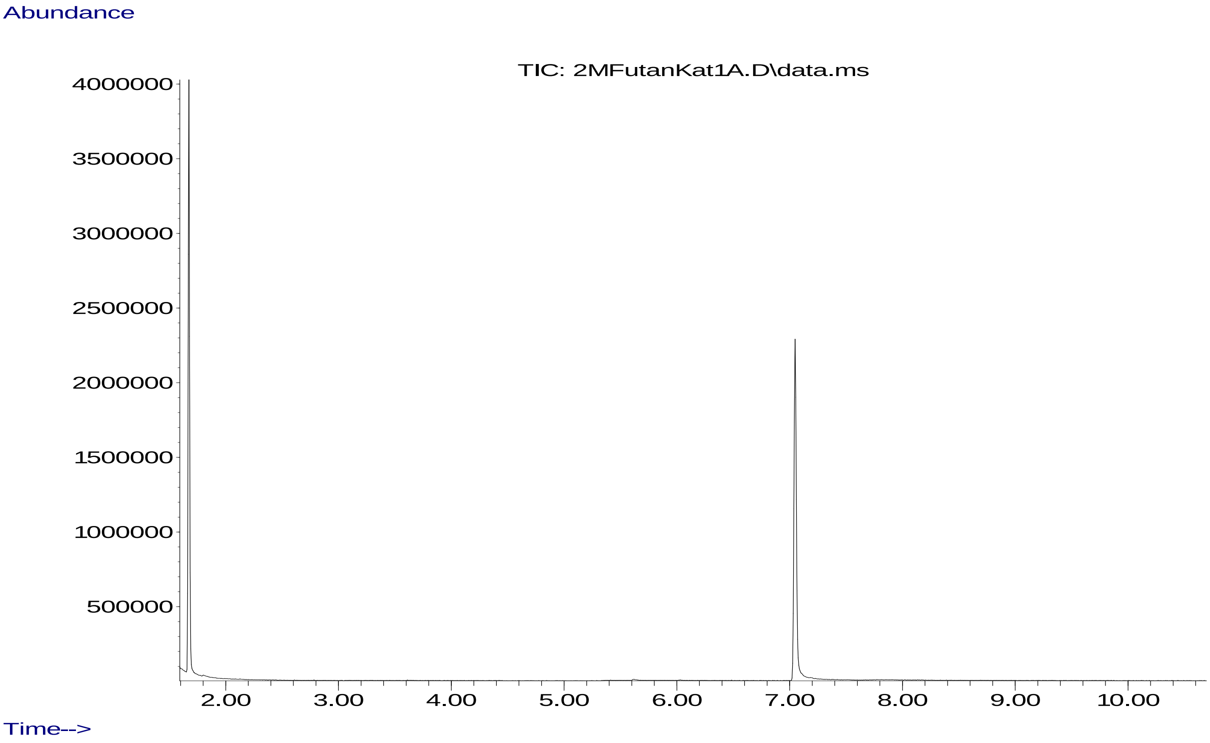


Figure 24 Expermental run with only 2MF without catalyst

The peak from the chromatogram shows that after 1,6 min 2MF is detected and at 7min the internal standard is detected. When the catalyst in added to the system the 2-MF is cracked into different molecule structures as is showed is figure 25

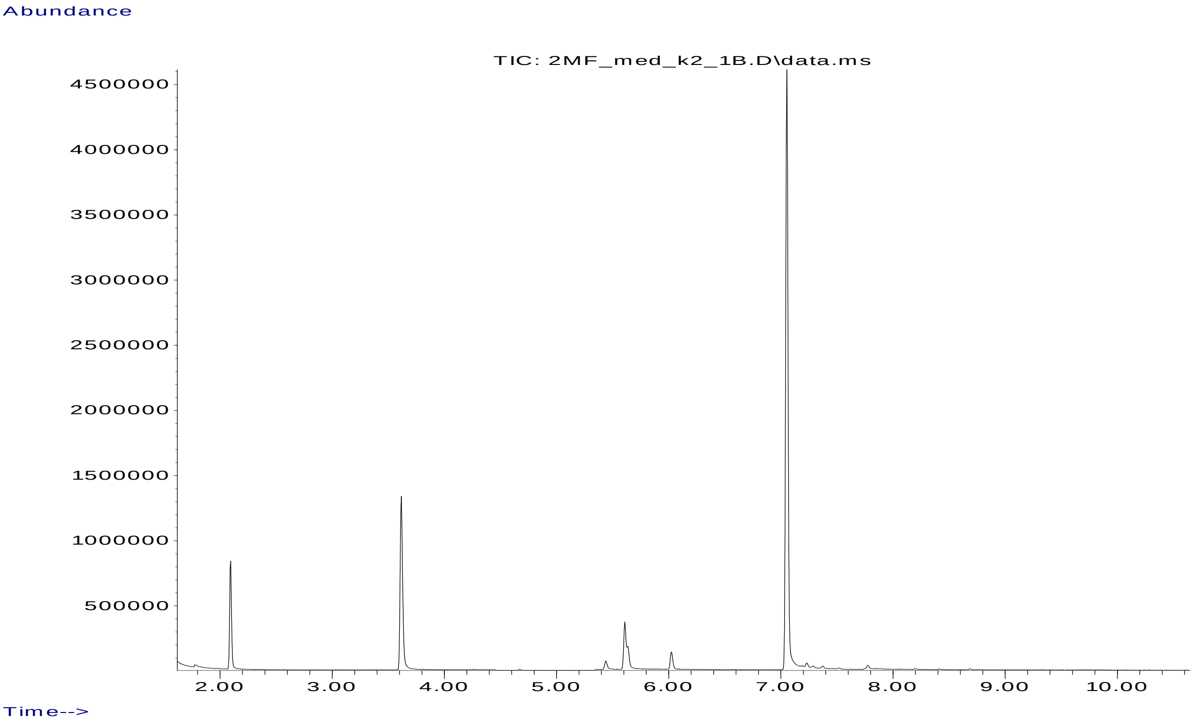


Figure 25 Experimental run 2MF with catalyst

The peak on 7min is the intern standard. As the chromatograph shows, 2-MF has reacted or being crack by the catalyst. The chromatograph shows that, at 2.1 min the benzene is shown, 3.8 min the compound toluene is detected and around 5.5min – 6.1min, ethyl-benzene, meta-xylene, p-xylene and o-xylene are detected and they have separated in that order. Only the catalyst and 2-MF together can form BTeX compounds but the yield is low. Over this sample series the average value is 15.1 mg BTeX of adding 70mg 2-MF. In order to find the reaction speed in the catalyst tests with two different argon flows were performed, one was on 22ml/min and the other one was 88ml/min, the result was that between 22, 44 and 88 ml/min there no different and because of the mole ratio between the reactants 44ml/min was chosen because it had a mole ratio on 1:1.

Then the propylene was added to the system and more reactions occurred and the yield increases (see figure 21).

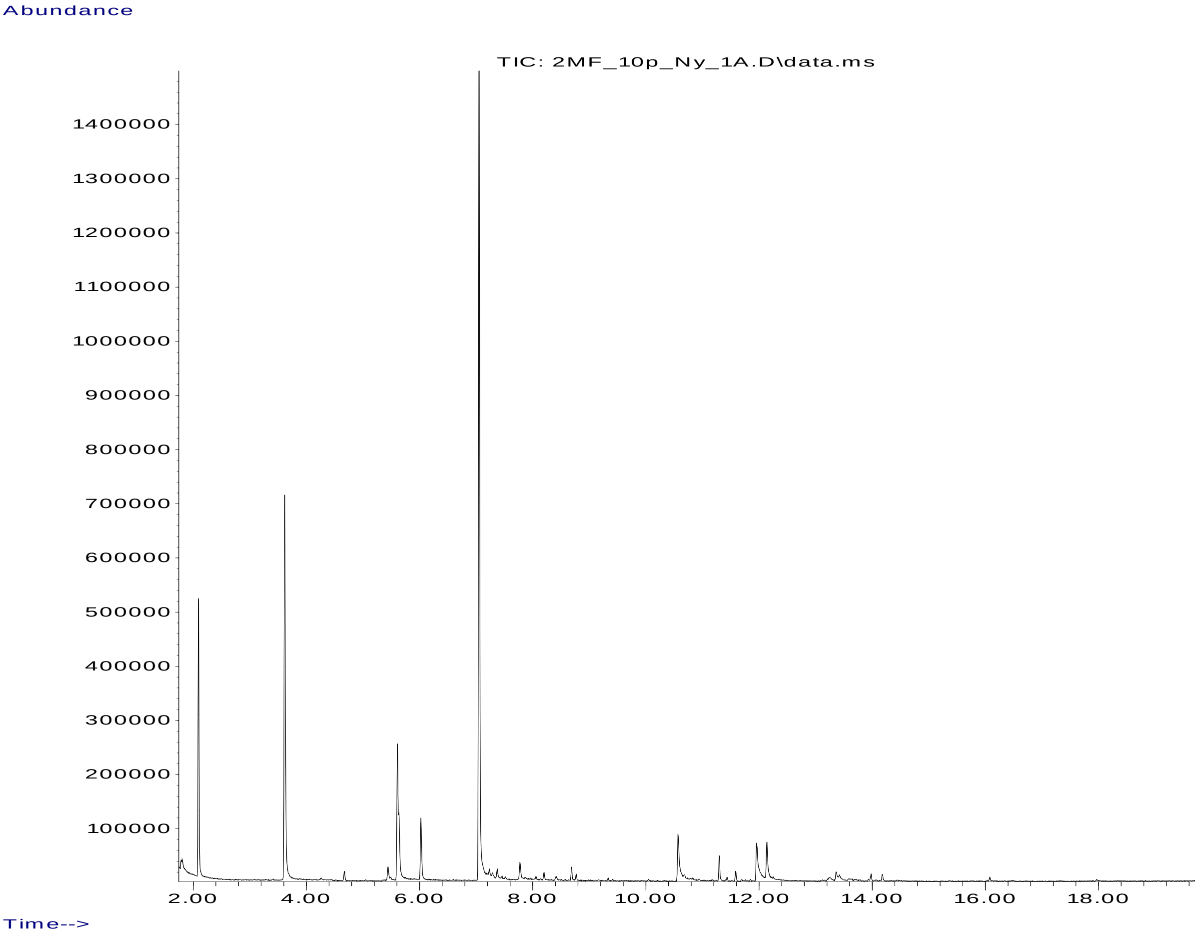


Figure 26 Chromatograph with 2MF and 10% propylene over a ZSM-5 catalyst

The BTeX compounds are before the intern standard and the compounds at 8min and forward are (see figure 22) detected on the GC-MS.

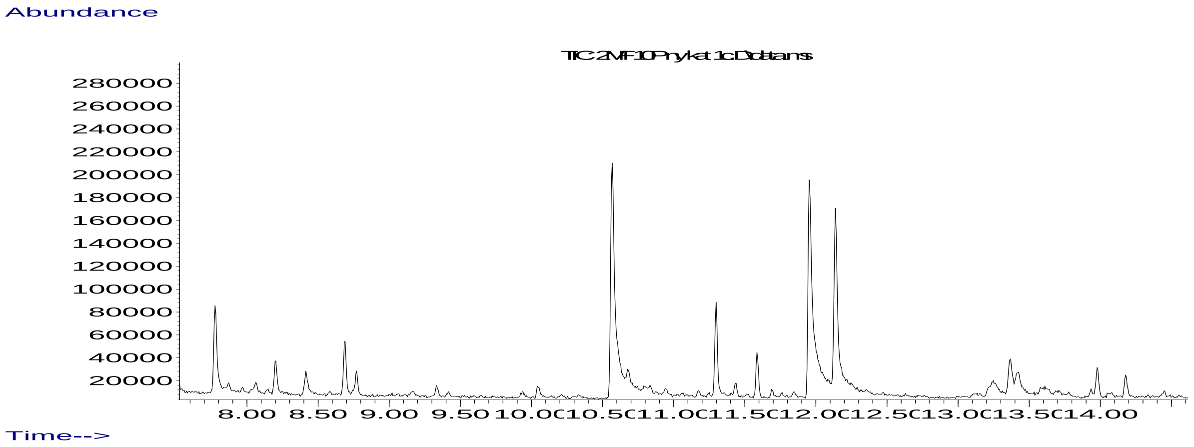


Figure 27 After 8 min in the 2MF and 10% propylene experimental run over a ZSM-5

The peak at 7.8 is 3-methylbenzene the peaks after has not been detected however they can be complex structure the GC-MS gives substance probability on 0.5%. At 10.5min naphthalene is detected and at 12.00-12.50 isomer of methylnaphthalene is detected. In this run series we got average 29mg and the total amount of products and the BTeX compounds was around 18mg.

The experiment shows that BTeX was the dominate products. The yield with only a catalyst is low but if propylene is added the selectivity increase with 350%.

The other experiment that was performed was using furfural over the ZSM-5. The catalyst the experiment was similar to the 2-MF. In the chromatography (see figure 23) is showed that BTeX was some of the products.

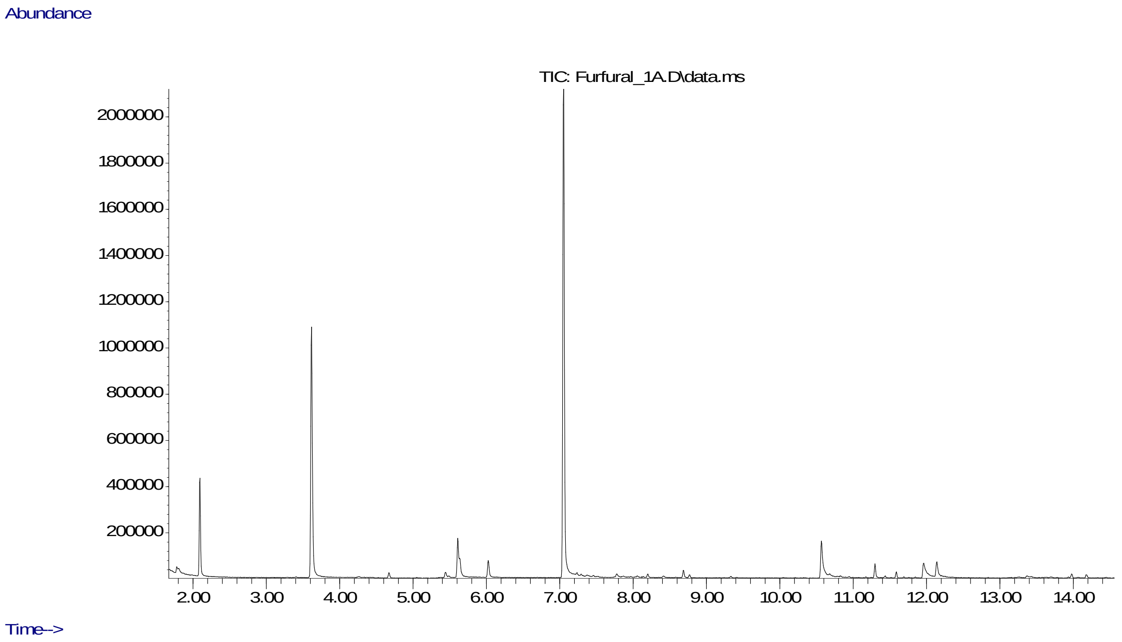


Figure 28 Chromatograph of furfural over a ZSM-5 catalyst

From the experiment, it was shown that BTeX compounds were gained, where toluene was the most dominant one. The average of the total amount detected was 26.2mg and the BTeX amount was 22.7mg. This experiment was performed without the propylene.

The whole result series is showed in table 3 below.

Chemical compound (yield)	Blank	2MF with catalyst	2MF with 10% propylene and catralyst	Furfural with catalyst
Benzene	<0,005	5,5	17,8	9,9
Toluene	<0,005	11,9	33,6	16,8
Ethylhexane	<0,005	0,1	0,9	0,8
Ethylbenzene	<0,005	0,5	0,6	1,5
m-Xylene	<0,005	1,8	5,0	1,8
p-Xyelene	<0,005	1,1	3,0	1,1
o-Xylene	<0,005	1,0	3,0	1,0
trimethylbenzene	<0,005	0,2	0,9	0,2
naphthalene	<0,005	<0,005	3,2	3,2
Methylnaphthalene	<0,005	<0,005	2,6	1,5
Methylnaphthalene	<0,005	<0,005	2,2	1,5
Methylnaphthalene	<0,005	<0,005	2,2	1,5
dimethylnaphthalene	<0,005	<0,005	0,5	0,4
dimethylnaphthalene	<0,005	<0,005	0,6	0,1
dimethylnaphthalene	<0,005	<0,005	0,5	0,2
Total sum BTeX	<0,005	21,7	62,9	32,0
Total sum	<0,005	21,9	76,5	41,2
Estimated experimental standard deviation is 25%				

Table 3 the experimental runs with different setups

6.3 Discussion

As the results show, there is a way to make green aromatics from both 2MF and furfural. The yield are approx. 50 % when propene is included in the transformations and 15 % when excluded. This suggests that the expected Diels-Alder reactions occur and improves the BTeX yield for 2MF. However, the BTeX distribution pattern is similar with and without propene. This suggests that the reaction products from the Diels-Alder reaction are transformed in the catalyst to form products similar to the products formed without Diels-Alders reactions. Results from the propene experiments also show that different types of methylnaphthalenes, dimethylnaphthalenes and etylhexane are found. Similar substances has been found, as intermediates ,by other groups studying the mechanism for m-xylene isomerization over ZSM-5[41]. The observation that furfural is transformed to BTeX without Diels-Alders reactions suggests that cracking mechanisms are important. This opens up for the use of less specific/purified substrates in future development.

The system was searched for leaks before the experiment was performed, and the gas flow was taken with bubble regulator before and after the run. One major problem with the system was that the mass flow regulators had wrong gas calculations. The gas in the experiment was argon and 10% propylene and argon but the mass flow regulator was calculated for oxygen (O_2) and nitrogen (N_2). The mass flow regulators were for 0-100ml but it preformed badly at low flow rate. In the 22l/min experiment was the flow rate difficult to keep stable but if there had been more stable the result maybe would have been different.

The result in table 3 shows that 2MF with only catalyst produce BTeX but in a small amount. It is shown that without propylene BTeX is produced so if the system is more optimize it can lead to better yield. This shows that it is possible to make green BTeX without using propylene.

An experiment over time was made to see if the catalyst will break at some point (figure 24). It was shown, that the highest yield was obtained after 2 hours, followed by a decrease. And that after 8 hours not much more was produced. This run was only performed ones and the experiment had some problem with the syringe because it broke unto the middle of the experiment. So the experiment was performed 4 h the day the syringe broke and continued the day after with the 4 h that remain on the experiment.

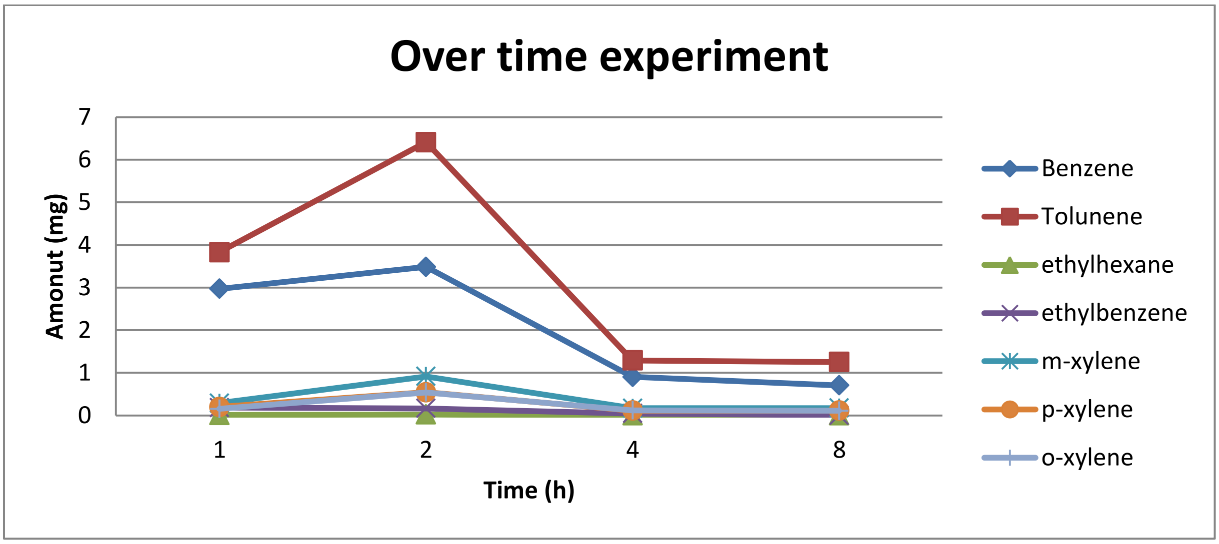


Figure 29 2MF and 10% propylene reacted over a ZSM-5 Over time to see then the catalyst fail to react more products

Another problem was that a beige wax was produce and it was runned on the GC-MS and was not able to be determined. It was round on the IR it showed that the functional groups was aliphatic of the wax (see figure 25).

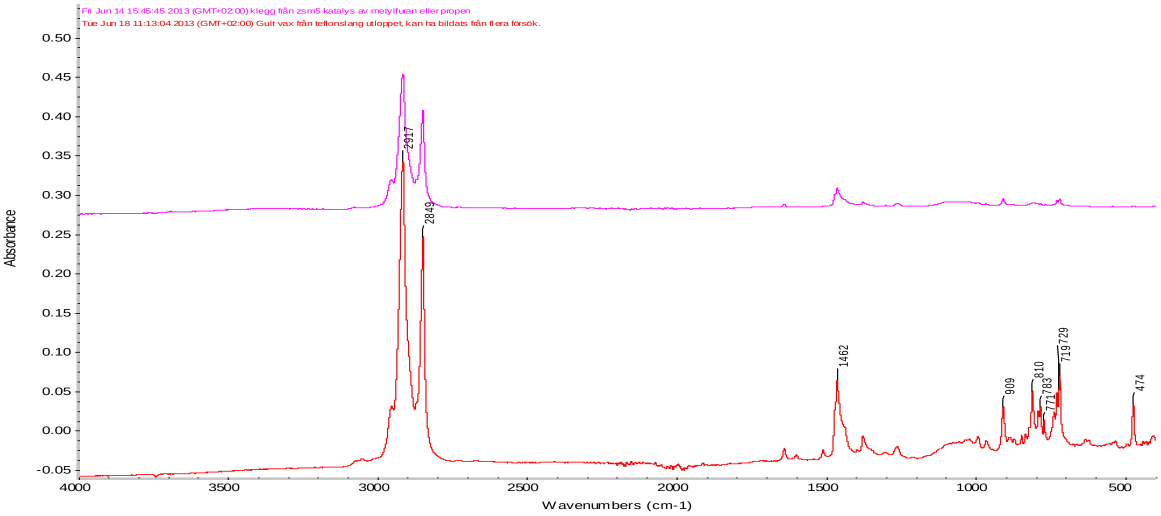


Figure 30 The beige wax on a IR-spectra

A picture was taken on the beige wax see Figure 31

Figure 31 Shown the beige vax that was produced under the experment

When the sample was taken there was a green unknown condensate inside the glass and the GC-MS detected it as naphthalene.

Then the gas was trapped on the coaltube there were some condense inside of the teflontube (the outlet stream from the glass tube), the condensate was not analyst. The problem could have been avoided by having better heating equipment. The heat tape was not the best choice, and maybe a heating tube with a regulator would have been a better option. The heat over the whole system was not preforming well. This could mainly affect xylene, as the boiling temperature of this compound is 139-144 °C. The glass tube cooled fast at the outlet of the reactor because it was hard to put heat tape there. The heat tape would have been damage from the heat from the reactor. The temperature out from the reactor decrease fast from 450ºC to 80ºC at the outlet and some gas condensate.

When the system was calcineted air was flowing through the system and the flow was around 100ml/min but sometimes the air bag did not fill up with air and the flow rate at 100ml/min was not correct all. The time the air bag experiment was performed but the total air in the bag was not calculated so the result is in percent of the total amount in each bag.

The meta-, and para-xylene peaks were integrated manually since they were hard to separate.

7 Conclusions

Furans and lignin have a great potential to form high-value chemical compounds. This study has, however, been focused on the furans.. The literature study found several activities concentrated around the conversion of polysaccharides (cellulose/hemicellulose). Some activities are still in the laboratory and some has moved on to demo scale. The most promising technologies are based on hemicellulose hydrolysates (furanes), transformed to xylenes supported by zeolite catalysis. The focus for many researchers is the production of p-xylene as a start material for PET polymer production. Experiments conducted in this study were based on the transformations of furans to xylenes. They show that it is possible produce green aromatic hydrocarbons from both 2-methylfuran and furfural. The yield is approx. 50 % when propene is included in the transformations and 15 % when excluded. This suggests that the expected Diels-Alder reactions occur and improves the BTeX yield for 2-methylfuran.

However, the BTeX distribution pattern is similar with and without propene. This suggests that the reaction products from the Diels-Alder reaction are transformed in the catalyst to form products similar to the products formed without Diels-Alders reactions. It was also shown that furfural is transformed to BTeX without Diels-Alders reactions. This suggests that other mechanisms than Diels-Alder (cracking mechanisms) are important. If this is the case, start substances for the production of green BTeX can be less specific than previously thought. For example furfural and 2-methylfuran gives the same products and yield. Future work could focus on conversion of start materials with origin somewhere between the hemicellulose polymer and highly purified furanes.

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