CHALMERS
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Thermochemical textile recycling

Investigation of pyrolysis and gasification of cotton and polyester

Master's thesis in Innovative and Sustainable Chemical Engineering

JULIA RITTFORS

Department of Space, Earth and Environment
CHALMERS UNIVERSITY OF TECHNOLOGY
Gothenburg, Sweden 2020

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Supervisor: Isabel Cañete Vela, Department of Space, Earth and Environment
Examiner: Martin Seemann, Department of Space, Earth and Environment

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Department of Space, Earth and Environment
Division of Energy Technology
Chalmers University of Technology
SE-412 96 Gothenburg
Telephone +46 31 772 1000

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Abstract

With a rising textile consumption worldwide comes in increased flow of textile waste. The existing recycling methods, mechanical and chemical recycling, are insufficient in many ways, and therefore only a small share of all textile waste is utilized for making new textiles or other materials. It is therefore of interest to investigate additional recycling methods, in this thesis gasification and pyrolysis are considered.

The first part of the report aimed to investigate mechanical and chemical recycling, by identifying suitable feedstocks for these methods, as well as their major limitations. The conclusion was that both methods solely can handle streams consisting of only one fiber type, and that this limits the ability to scale up the recycling, as the textile waste found in municipal solid waste, MSW, is exceptionally heterogeneous.

Secondly the report aimed to investigate the possibility to recycle textile waste found in MSW by thermochemical methods. Applications for the gas, liquid and solid product was evaluated and the expected composition of the gas and liquid were investigated by reviewing existing gasification and pyrolysis experiments, as well as by performing new tests of cotton and polyester pyrolysis. As the oxygen content in both cotton and polyester is relatively high, the existing experiments reviewed showed that the dominating specie in the gas produced will be CO_2, which lowers the quality of the gas. The focus of the thesis was therefore to recover mono-aromatic compounds from the pyrolysis oil, as these are desired in the chemical industry and can be utilized when manufacturing several chemical compounds.

Keywords: Textile waste, textile recycling, gasification, pyrolysis, thermochemical recycling, pyrolysis oil, cotton, polyester.

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Julia Rittfors, Gothenburg, June 2020

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Introduction

1.1 Background

The textile industry plays an important role in the world economy, employing more than 300 million all over the world, and annually more than 100 million tonnes of textiles are produced[1],[2]. Textile consumption is however strongly associated with many negative environmental impacts, connected to both the production and user phase. Cotton, which accounts for approximately 25% of all produced textile fibers, requires large amounts of water, fertilizers and pesticides when cultivated, which causes ground water depletion, and contamination of soil and water[3]. Around 50 % of all fibers produced are polyester, which is a synthetic fiber usually made from fossil oil[2]. Besides impacts related to the fiber production, manufacturing of fabric and finished textiles, as well as the use of textiles is energy and electricity demanding, which increases the carbon footprint even further[3]. Every year the textile industry consumes 98 million tonnes of fossil resources, and is responsible for emitting 1.2 Gt CO_2-eqv, which is approximately 3% of the total emissions of green house gases[2].

Over the last years the textile consumption has increased rapidly, and a frequently used term in the textile and clothing industry is "fast fashion". It is used to describe the trend seen within the fashion industry, where the price of garments is continuously decreased and brands release new collections and garments as often as every week. This encourages consumers to constantly purchase new clothes, and garments are on average used less times[4][2]. This together with a growing middle class world wide has made the clothing sales increase drastically, between 2000 and 2015 the consumption has doubled[2].

With an increased consumption and and decreased utilization comes a rising flow of textile waste, but the recycling rate is very poor. Approximately 13% of all waste is being recycled in some way, but less than 1% is utilized for producing new textiles[2],[4]. The majority of all waste is disposed in the Municipal Solid Waste (MSW) and is then incinerated or sent to landfill.

Both sustainable consumption and waste management are topics that are being widely discussed. The United Nations has formulated 17 goals to achieve a more equal and sustainable society, namely the "Sustainable Development Goals". Goal 12; "Responsible consumption and production" aims to minimize the effect that material consumption has on water, air and soil as well as promoting a more efficient use of resources[5]. This goal is strongly related to textile consumption and the waste that is created, as a more efficient utilization of the waste would enhance a more sustainable production chain since less virgin material would be required.

The European Union has created a waste hierarchy in order to illustrate how to best prevent waste and increase resource efficiency, see Figure 1.1 below. This hierarchy states that the best ways to minimize waste is simply to prevent it by consuming less and re-using material. These options are followed by material recycling, which is done by recycling of monomers and polymers in the material. As mentioned previously, the majority of all textile waste is today incinerated of sent to landfill, which are the least favored options.[6]

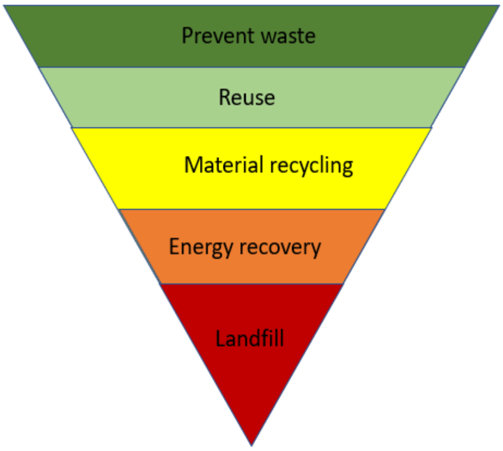


Figure 1.1: The European Union's waste hierarchy.

In Sweden every person consumes 13.9 kg textiles annually and 7.5 of this is disposed in the MSW, and then sent to incineration. The Swedish Environmental Protection Agency,Naturvårdsverket, proposes that this number should decrease by 60% until 2025 and that 90% of all textile waste should be collected separately[7]. To reach this goal, as well as the goals set up by the EU and the UN, both political and technical solutions will play an important role. There will be a need for systems to collect and sort textiles, and for recycling methods that can handle an exceptionally heterogeneous stream, as textile waste consists of a large variety of fiber types, chemicals and other materials, such as metal and plastic. Today two types of recycling methods exists, mechanical and chemical recycling. However, these methods face many challenges, such as issues with handle a heterogeneous waste stream and a decrease of the material quality. This will be described further in Chapter 3. Due to their insufficiency there is a need to explore and evaluate new recycling methods.

The method being investigated in this thesis is thermochemical recycling. This method has the potential to handle heterogeneous carbon-containing material and convert it into monomers that can be used for many purposes, such as for fuel production and as building blocks in the chemical industry[8].

1.2 Aim

The main purpose of this thesis is to explore how thermochemical recycling can contribute to an increased textile recycling. Firstly the report aims to gather information concerning existing recycling methods, i.e mechanical and chemical recycling. The aim will be to identify their strengths and weaknesses, by investigating which fiber types that are currently suitable for these methods and which are not, and why. This will be used to assess the possibility and limitations to expand the current textile recycling so that a significantly larger share of all waste can be recycled. The objective is also to explore which end products that are generated in the two processes, in order to assess their possibility to contribute to a more circular textile production chain.

Secondly, the aim is to investigate the possibility to use gasification and pyrolysis as alternative recycling methods. Although gasification and pyrolysis are well researched topics, and many studies and experiments have been performed on gasification and pyrolysis of e.g. biomass and municipal solid waste (MSW) very little literature exists on thermochemical treatment of textile waste. The aim is to identify and cover this knowledge gap, by investigating the feasibility of using gasification or pyrolysis as a recycling method. More specifically, this part of the thesis aims to:

- *Investigate what the product stream from gasification and pyrolysis of textiles in MSW will look like.* This includes the yield of gas, liquid and solid product as well as the composition of the gas and which components to expect in the liquid product. This will be done by reviewing existing literature on gasification and pyrolysis on both textiles and similar materials, as well as by performing new experiments.
- *Identify and describe different end uses for gasification and pyrolysis products.* This includes the possible use of both the gaseous, liquid and solid product, and the purpose is to evaluate which end uses that are possible for a product stream that is characteristic for the one from thermochemical treatment of textiles.This will be done by studying literature on the use of gasification and pyrolysis products from other feedstocks.
- *Investigate the feasibility of the end product that is chosen as the best option when using textiles as a feedstock.* A method to assess the feasibility of the suggested recycling path will be developed, focusing on the circularity and to what extent the material is utilized for products of high value.

2

Methods

In the following chapter the literature study of existing recycling methods and experiments on pyrolysis and gasification will be described, as well as the experimental set-up.

2.1 Literature Review

The literature review aimed to gather information regarding two focus areas; existing recycling methods and thermochemical treatment of textiles.

When studying literature about existing recycling methods the focus was mainly to gather information regarding their strengths and weaknesses, in order to evaluate which textile steams are suitable for these methods and which requires some other recycling method. The review also aimed to quantify the flow of textile waste that has little potential to be recovered by existing methods as well as exploring the composition of this stream in terms of fraction of different textile fibers and what chemical structures that could be expected.

Lastly the literature study aimed to review existing experiments on gasification and pyrolysis of textiles, in order to gather information about what syngas quality to expect and which valuable compounds that could be retrieved in tar or pyrolysis oil. In addition different end-uses of the products from gasification and pyrolysis was investigated. The literature that was reviewed should cover thermochemical treatment of cotton or cellulose and polyester of PET. The paper or study should also include the yield of gas, pyrolysis oil and solid product, as well as quantifying the yield of different tar species.

2.2 Experiments

The pyrolysis experiments were conducted in a lab scale fluidized bed reactor, which had a height of 1.27 m and an inner diameter of 79 mm. The gasifying agent, which in this case was N_2, was introduced at the bottom of the reactor. This gas was fed through a plate with holes, that would distribute the gas and enable an even fluidization of the bed. Helium was used as a tracer gas, and was fed to the reactor at the bottom as well. The fuel was manually fed from the top by dropping the desired amount of textile sample into the reactor. The produced gas would exit the reactor at the top. A gas sample was taken with a syringe from the side of the reactor. The sample was pulled through a packed column where the tars were extracted by letting them condense and adsorb on a solid material, while the gases passed the column and were collected in a separate gas bag. The reactor set-up can be seen in Figure 2.1.

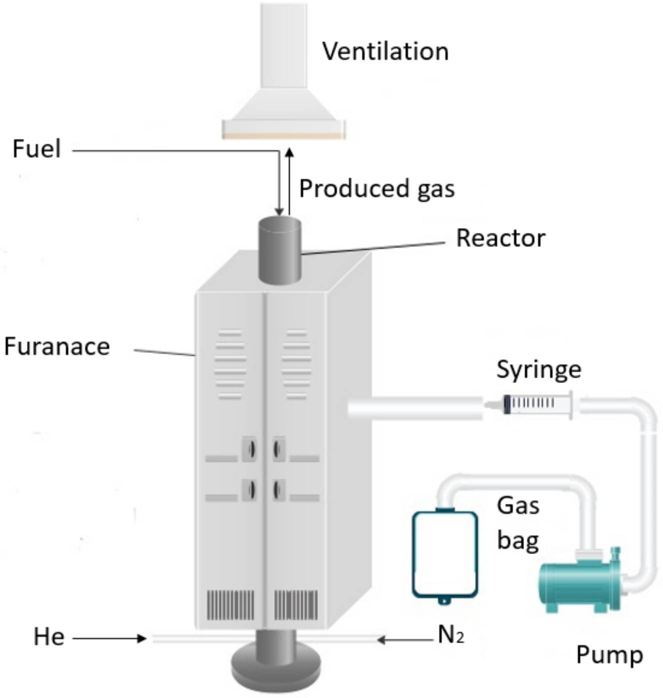


Figure 2.1: Reactor set-up for the experiments performed

Three different textile samples were tested in this experiment; pure cotton, pure polyester and a mixed fabric consisting of 50% cotton and 50% polyester. All fabric samples originated from used clothes and the pure polyester sample and the mixed fabric was dyed. Before being fed to the reactor the fabrics were cut into smaller pieces and then compressed into pellets, with a weight of approximately 0.2 g each. For each experiment 2 grams of pellets was used. The cotton and polyester samples were pyrolyzed at 400°C and 500°C and for the mixed fabric two runs were performed at 500°C. The nitrogen and helium flows were constant throughout all experiments. The conversion time varied for all experiments, ranging between 200 and 600 seconds. The conversion was assumed to be complete when no gases could be seen at the top of the reactor, which is where the produced gas would exit. The process conditions for all experiments, as well as the order of experiments is summarized in Table 2.1.

Fabric	Temperature	Residence time	Nitrogen flow	helium flow
Cotton	400 °C	300 s	5 l/min	0.05 l/min
Polyester	400 °C	600 s	5 l/min	0.05 l/min
Cotton	500 °C	200 s	5 l/min	0.05 l/min
Polyester	500 °C	200 s	5 l/min	0.05 l/min
Mixed 1	500 °C	200 s	5 l/min	0.05 l/min
Mixed 2	500 °C	200 s	5 l/min	0.05 l/min

Table 2.1: Process parameters for all experiments

Sampling of the produced gas and pyrolysis oil continued throughout the whole conversion time. The products can be divided into non-condensable and condensable gases; i.e. tars. The non-condensable gases, which includes H_2, CO, CO_2, CH_4 and C2-C3 hydrocarbons were collected in a sample bag and analyzed using micro gas-chromatography (µ-GC). The condensable products includes aromatic and phenolic species, which are collected by Solid Phase Adsorption, SPA. In SPA tars in gaseous form are condensed and adsorbed on a solid phase in a packed column. The tars are then desorbed by a solvent before being analyzed.

The tars collected were separated using gas chromatography (GC). In GC a column is packed with a polar stationary phase, often solid particles, and a mobile phase consisting of an inert gas. The compounds are separated based on how strongly they interact with the stationary phase. Polar substances will have a stronger interaction with with the stationary phase and therefore have a longer retention time. As the boiling point of a substance is related to the polarity, molecules with similar boiling points will have similar retention times.

The separated tars were the quantified using Flame Ionization Detection, FID, where the tar sample passes through a flame and the substances becomes ionized. The ions generates an electric current that is proportional to the concentration of molecules in the sample treated.

The outcome of the GC-FID analysis is a diagram where the detected species are represented as peaks, with response height on the y-axis and retention time for the species on the x-axis. From the retention time the species can be known and the area of each peak is proportional to the concentration of the species. In this case the aromatic components consisting of 1-4 rings could be detected. The substituent groups that could be seen was primarily alkyl groups (-CH_3) as well as hydroxy groups (-OH), as the retention time for these species was known. For some species present in the pyrolysis oil the retention time was unknown, and the components could therefore not be specified, although the concentration could be calculated, as the peak was seen in the diagram. Compounds that could be measured but not specified include aromatic species with carboxyl groups.

One important concept being used in FID is response factor. This is the ratio between the signal from a compound and the actual concentration, where the signal usually is the peak area generated, see following equation;

$$\text{RF} = \frac{\text{Peak Area}}{\text{Concentration}} \tag{2.1}$$

The response factor determines the sensitivity of the analysis and is dependent on the combustion efficiency of the compound. Saturated hydrocarbons are easily burnt in the flame, and will therefore generate a high response, i.e large peak area. When functional substituent groups are present, such as carboxyl or hydroxyl groups, the efficiency of the combustion is decreased, and therefore also the response factor. This might be an issue in these experiments, as many of the compounds analyzed are alcohols and acids that will have a low response factor.

2.3 Review and processing of data from literature and experiments

From the existing papers on pyrolysis of cotton and polyester the yield of gas, liquid and solid product was compiled so that the mass% was obtained. Based on which tar components that was reported in the reviewed literature, the five most common were chosen for further processing. The yield of each component was plotted, expressed in [kg/kg cotton or polyester]. In addition the carbon yield and efficiency with respect to the recovery of the five components were calculated, these calculation will be further described in Chapter 5.

As mentioned previously, both the gas and the liquid obtained in the new experiments performed was analyzed. The gas analysis yielded the volume% of CO_2, CO, CH_4, H_2, H_2S, C2-C3 hydrocarbons as well as the nitrogen used as fluidization gas and the helium used as carries gas. As the flow of helium into the sampling equipment was known, the total volume of gas produced could be calculated, see the equation below:

$$V_{tot} = \frac{\dot{V} \cdot t}{\frac{\alpha}{100}} \tag{2.2}$$

$\dot{V}$ is the volumetric flow of helium in [m^3/min], t is the sampling time in minutes and α is the vol% of helium detected. As the fraction of the remaining gases is known, their volume can now be calculated. By using the ideal gas law, the molar yield of each species was calculated, and by multiplying by the molar mass the total mass for the gas species obtained in each run calculated. Since two grams of fuel was used in each run, this number was multiplied by 500 to obtain the mass gas in [kg/kg fuel] see Equation 2.3

$$m_i = \frac{V_{tot}}{\frac{\alpha_i}{100}} \cdot \frac{P}{RT} \cdot M_i \cdot \frac{1000}{2} \tag{2.3}$$

m_i is the mass of species i in [kg/kg fuel], α_i is the vol% of component i, P is the pressure is Pa, which in this case was 101325 Pa, R is the ideal gas constant; 8.314

$[\frac{J}{mol \cdot K}]$, T is the temperature in Kelvin, which in this case was 298 K, i.e. the assumed room temperature. M_i was the molar mass of gas species *i* in [kg/mol]

The results from the tar analysis were given in [kg tar/ m^3] for each species that was detected. This value was multiplied by the total amount of gas produced, including He and N_2, to obtain [kg tar species/kg fuel]. As mentioned previously, some componets detected could not be specified, but from their peak area the mass yield could still be known.

Lastly the recovery of carbon, hydrogen and oxygen in the gas and liquid product was calculated, using the following equation:

$$X_{j,i} = \frac{m_i \cdot \frac{1}{M_i} \cdot n_{j,i}}{\frac{1}{M_f} \cdot n_{j,f}} \tag{2.4}$$

$X_{i,j}$ is the fraction of recovered carbon, hydrogen or oxygen in species *i*, m_i is the yield of *i* in [kg/kg fuel], M_i is the molar mass of *i* and $n_{j,i}$ is the number of C,O or H atoms in 1 molecule of *i*. M_f is the molar mass of the fuel and $n_{j,f}$ is the number of C,O or H atoms in 1 molecule of the fuel.

For the unknown tars, M_i and $n_{j,i}$ was not known, and an estimated value had to be used. It was therefore assumed that the value for M_i and $n_{j,i}$ was the same as for the closest peak were the species was known.

3

Production and recycling of common textiles

In this chapter the production chain for textiles will be explained, as well as the characteristics of the four most common fiber types. The existing recycling methods will be desribed, aiming to illustrate their potential and limitations.

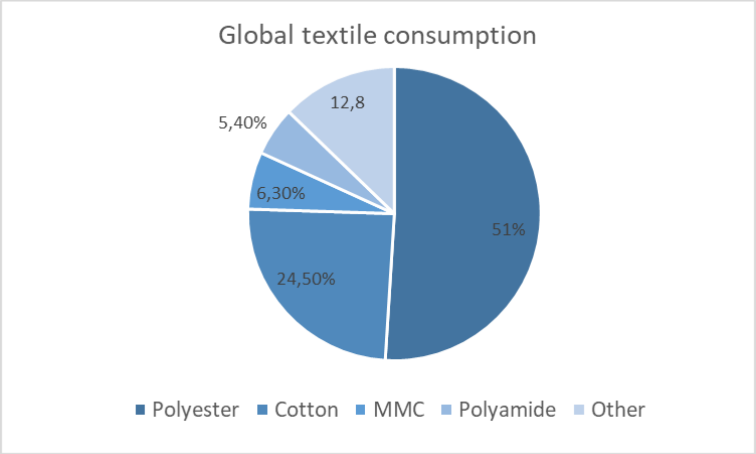
3.1 Textile production

3.1.1 Global and Swedish textile consumption

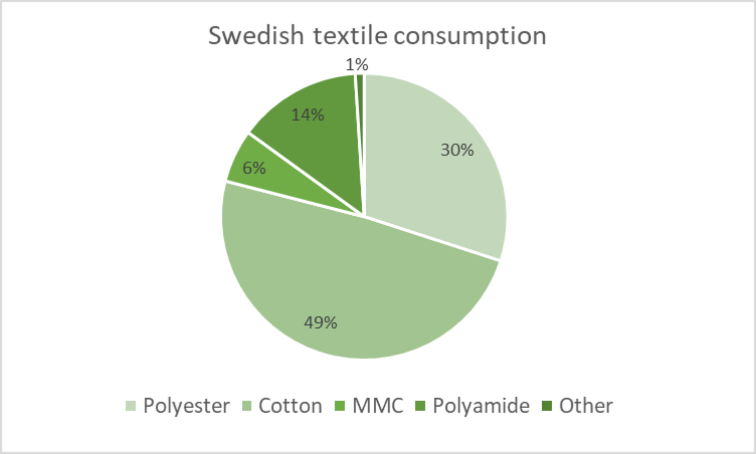
The textile consumption has increased drastically during the last decades and has now exceeded 100 million tonnes annually[1]. Clothing sales, which represents approximately 60% of all textiles produced, has more than doubled between 2000 to 2015[2]. In Sweden the textile consumption is 140000 tonnes annually[7]. Around 75000 tonnes are found in the MSW every year, which is approximately 7.5 kg/person[7].

Cotton and polyester are the two fiber types that dominate the textile market, with polyester being the most common fiber type since the middle of the 1990s. Today polyester production accounts for 51% of all textile fibers being produced, followed by cotton at 24,5%. Man-made cellulosic (MMC) material and polyamides constitutes 6.3% and 5.4% of the global fiber market respectively[1]. In Sweden cotton accounts for 49% of the textile consumption, polyester stands for 30%, and polyamide and MMC fibers for 14% and 6% respectively[3]. The share of the four most produced and consumed textiles is illustrated in figure 3.1.

Polyester and polyamide are synthetic fibers, almost exclusively made from fossil resources[2]. Polyester, also known as polyethylene terephthalate, has the chemical formula $(C_{10}H_8O_4)_n$ and is manufactured from ethylene glycol and dimethyl terephthalate[3]. The molecular structure can be seen in the Figure 3.2. Polyester fabrics are known to be resilient and resistant to wrinkling, but has bad water absorption ability. Polyamide is a name for polymers with amide groups attached to the chain. Their exists several types of polyamides, the most important in the textile industry being polyamide-6 and polyamide-6.6. Polyamide is often referred to as nylon. This fabric is extremely durable and is often used in car tires, fishing nets and carpets. It can also resemble silk, and is therefore popular in more delicate textiles.



(a) Share of the four most common fiber types in the global textile consumption



(b) Share of the four most common fiber types in the Swedish textile consumption

Figure 3.1: Consumption of the four most common fiber types globally and in Sweden[1].

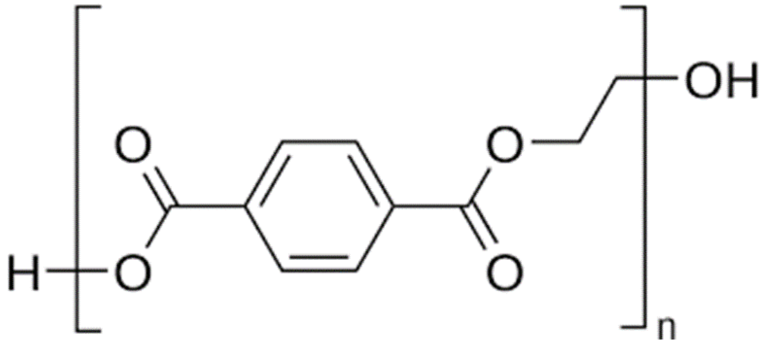


Figure 3.2: Molecular structure of polyester

Cotton and MMC fibers are both classified as natural fibers. Cotton consists of pure cellulose and is harvested from the cotton plant, which is native to North and South America, India and Pakistan among other countries. The molecular formula of cellulose is $(C_6H_{10}O_5)_n$, and the structure can be seen in Figure 3.3.

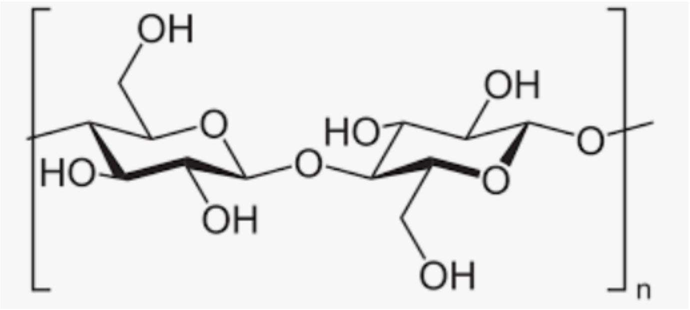


Figure 3.3: Molecular structure of cellulose

Cotton fabric has great water absorption and transportation ability, and is therefore popular in home textiles, such as towels and bed-linen. It is not however, as resilient and durable as many synthetic fibers, and is therefore often blended with polyester, in order to obtain a fabric that has good breathability as well as resilience.

Man-made cellulosic fibers, also called regenerated cellulose, is obtained by dissolving cellulose from wood pulp, often from birch or eucalyptus. Some common MMC fibers are viscose, tencel and lyocell.

3.1.2 Production chain

The first step in the production chain of textiles is the fiber production. For cellulose based textiles this means cultivation of cellulosic material, such as cotton plants or trees and in some cases, dissolving of the fibers[9]. The cultivation of cotton is very water intensive and may cause water depletion[3]. The cultivation also requires large quantities of pesticides, herbicides and fertilizers, which can leach into the surrounding environment and cause ground water contamination as well as eutrophication[3]. Synthetic fibers are chemically manufactured and in most cases based on fossil resources,[2][9].

Once textile fibers are obtained they are sent to yarn manufacturing. This production step involves spinning of the fibers, which requires electricity and often also dying of the thread, a process that is very water and chemical intensive.[9], [3]

Yarn production is followed by fabric manufacturing. This step involves knitting and weaving of the yarn as well as dying and bleaching of the fabric[9]. The next step in the production chain is cutting and sewing the finished textiles into garments. In this step a lot of waste is produced, so called pre-consumer waste.

As the production of fibers, yarn and finished textiles often occurs in countries where a large share of the electricity is fossil based and water is scarce, these production steps have a huge environmental impact.[9]

Before the textiles reach the consumers they are sent to retailers. At retailers electricity and heat is consumed. In the user phase water and electricity is required for washing and drying of the textile, and the washing causes the release of microplastics as well as chemicals in the fabric.[2],[3]

The environmental impact of the user phase is difficult to estimate as it is dependent on how often the textile is washed, whether or not it is dried in a dryer, the lifetime of the textile and whether or not the electricity used is produced from fossil resources or not[3].

The last step is most often waste disposal. In some cases this waste is burnt and the heat might be recovered for district heating. The waste might also be sent to landfill. In this case chemicals found in the textiles, such as flame retardants, dyes and traces of pesticides from the cultivation might leak into the ground water and anaerobic digestion of the material causes emissions of methane, which is a greenhouse gas approximately 30 times stronger than CO_2.

In Figure 3.4 the production chain descried is summarized. The boxes to the left show the most important resources for each step in the production chain. The boxes to the right summarizes the emissions and environmental effects connected to the different stages.

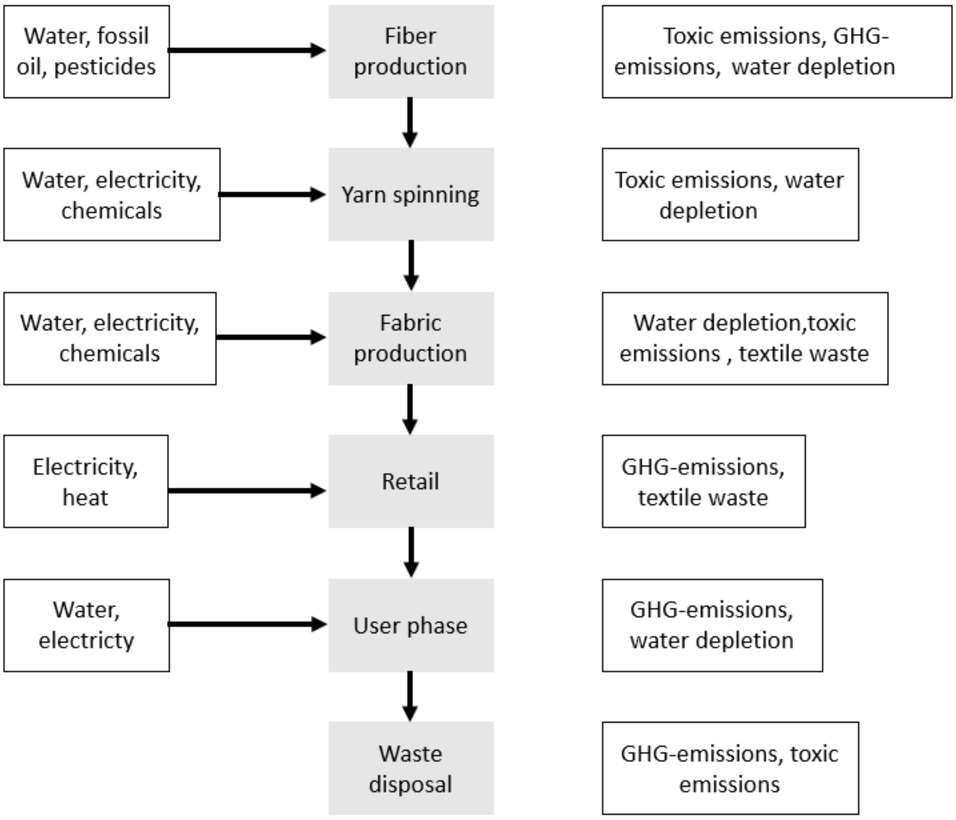


Figure 3.4: Mass and resource flows in the textile production chain and the most important environmental impacts for each production step

3.2 Existing recycling methods

By recycling used textiles some of the negative environmental impacts of textile production can be mitigated as less virgin material has to be produced. As mentioned previously there are currently two available recycling methods ; mechanical and chemical recycling. The mechanism for these two methods will be described in the following sections, as well as which fabrics that can be recycled this way, and the limitations of both methods.

3.2.1 Mechanical recycling

Mechanical recycling is the most common recycling method and approximately 12% of all clothing textiles are recycled this way[2].Most mechanical recycling methods are down-cycling methods, meaning the fibers or fabrics are recycled into materials with a lower quality compared to the original product[10].

Mechanical recycling can be divided into two processes; thermomechanical recycling and mechanical processing. Thermomechanical recycling can only handle synthetic fibers, such as polyester and different types of nylon. The fibers are melted into granulates, which are then spun into new fibers with the same quality as virgin fibers. One drawback of this method is that it is very sensitive to contamination, and e.g. surface treatments and dirt can therefore cause problems. Furthermore, this method cannot handle any blended materials and some polymers, such as elastane, are impossible to melt.[11]

In mechanical processes the end product is usually one with less value, as the fiber quality is decreased in the process. The first step is cutting and tearing the textile waste into smaller pieces, which can be used for cleaning clothes and wipes. The pieces can be processed even further by feeding them to a shredder, which releases the fibers. These can then be used as stuffing material and insulation.[10],[11]

For this type of recycling most types of textile fibers can be utilized, as well as many types of fiber blends. However, one limitation is that synthetic fibers are stronger than natural and therefore require more processing in order to be released. Fiber blends between natural fibers and polyester are therefore not mechanically recycled. As the fiber quality is severely decreased in the process, the end products of this type of processing cannot be recycled again.[11],[10]

For some materials the recycled fibers can be used in the manufacturing of yarn for new textiles. For this type of recycling cotton and wool are suitable fabrics. As the fiber quality is degraded both in the user phase of the textile as well as in the recovery of the fibers, virgin fibers usually has to be blended with the recycled fibers. One application for mechanical fiber-to-fiber recycling, which today exists at demo-scale, is denim products, where the cotton fibers from waste denim is used when spinning yarn for new jeans. In that case 20% of the fibers in the new garment are recycled fibers, while 80% has to be virgin, in order to ensure a good quality of the fabric. [10]

3.2.2 Chemical recycling

In chemical recycling both monomers and polymers, i.e. textile fibers, can be regenerated through various processes. For most fiber types chemical recycling only exists at small scale, but for some synthetic materials commercial scale recycling is available. In these processes the fabric fiber is depolymerized into its monomers. This step is followed by a purification step, in which contaminants such as dyes are removed. The monomers are then used for building new polymers, which will have the same quality as virgin fibers.[11]

Today the only materials that can be recycled this way, at commercial scale, is polyester and nylon-6. Apart from polyester and nylon-6 textiles, important material inputs in these depolymerization processes are PET-bottles for polyester recovery and carpets and fishing nets for nylon-6 recovery. As the depolymerization process is different for different polymers, there are restrictions on which fiber blends that can be treated. For polyester recycling up to 20% of cotton is allowed in the fabric, but this fraction will no be recycled. However, polyester textiles containing wool, leather or elastane cannot be treated. For nylon recycling only pure nylon 6 is possible to process.[10],[11]

The recycling of cellulose based fibers is possible by dissolving the cellulose fabric in a pulping process, creating dissolving pulp, which is then used to generate new cellulose fibers[11]. This type of process can handle pure materials, as different chemical processes are required to dissolve different fiber types. There might be problems with dyes and other additives, as these chemicals can interfere with the dissolving reactions. Chemical recycling is not possible for viscose and lyocell, as these are already regenerated fibers[11].

Processes that can handle blended materials are being developed, one example is Blend Re:wind, where textiles consisting of polyester and cotton, so called polycotton is treated[4]. In this process the fabric is treated with sodium hydroxide, NaOH. This degrades the polyester into two monomers, terephthalic acid and ethylene glycol, which can be utilized when manufacturing new polyester. The cellulose is not degraded in the process and can be separated. [4],[12],[13].

Figure 3.5 illustrates the material flow for textile production when the product flows from the described recycling methods are included. The dashed line represents the system boundary. In chemical recycling the outcome from recycling of natural fibers will enter the yarn spinning-step, while recycling of synthetic fibers generates monomers that will go to fiber production. The product from mechanical down-cycling will exit the system, while the outcome from mechanical fiber-to-fiber recycling will go to yarn spinning.

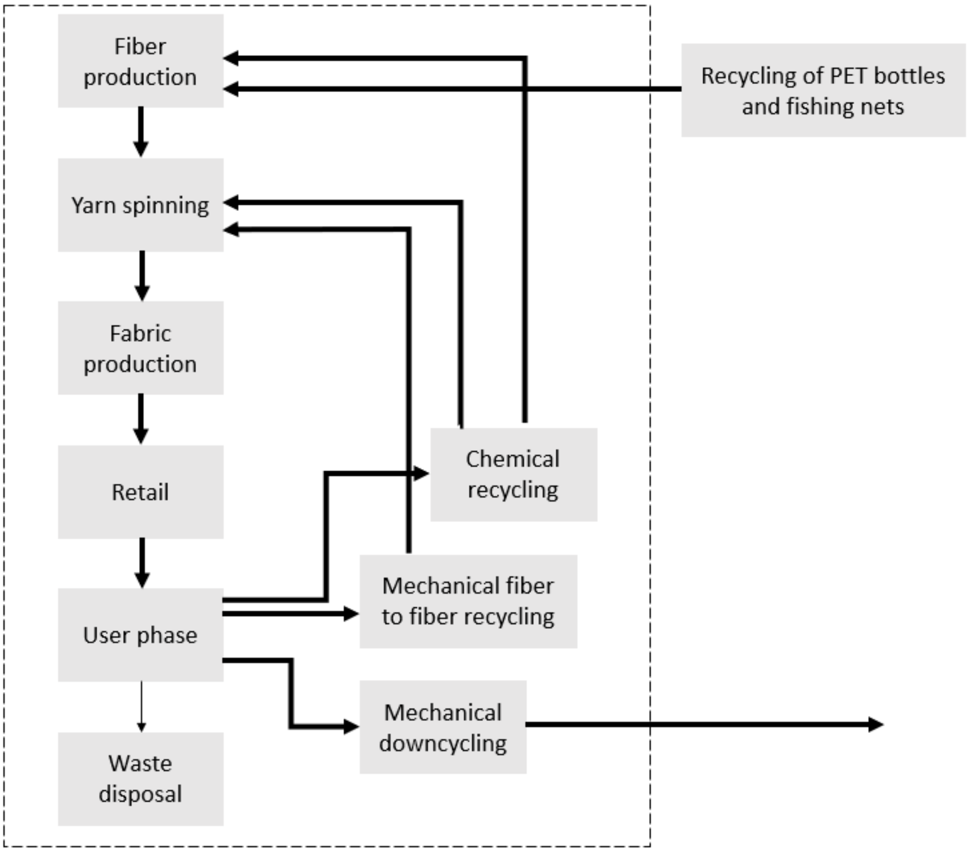


Figure 3.5: Material flows for the recycling methods available.

3.2.3 Limitations with existing methods

In Table 3.1 the recycling methods described above are summarized in terms of most important process step, restrictions of the textiles being recycled, outcome of the process and whether the recycled material is introduced in the textile industry once again (closed loop recycling) or sent to another industry (open loop recycling).

The benefit with mechanical recycling methods is that they allow a greater heterogeneity in the material, and therefore have the ability to treat blended fabrics, which is the type of fabric found in MSW. However, since the fiber quality is decreased in the recycling process closed loop recycling is not possible.

Although several of the methods described enable closed loop recycling of some waste textiles there are many limitations that prevents them from working at larger scale. All closed loop recycling routes existing today are only able to handle pure or almost pure fabrics, with strict limitations on the presence of other types of fibers and contaminants, e.g. dyes and flame retardants.

As mentioned previously, for mechanical fiber to fiber recycling, used denim textiles are the most common applications. For chemical cotton recycling waste textiles from the health care sector, such as hospital clothes, towels and sheets, is an important input[4]. Both denim textiles and textiles from the health care sector are niche

Type	**Process**	**Waste**	**End use**	**Closed/Open loop**
Mechanical	Cutting/tearing	Blended, mostly cotton based	Cleaning cloths	open loop
Mechanical	Shredding	Blended fabric	Stuffing material, insulation	Open loop
Mechanical	Shredding	High cotton fabric	Cotton fabric, often denim	Closed loop
Mechanical	Melting and spinning	pure polyester and nylon	polyester and nylon fabric	Closed loop
Chemical	Depolymerization	Pure nylon-6, polyster with <20% cotton	Polyester and nylon-6 monomers	Closed loop
Chemical	Dissolving	Pure cotton	Regenerated cellulose fibers	closed loop
Chemical	Depolymerization and dissolving	polycotton	Regenerated cellulose fibers,polyester monomers,	Closed loop

Table 3.1: Summary of existing recycling methods

markets, and other sources of textiles are required to scale up[4], which is difficult due to the purity restrictions.

The textiles found in MSW are highly heterogeneous, both in terms of fibers and chemical additives, and can therefore not be recycled into new textiles without extensive sorting. Today much of the sorting is done manually, by color sorting and tags attached to textiles stating the fiber composition[10]. This is very time consuming and not viable on a large scale, and today no automatic sorting methods are implemented.

Due to the many limitations and restrictions of above mentioned recycling methods, it is evident that more recycling methods should be investigated, where a more heterogeneous feedstock can be processed.

4

Thermochemical Recycling

The thermochemical processes that will be investigated in this thesis is pyrolysis and gasification. In both cases carbonaceous compounds are degraded by heat to monomers. The temperature in these processes is high, usually between 400-1000 °C and the reactions take place in an oxygen deficit or oxygen free environment.[14],[15]

In gasification the desired product is synthesis gas, often referred to as syngas. This is a gas mixture consisting of hydrogen (H_2), carbon monoxide (CO), carbon dioxide (CO_2) and methane (CH_4). Apart from this gas mixture some larger hydrocarbons, e.g ethylene, as well as tar and ash is produced. Ash consists of compounds from the feedstock that cannot be gasified and tar is a mixture of condensable larger hydrocarbons. [8],[16]

In pyrolysis, where the temperature is typically lower compared to in gasification, a larger share of the material is converted to condensable compounds. This desired product is often referred to as pyrolysis-oil or pyrolysis-liquid. Just as with gasification syngas and ash is produced as well.[17]

Gasification and pyrolysis are fuel flexible processes, and common feedstocks are coal, biomass, sewage sludge, agriculture- and forest residue and municipality solid waste,[18], [14]. Depending on the feedstock unwanted compounds will be formed, such as hydrogen sulfide (H_2S) and ammonia (NH_3)[19].
The choice of feedstock, as well as operating conditions, influences the yield of tar, syngas and solid products[19],[20].

4.1 Reactions

In the following section the reactions occurring in gasification and pyrolysis will be explained.

4.1.1 Pyrolysis

Pyrolysis is an endothermic process that takes place in the absence of oxygen or air. Carbonaceous material is degraded by heat and the product consists of a solid, a liquid and a gaseous fraction. The solid fraction consists of ash and unreacted organic compounds, and is also called char. The gaseous fraction consists of syngas and small amounts of light hydrocarbon and the liquid fraction, tar, is made up of larger hydrocarbons, such as mono- and poly aromatic compounds and oxygen containing hydrocarbons, such as carboxylic acids, aldehydes, alcohols and ketones. The liquid fraction is often referred to as pyrolysis oil or pyrolysis liquid. [19], [18] The pyrolysis process can be summarized with the reaction below:

$$C_xH_y \rightarrow CO + CO_2 + H_2 + CH_4 + H_2O + \text{tar} + \text{char} + \text{ash} \tag{4.1}$$

4.1.2 Gasification

In gasification the feedstock reacts with a so called gasifying agent, which can be CO_2, steam or air, to produce mainly syngas. Although oxygen may present in the process only partial oxidation is allowed as the amount of oxygen should be less than what is required for stoichiometric combustion.[8],[19]

The process is divided into four different stages; pyrolysis, oxidation, reduction and tar reforming. The pyrolysis step is the same as described above. In the reduction reactions char reacts with steam or CO_2, which produces the desired CO and H_2. Some of the produced H_2 might react with char and CH_4 is formed. All reducing reactions are endothermic. In the oxidation step char and volatile compounds react with oxygen and CO_2 is created. These reactions are exothermic and the produced heat provides some of the energy required for the reducing reactions described above.[8], [21], [14]

In the tar reforming step tar and steam reacts and produces volatile compounds and lighter hydrocarbons[14]. In Table 4.1 below the different oxidation and reduction reactions are summarized.

Table 4.1: Summary of the gasification reactions described[8],[14],[18],[19],[21].

Reaction type	Reaction	
Exothermic	$C + O_2 \rightarrow CO_2$	Oxidation
	$C + \frac{1}{2} O_2 \rightarrow CO$	Partial oxidation
	$H_2 + \frac{1}{2} O_2 \rightarrow H_2O$	Hydrogen oxidation
	$CO + 3H_2 \rightleftharpoons H_2O + CH_4$	Methanation
	$2CO + 2H_2 \rightleftharpoons CO_2 + CH_4$	Methanation
	$CO + H_2O \rightleftharpoons CO_2 + H_2$	Water Gas Shift (WGS)
Endothermic	$C + CO_2 \rightleftharpoons 2\,CO$	Boudouard reaction
	$C + H_2O \rightleftharpoons CO + H_2$	Steam gasification
	$C + 2\,H_2 \rightleftharpoons CH_4$	Hydrogen gasification
Tar reforming	$\text{Tar} + H_2O \rightleftharpoons H_2 + CO + CO_2 + C_xH_y$	

4.2 Tars and pyrolysis oil

One of the products from gasification is tar, which is a complex mixture of mono- and poly-aromatic compounds as well as other oxygenated hydrocarbons[16]. There does not exist one single definition of tar but it is often defined as all organic compounds with a molecular mass larger than 78 [g/mol], which is the molar mass of benzene[16]. Some definitions include lighter hydrocarbons, meaning all types of acids, aldehydes, alcohols etc. are included in the concept as well[22].

The liquid product formed in pyrolysis is often referred to as pyrolysis oil or bio-oil[15]. This liquid has many similarities with tar and consists of oxygenated hydrocarbons and form of e.g. acids, alcohols, aldehydes and mono- and poly-aromatic species, but contains a water phase as well[15].

The formation of tar and pyrolysis oil is highly dependent on both process conditions and feedstock. Temperature affects the total amount condensable species that are produced as well as its composition[16]. At temperatures below 500°C both linear and aromatic oxygen-containing hydrocarbons will be found[22]. At 600 °C alkylphenols, such as cresol will be formed, and at even higher temperatures, above 800 °C, the yield of oxygen-containing compounds will start to decrease[22],[16]. At these temperatures the condensable species will consist of primarily aromatics without substituent groups, as benzene, naphthalene[16]. At around 850 °C 3- and 4-ring aromatic hydrocarbons are formed[16].

The components in tar and pyrolysis oil is often classified into primary, secondary and tertiary tar, where primary tars includes the species formed at lowest temperature and tertiary tars are the species formed at the highest[22],[23].

4.3 Applications

The gasification and pyrolysis products can be used for several purposes. The gases and tars formed are combustible and can be utilized in an engine, gas turbine or boiler to produce heat and power. The products can also be used as building blocks when synthesizing chemicals and fuels. [21] In the following sections some of these applications will be described.

4.3.1 Heat and power production

The syngas produced in gasification and pyrolysis is combustible and can be used as a substitute for natural gas in heat and power applications such as engines, gas turbines and burners[24].

There are several benefits with thermochemical treatment of a fuel prior to combustion, compared to direct combustion of the fuel. The excess air is typically lower , thus over all efficiencies are higher. Less NO_x is formed and the presence of fly ash is lower is the syngas, which reduces the risk of fouling. Another advantage is that, in the case of strict environmental regulations, the syngas can be cleaned prior to combustion which is less energy demanding compared to cleaning the flue gas, as the flow of typically is twice as large.[24]

Syngas can be used as fuel in CHP-plants, and for small scale applications where the electrical output is less than 10 MW the technology is promising[25]. The electrical efficiency for these plants is usually between 35-40%, which is high compared to in conventional plants based on direct combustion of the fuel[25].

In addition to the syngas, the pyrolysis oil can also be combusted and thus have the potential to replace fossil oil in heat and power applications, although their properties differ significantly[26]. The water content is often higher, especially if the feedstock pyrolyzed has a high moisture content[26]. For wood, the water content in the obtained pyrolysis oil can be up to 30 wt% [15]. Also the oxygen content is higher in pyrolysis oil, due to the oxygenated hydrocarbons formed [15]. The high concentration of oxygen and moisture leads to a much lower energy content in pyrolysis oil compared to fossil oil [26]. It also makes the pyrolysis oil polar, and therefore immiscible with the non-polar fossil oil that mostly consists of hydrocarbons [15].Due to the presence of carboxylic acids the pH of pyrolysis oil is often low, typically around 2-3, which makes the oil corrosive.

One benefit with the high water content is that the adiabatic flame temperature decreases, which lowers the production of thermal NO_x. In addition, the combustion of pyrolysis oil generates almost no emissions of SO_x[26].

4.3.2 Fuel production

By catalytic reactions or anaerobe digestion syngas can be converted into both liquid fuels, such as Fischer Tropsch-fuels, ethanol and methanol as well as gaseous fuels, e.g. hydrogen and synthetic natural gas (SNG) [14].

In Fischer-Tropsch synthesis carbon monoxide and hydrogen is converted to hydrocarbons according to the reactions below[14],[27].

$$(2n+1)H_2 + nCO \rightarrow C_nH_{2n+2} + nH_2O \tag{4.2}$$

$$2nH_2 + nCO \rightarrow C_nH_2n + nH_2O \tag{4.3}$$

$$nCO + (n+\frac{m}{2})H_2 \rightarrow C_nH_m + nH_2O \tag{4.4}$$

Some of the most important products from Fischer-Tropsch synthesis are biofuels such as gasoline, diesel and kerosene[14].

CO and H_2 can also be used to synthesize alcohols, which can be utilized as additives in gasoline. The reaction is described below:

$$nCO + 2nH_2 \rightarrow C_nH_{2n+1}OH + (n-1)H_2O \tag{4.5}$$

Ethanol has been used as vehicle fuel since the end on the 19th century can can be used as an additive in gasoline[28]. Adding ethanol to the gasoline has many advantages, such as an reduction in CO, sulfur oxides and volatile organic compounds

(VOC) as well as an increased engine efficiency[29],[28].

Another important alcohol that can be manufactured from syngas is methanol, CH_3OH, which can be used directly as a fuel or used to synthesize hydrocarbons[27]. Some of the useful hydrocarbons that can be manufactured from methanol is gasoline, diesel and olefins, such as ethylene and propylene[27]. By dehydration of methanol dimethyl ether (DME) can be produced, which is a fuel that can be used as a substitute for diesel[27], [30]. This reduces the emissions of CO, NO_x and hydrocarbons[30].

As mentioned previously, syngas can be used to synthesize gaseous fuels as well. By the Water Gas shift reaction in Table 4.1 hydrogen is formed, which can then be used in e.g. fuel cells to produce electricity[8]. Another application for syngas is the production of synthetic natural gas, SNG, which is produced in the methanation reactions in Table 4.1. The methane produced can be used as a substitute for fossil natural gas.

The pyrolysis oil produced in the pyrolysis process can also be used as a fuel, although modifications are required before it can be added to or substitute conventional fuels. As mentioned previously pyrolysis oil is highly corrosive due to its low pH-value, low energy density and polar nature [15],[26]. In addition pyrolysis oil has a high content of solid particles and low chemical stability [31]. Some common upgrading methods are filtration to remove solid particles, addition of organic solvents and surfactants in order to increase the chemical stability and the miscibility with hydrocarbon fuels, such as diesel[31]. By treating the oil with hydrogen, oxygen is removed as CO_2 and H_2O, which improves the energy density of the fuel[15],[31].

4.3.3 Production of chemicals

The condensable products produced in pyrolysis contain a variety of oxygenated hydrocarbons such as alcohols, acids, ketones, aldehydes, sugars and phenolic compounds which can useful as chemicals or in the manufacturing of chemicals[15].

5

Thermochemical recycling of textiles

In this chapter the results regarding thermochemical textile recycling is presented. In Section 5.2.1 the reviewed literature is summarized and in 5.2.2 the data from the literature is processed and analyzed. In Section 5.3 the result from the pyrolysis experiments performed is presented and discussed.

5.1 Review of experiments found in literature

As mentioned previously the focus of this thesis is Swedish textile waste. No reliable data was found regarding the composition of different fiber types of disposed textiles found in the MSW, and it was therefore assumed that the waste composition resembles the composition of consumed fibers. Since cotton and polyester are by far the most dominant fibers, the focus was to review literature and perform experiments on thermochemical treatment of those. Cotton consist of almost pure cellulose, thus literature regarding both pyrolysis of cotton fabric and pure cellulose was reviewed. As polyester has the same molecular structure as PET-plastic, literature on PET pyrolysis was also included.

As mentioned in Section 1.2, not many experiments on textile gasification has been performed, and in the majority of the literature reviewed the focus was to establish a kinetic model for the gasification, rather than measuring yield of gas, liquid and solid product, as well as what the gas and liquid composition would be. However, this has been investigated in [32], where three samples of textile waste was gasified at 650°C, 750°C and 850°C. The textile samples consisted of pure cotton pure polyester and a mix of 50% cotton and 50% polyester, and were gasified in a lab scale reactor using steam as gasification agent.

Table 5.1 shows the yield of CO_2, CO, H_2 and CH_4 in vo%. As can be seen CO_2 is the dominating species in all cases, followed by CO.

		CO_2	CO	H_2	CH_4
Polyester	650 °C	59.7	31.5	2.2	6.5
Polyester	750 °C	63.1	21.5	10.4	5.0
Polyester	850 °C	50.9	21.6	20.5	7.0
Cotton	650 °C	33.2	31.2	27.8	7.8
Cotton	750 °C	34.9	31.6	23.9	9.7
Cotton	850 °C	47.1	20.0	29.5	3.4
Mixed	650 °C	54.2	30.7	10.0	5.2
Mixed	750 °C	49.7	27.2	14.8	8.2
Mixed	850 °C	35.8	30.3	23.2	10.7

Table 5.1: Yield of CO_2, CO, H_2 and CH_4 in vol%, reported in [32]

Since the content of oxygen is relatively high in both cellulose and polyester, the high yield of CO_2 was expected. This will be a limitation if the aim is to utilize the gasification product to produce fuel, as the desired gases in that case would be CO and H_2, see section 4.3.2. In addition, the high concentration of CO_2 decreases the heating value of the gas, thus making it less suitable for heat and power purposes.

With this in mind it became evident that a good option is to focus on the extraction of chemicals from pyrolysis oil, and thereby maximize the amount of carbon recovered in useful products. By keeping the temperature lower the aromatic structures found in textile fibers are not degraded to the same extent as at a higher temperature. Many of the aromatic compounds that can be expected from the pyrolysis serve as important building blocks in the chemical industry today[33]. Focusing on increasing the yield of pyrolysis oil, and especially mono-aromatic species, is therefore the best option if one wants to maximize the recovery of complex chemical structures. Recalling Figure 3.2 and 3.3, both polyester and cellulose monomers are aromatic, and it can therefore be expected that aromatic compounds resembling these original structures will be found in the pyrolysis oil.

5.1.1 Summary and results from five pyrolysis experiments

The following section presents the result from five pyrolysis experiments that could be found in literature. The purpose of reviewing these experiments is to obtain an overview of the yield of gas, pyrolysis oil and char and which mono-aromatic components to expect in the pyrolysis oil. Five component that appeared most frequently were chosen to be studied. These are benzoic acid and its derivatives, furan and derivatives, phenol, terephthalic acid and levoglucosan. Three of the studies investigated cotton/cellulose and two investigated PET, which is the same molecule as the most common type of polyester used in textiles.

Characterisation of slow pyrolysis products from segregated wastes for energy production

In [34] the pyrolysis of a textile sample, consisting of cotton on a minor amount polyester (<5 %), was investigated in a 125 mm × 500 mm reactor reactor. The experiments were conducted at five different temperatures; 350, 400, 500, 600 or 700

°C and 150-200 g of sample was treated in each test. The sample was put in the over at ambient temperature and the heated by 10 °C/min until the final temperature was reached, and then kept at this temperature for 2 hours. The char, liquid and gas produced were analyzed to obtain mass yield, elemental analysis and to identify chemical compounds. The results showed that the char fraction decreased with increasing temperature, from 31.6 mass% to 19 mass%. Liquid fraction peaked at 600 °C,where the yield was 47%.The gas yield increased with temperature.

The pyrolysis liquid was analyzed using GC-MS for 350, 500 and 700 °C. The chemical compounds found in the oil was substituted furans, Anhydrosugars (mainly levoglucosan), phenolic compounds and ketones, where all species except ketones are aromatic. The table below displays the yield of the components in the pyrolysis oil. The numbers are in mass% of the oil.

Compound	350	500	700
Ketones	2.9	2.9	2.8
substituted furans	22.7	20.7	22.1
Anhydrosugars	16.4	29.5	4.2
Phenolics	32.2	24.7	44.9

Table 5.2: Yield of oil components at different temperatures reported in[34]. The values are in mass% of the oil obtained.

The composition of the gas phase was measured at 650 °C, which can be seen in Table 5.3

	CO	CO_2	H_2	CH_4	C2-C3
vol%	34.7	35.6	5.4	19.2	5.1

Table 5.3: Composition of the gas produced at 650°C

Pyrolysis gasification reactivities of primary tar and char fractions from cellulose and lignin as studied with a closed ampoule reactor

In [35] the thermal conversion of cellulose powder is studied in an N_2-atmosphere and at 600 °C. 10 mg of the cellulose was placed in a pre-heated reactor with the dimensions 8 mm x 120 mm and the residence time was varied between 50-120 s. Tar and gas was then sampled in order to be analyzed.

The experiments revealed that the gas yield increased with increasing residence time, while the yield of pyrolysis oil decreased. The yield of char did not vary significantly. Analysis of the gas showed that CO, H_2 and CH_4 all increased with an increasing residence time, while the CO_2-formation was almost complete at 50 s and the yield of this component was therefore independent of residence time. When analyzing the pyrolysis oil the major components were levoglucosan, furfural, 5-hydroxymethylfurfural, glycolaldehyde, hydroxyacetone, formic acid and acetic acid, where the three former are mono-aromatic. The yield of all components except acetic acid and hydroxyacetone decreased with increasing residence time.

As residence time is not a parameter being investigated in this report, only the data from the experiment with the shortest residence time is included, as this experimental point had the highest yield of pyrolysis oil.

The disposal of combed cotton wastes by pyrolysis

In [36] cotton textiles are pyrolyzed at 450, 500, 550 and 600 °C. 100 g of textile sample was placed in a cold reactor, then heated at to the goal temperature at a rate of 5 °C/min. The reactor was then kept at the final temperature for one hour. For each temperature two different catalysts,Na_2CO_3 and $CaCO_3$, as well as no catalyst was investigated.

To maximize the liquid yield the optimal temperature was 550°C and the use of a catalyst was favorable. Na_2CO_3 had the highest liquid yield at all temperature except for at 600°C. Table 5.4 displays the yield of gas, liquid and solid product when Na_2CO_3-catalyst.

	Char	Liquid	Gas
450 °C	30	18	52
500 °C	28	29	43
550 °C	20	35	45
600 °C	22	27	51

Table 5.4: Yield of gas, liquid and char at different temperatures, using Na_2CO_3-catalyst.

The pyrolysis oil acquired at 550 °C using Na_2CO_3-catalyst was analyzed to reveal its main components. The analysis showed that the oil contained 28.18% furans, 25% ketones, 13.51 % aldehydes, 7.01% carboxylic acids, and 7.05 %hydrocarbons, where the furans are the only aromatic species.

Pyrolysis of poly(ethylene terephthalate) in a fluidised bed plant

Yohioka et al. [37] investigated the pyrolysis of polyethylene terephthalate (PET) in a fluidized bed reactor at 510 and 630 °C. The reactor had an inner diameter of 154 mm and was continuously fed with 471-3995 g/h. The gas and pyrolysis oil was analyzed to obtain the yield and major compounds. The distribution between gas, solid and liquid product can be seen in the table below.

		510	630
Gas		**37**	**39**
	CO	23	18
	CO_2	13	17
	H_2	0.09	0.13
	CH_4	0.87	1.9
	C2-C4 hydrocarbons	2.6	1.33
Liquid		**51**	**50**
	Aromatic hydrocarbons	1.3	3.4
	Oxygen containing components	24	20
	NaOH-soluble components	24	13
Char		**12**	**11**

Table 5.5: Mass% gas, liquid and char, and main components in the gas and liquid at different temperatures, reported in [37].

The aromatic hydrocarbons consisted almost exclusively of benzene and benzene derivatives. Among the oxygen containing compounds aldehydes, ketones as well as benzoic acid was found. The NaOH-soluble compounds contained mainly terephthalic acid.

Comparative pyrolysis of polyolefins (PP and LDPE)and PET
Cit et al.[38] investigated pyrolysis of PET and measured the yield of tar, char ad gas at four temperatures; 400,500,600 and 700 °C. The composition of the liquid and gaseous product was analyzed at 700 °C. The PET-sample was placed in the reactor at ambient temperature and then heated with 10 °C/min until desired temperature was reached, and then kept at this temperature until no liquid was produced. The yield of liquid, char and gas is shown in the Table 5.6

	Char	Liquid	Gas
400 °C	15	60	25
500 °C	11	62	27
600 °C	7	58	35
700 °C	8	50	42

Table 5.6: Yield of gas, liquid and char in [38]

The gas was analyzed in order to establish the distribution between gaseous carbonaceous compounds. The analysis showed that 40% of the gas was C1+C2 compounds. The yield of C3,C4 and C5 was slightly less than 20 % for each category and the yield of C6+C7 compounds was approximately 10 % .

Analysis of the liquid product showed that approximately 37 % of the liquid product was in the form of benzoic acid or derivatives of this compound, such as methy-, ethyl- and acetyl-benzoic acid. Other mono-aromatic compounds that was found in less significant amounts was styrene and 1-Phenyl-1,2-propanedione. The remaining liquid product was in the form of 2- and 3-ring aromatic compounds, biphenyl being the most common with a yield of 17%.

In Table 5.7 the composition of gas, pyrolysis oil and solid product found in literature is summarized and presented. All numbers are in mass%.

			Char	Liquid	Gas
[34]	Cotton	350 °C	31.6	38.4	30
		500 °C	22	46.1	31.9
		700 °C	19	35.2	45.8
[35]	Cotton	600 °C	19	60	21
[36]	Cotton	450 °C	30	18	52
		500 °C	28	29	43
		550 °C	20	35	45
		600 °C	22	27	51
[37]	Polyester	510 °C	13	51	37
		630 °C	11	50	39
[38]	Polyester	400 °C	15	60	25
		500 °C	11	62	27
		600 °C	7	58	35
		700 °C	8	50	42

Table 5.7: Yield of gas, liquid and char in the different pyrolysis experiments studied.

In Figure 5.1 the yield of liquid product obtained in the five studied pyrolysis experiments is summarized. To easier illustrate trends in the data, four temperature ranges has been created. The yield is displayed in kg pyrolysis oil/kg fuel.

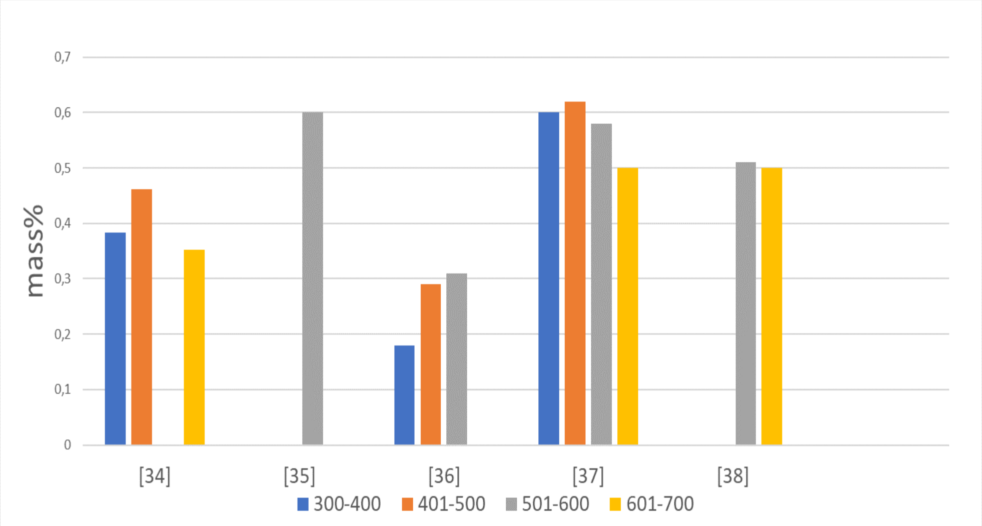
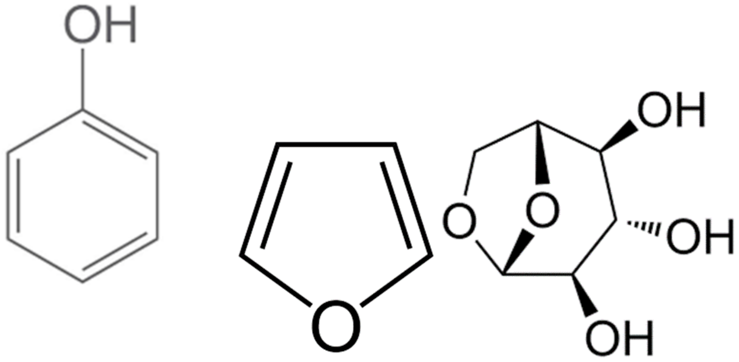


Figure 5.1: Yield of pyrolysis oil at different temperatures reported by the five pyrolysis experiments reviewed. Reference [34]-[36] cellulosic, reference [37]-[38] polyester.

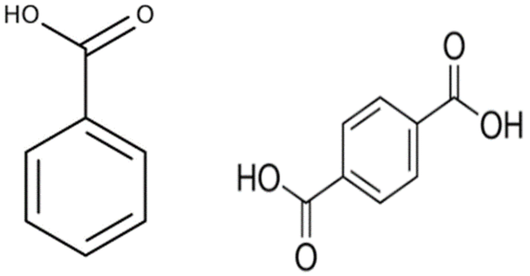
As can be seen in Figure 5.1 all studies showed that the maximum liquid yield is obtained at a temperature between 400 and 600 °C, and further experiments should therefore be conducted around this interval.

5.1.2 Processing and analysis of data from literature

Based on the composition of the pyrolysis oil obtained in the studied literature five groups of aromatic components were chosen for further investigation, namely phenol, furan derivatives and levoglucosan, which were found in the liquid produced from cotton pyrolysis, as well as benzoic acid derivatives and terephthalic acid which was found in the liquid produced in PET pyrolysis.



(a) Phenol (b) Furan (c) Levoglucosan



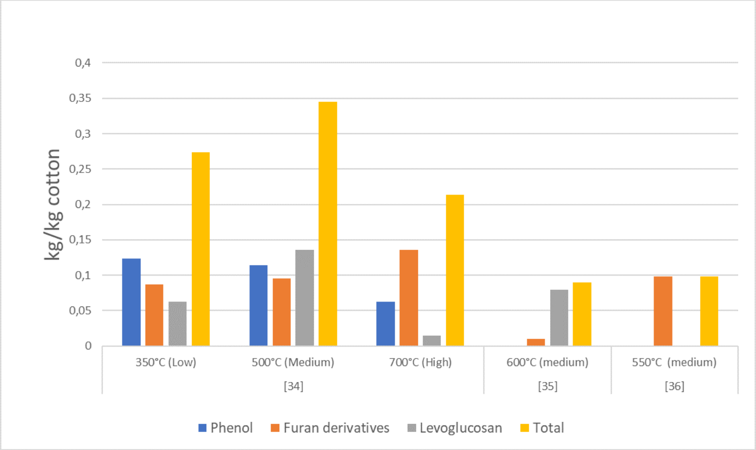
(d) Benzoic acid (e) Terephthalic acid

Figure 5.2: Molecular structure of phenol, furan, levoglucosan, benzoic acid and terephthalic acid

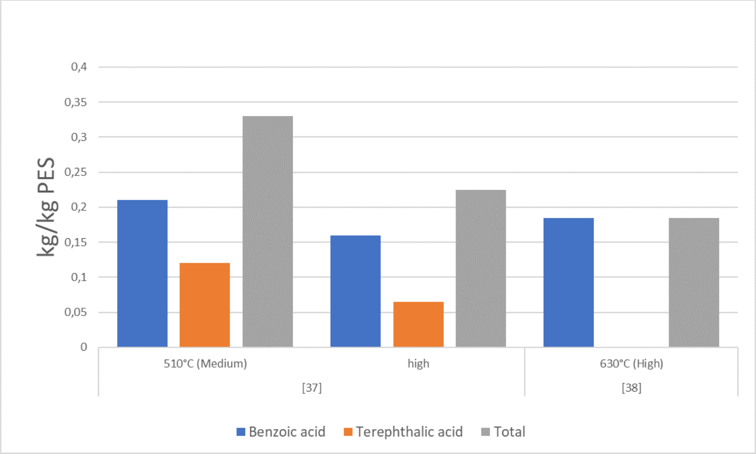
Furan derivatives appear in all cotton pyrolysis experiments, but the exact species is only specified in [35], where furfural is detected. In [34] and [36] it is mentioned that furan derivatives are detected, but not specifically which ones. For simplicity all furan derivatives detected will therefore be assumed to have the same molecular structure as furan. The same approach is applied for the benzoic acid derivatives found in [38], where all derivatives are assumed to have the same molecular structure as benzoic acid.

All components chosen are mono-aromatic compounds with one or two substituent groups, and could therefore be interesting in the chemical industry as they can act as building blocks in the manufacturing of more complex chemicals.

Figure 5.3a show the mass of phenol, furan derivatives and levoglucosan that is produced in the pyrolysis of 1 kg cotton, based on the three experiments on cotton pyrolysis reviewed. Figure 5.3b mass of benzoic acid derivatives and terephthalic acid produced based on the two reviewed experiments on PET pyrolysis. "Low", "Medium" and "High" refer to three different temperature ranges, where "Low" are experimental points where the temperature is below 500°C, "Medium" are experimental point where the temperature is between 500 and 600 °C and "High" are points taken at temperatures above 600 °C.



(a) The yield of phenol, furan derivatives and levoglucosan from cotton pyrolysis



(b) The yield of benzoic acid and terephthalic acid from PET pyrolysis

Figure 5.3: Yield of the five studied components. The values are given in mass% of the total product.

As can be seen in Figure 5.3 the total yield of the chosen components is approximately 10-35% for the cotton experiments and 17-33% for the PET experiments. For some of the experiments for amount of species that are recovered is relatively low, especially in [35], [36] and [38].

When comparing these results with the result shown in Figure 5.1 one can see a gap between the total yield of pyrolysis oil and the yield of the five species studied. In [35] the total yield of pyrolysis oil was 60%, which is significantly more than the yield of furan and levoglucosan showed in Figure 5.3. In [36] the pyrolysis oil obtained at 550°C was analyzed. At this temperature the total yield was slightly more than 30%, while the total yield of the species investigated is 10%. Also in [37] and [38] the yield gap is large, approximately 25 percentage points and 33 percentage points respectively. The conclusion that can be drawn from these results is that the yield of the chosen components is not exceptionally high but considering the yield gap mentioned the potential to recover more valuable compounds from the oil, such as other mono-aromatic species, is high.

As previously described, carbon emissions connected to to the textile production and use is one of the environmental issues related to the industry. It is therefore of interest to calculate the mass of carbon in the form of the five studied components, as this is the carbon that can be utilized when manufacturing new materials of high value.

To calculate this the mass of carbon in each compound, as well as the carbon in cotton and polyester was required, see Equation 5.1 and 5.2

$$\mathrm{m}_{c,i} = \frac{m_i \cdot n_{C,i} \cdot M_C}{M_i} \tag{5.1}$$

$\mathrm{m}_{C,i}$ is the mass of carbon in species i, m_i is the yield of species i in [kg/kg fuel], i.e the one displayed in Figure 5.3. $\mathrm{n}_{c,i}$ is the number of carbon atoms in one molecule of species i, M_C is the molar mass of carbon in [kg/mol] and M_i is the molar mass of species i. $\mathrm{n}_{c,i}$ and M_i for the five compounds can be seen in Table 5.8

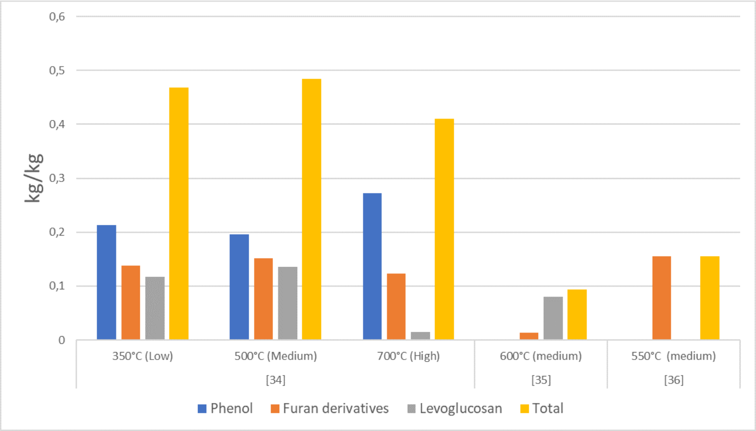
	Phenol	Furan	Levoglucosan	Benzoic acid	Terephthalic acid
n	6	4	6	7	8
M [x10^3 kg/mol]	94.11	68.07	162.14	122.12	166.13

Table 5.8: number of carbon atoms per molecule and molar mass in kg/mol

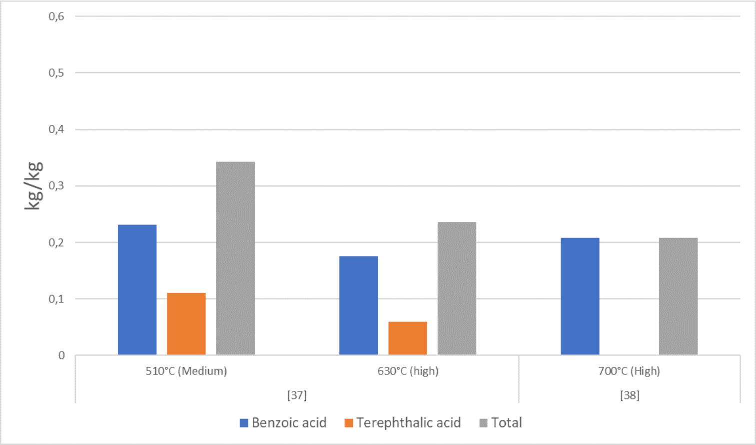
$$m_{c,fuel} \frac{n_{C,fuel} \cdot M_C}{M_{fuel}} \tag{5.2}$$

$\mathrm{n}_{c,fuel}$ is the number of carbon atoms in one molecule of cellulose and polyester, which is 6 and 10 respectively and M_{fuel} is the molar mass of cellulose and polyester.

To obtain the fraction of recovered carbon in each compound $m_{c,i}$ was divided by $m_{c,fuel}$. The result was plotted and is displayed in Figure 5.4.



(a) Carbon recovery in Cotton experiments



(b) Carbon recovery in PET experiments

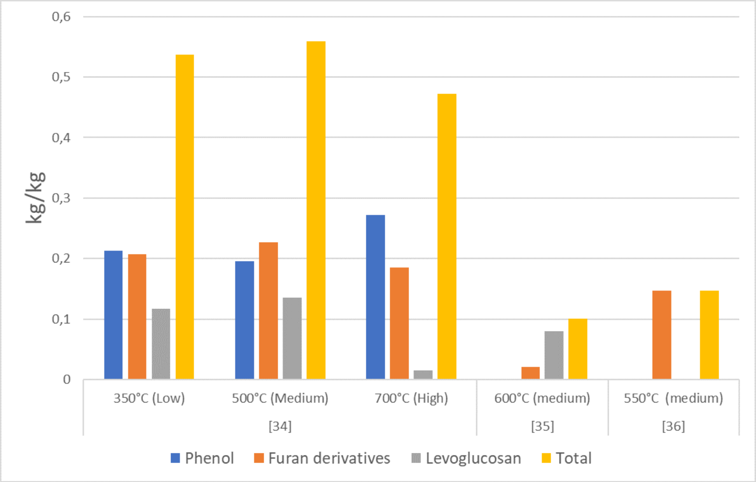
Figure 5.4: Mass of carbon in the five species divided by the carbon in cotton and polyester

These results show that approximately 10-50% of all carbon in the cotton fuel can be found in the phenol, furan and levoglucosan produced and for polyester between 20% and 35% of the carbon is found in benzoic acid or terephthalic acid. By gaining knowledge regarding the expected amount of carbon recovered in useful products, one can draw conclusions about the expected magnitude on the CO_2 emissions.

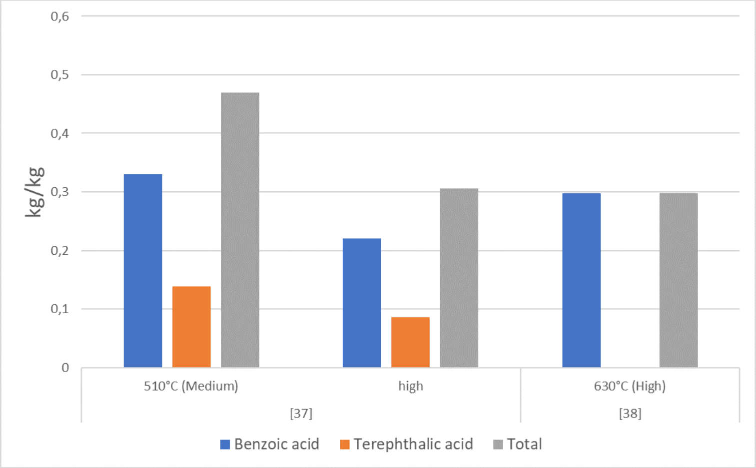
However, not all carbon in the original material is available in the formation of the compounds studied. In the formation of furan, only four of the six carbon atoms from the cellulose molecule can be utilized. The polyester molecule contains 10 carbon atoms, but only seven and eight is available in the formation of benzoic acid and terephthalic acid respectively. Following equation ca be used to calculate the recovered fraction:

$$X_i = \frac{m_{c,i}}{\frac{n_{c,i}}{n_{c,fuel}} \cdot m_{c,fuel}} \tag{5.3}$$

The results is displayed in 5.5



(a) Recovery of compounds in cotton



(b) Recovery of compounds in polyester

Figure 5.5: Efficiency of the recovery of the studied compounds, displayed in [kg carbon/kg carbon available]

In contrast to the result shown in Figure 5.4, these result are of interest when investigating how close to maximum utilization of the complex structures the recovery is. It can therefore be interpreted as a way to measure the efficiency of the recovery.

5.2 Experimental results

In the following section the results from the pyrolysis experiments will be presented and discussed. The figure below show the composition of the gas produced in the experiments were cotton, polyester and a mixed fabric was pyrolyzed. The gas contained various hydrocarbons with two and three carbon atoms. These species are presented together, here denoted HC.

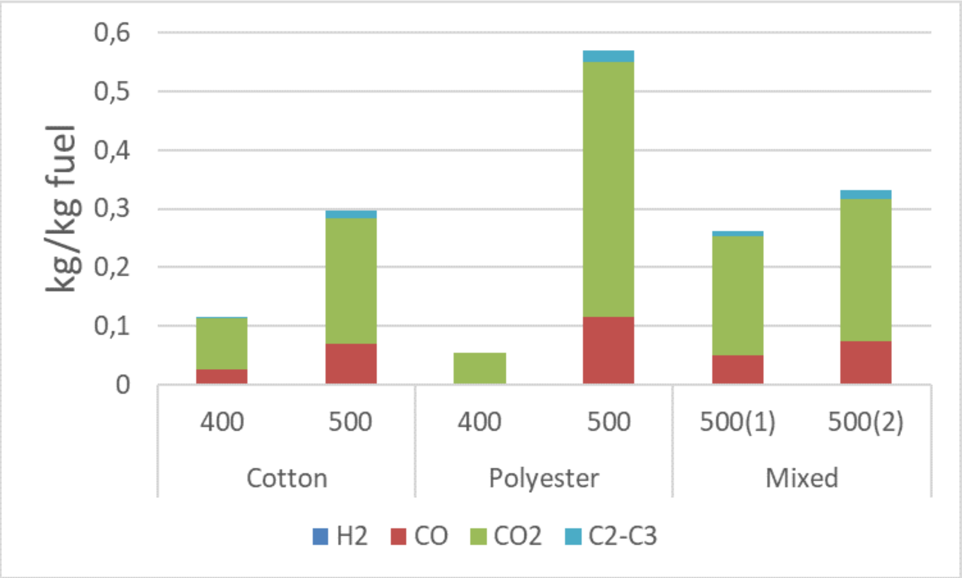


Figure 5.6: Yield of H_2, CO, CO_2 and C2-C3 hydrocarbons for experiments with cotton, polyester and mixed fabric

As can be seen in the figure, CO_2 is the dominant gas species in all experiments, followed by CO. Similar results can be seen in [34], where CO_2 and CO together make up 70.3% of the total gas produced and in [37], where nearly all gas is CO_2 and CO, see Figure 5.3 and 5.5. Unlike in the literature reviewed, no CH_4 could be detected. H_2 could only be measures in very small quantities in the cotton pyrolysis at 500°C and for the mixed fabric. In all experiments the gas yield was favored by an increased temperature, which is a trend seen in the reviewed experiments as well, see Table 5.7.

When looking at the molecular structure of polyester, see Figure 3.2, one can see that two molecules of CO_2 can be formed from each molecule of polyester. On mass basis this equals to 0.456 kg CO_2 for each kg of polyester. For the experiment with polyester at 500 °C 0.436 kg of CO_2 has been formed, which means almost all molecules has been de-carboxylated. However, for the polyester experiment at 400°C, only 0.056 kg CO_2 has been formed.

Table 5.9 shows the yield of aromatic species detected in the pyrolysis oil obtained in the experiments with cotton and polyester. In order to simplify the data, the compounds were sorted into four categories; benzene, mono-aromatic compounds, poly-aromatic compounds and phenolic species. The unknown species were put in the same category as the closest peak corresponding to a known compound. All values are given in [g/kg].

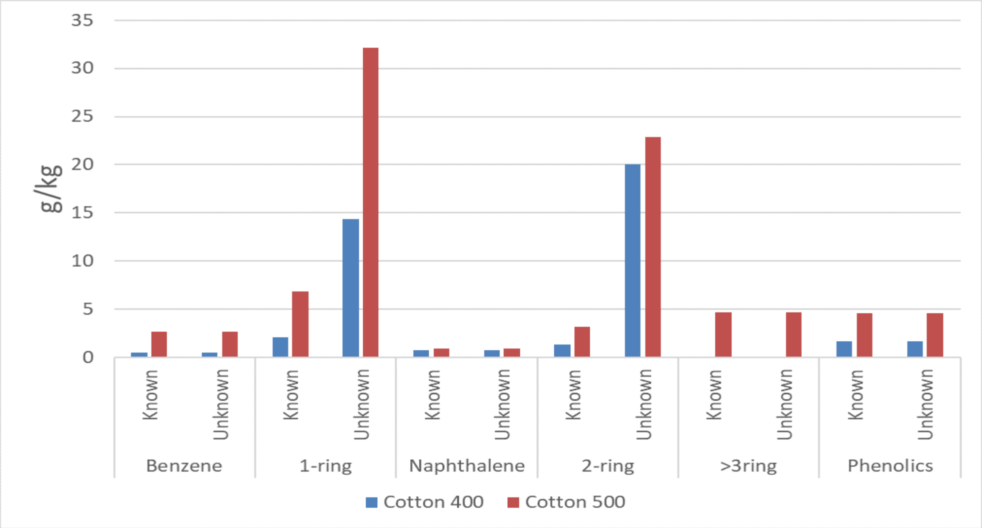
As can be seen in the table the total yield of pyrolysis oil from cotton is approximately 3.75% at 400 °C and 6.78% at 500°C. The majority of this is however unknown species, especially for mono- and poly-aromatic species. The measured yield is significantly lower compared to the one observed in literature. In [34] the liquid yield 38.4% and 46.1 % at 350 and 500°C respectively. In [36] the reported yield is 18 % at 450 °C and 29% at 500°C. Neither furan nor levoglucosan can be detected with the analysis method used for these experiments, and these species might therefore be displayed as one of the unknown species or not be seen at all. For polyester the total yield is higher; 8.36% and 35.4% for 400°C and 500°C respectively, and similarly to the cotton experiments, the majority of the tar species are unknown.

	Benzene	1-ring	>1-ring	Phenolic	Total
Cotton 400	0.54	2.06	2.23	1.68	6.51
Including unknown	0.54	14.38	20.89	1.68	37.49
Cotton 500	2.63	6.86	8.75	4.58	22.83
Including unknown	2.63	32.16	28.42	4.58	67.80
PES 400	1.31	0.34	2.64	0.84	5.13
Including unknown	1.31	4.89	76.53	0.84	83.58
PES 500	23.69	3.63	19.41	8.17	54.89
Including unknown	23.69	28.30	294.02	8.17	354.18

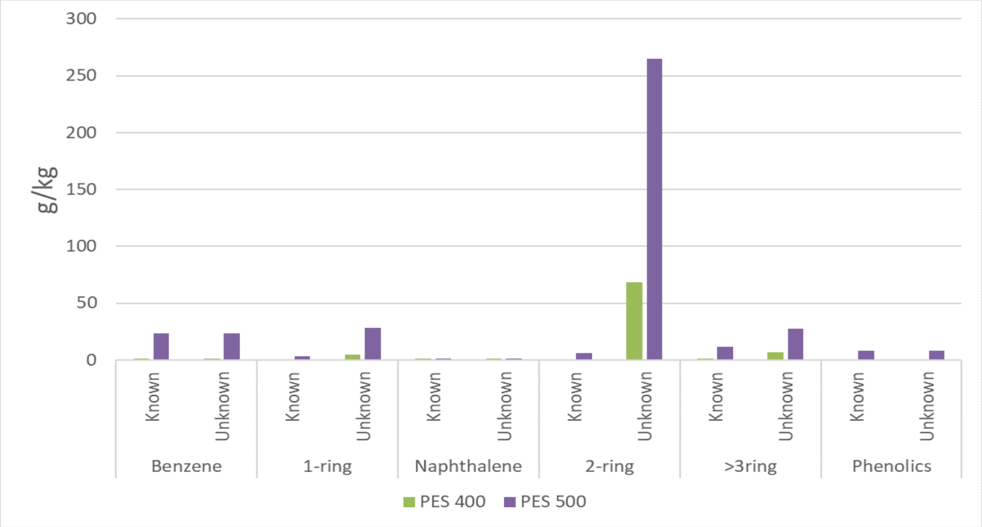
Table 5.9: Yield of aromatic species in the pyrolysis oil obtained in cotton and polyester experiments in [g/kg]

In Figure 5.7 the yield of known and unknown tar species from the cotton and polyester experiments is shown. Unlike in Table 5.9, naphthalene, 2-ring components and components with more than two rings are not grouped together in one category, but displayed individually. From the figures it can be seen that the majority of the tar species from cotton pyrolysis are unknown 1- and 2-ring aromatic compounds, and for polyester the tars are almost exclusively unknown 2-ring compounds.

In [37] and [38] benzoic acid is reported, with a yield between 10-20% and in [37] terephthalic acid is also detected. Both compounds are organic acids that was not detected with the applied analysis method, as described in Chapter 2. For the polyester experiments at 400°C, the yield of species with 2 rings or more was 76.53 [g/kg]. When analysing the data further it was observed that approximately 26 [g/kg] of this is in the form of a species with a retention time close to 2-methyl naphthalene. As the boiling point for benzoic acid is close to the boiling point for 2-methyl naphthalene, the retention time for these two species should be close, and there is therefore a reason to believe that the unknown compound is benzoic acid. For the polyester experiments at 500°C the yield of the same unknown compound is 180.2 [g/kg], which is similar to the yield reported in [37] and [38].
Out of the five components investigated in Section 5.2 only phenol could be detected using FID, but there is still a reason to believe that the remaining are present in the oil obtained in the experiments presented, as multiple studies has reported their presence in similar experiments.



(a) cotton



(b) Polyester

Figure 5.7: Yield of different groups of aromatic species as well as unknown species for cotton and polyester pyrolysis.

Figure 5.8 shows the total yield of gas and liquid product. For both cotton experiments, as well as for polyester at 400°C, the total yield is very low. For cotton the majority of the product is gas, while the tar fraction is significantly higher for the polyester.

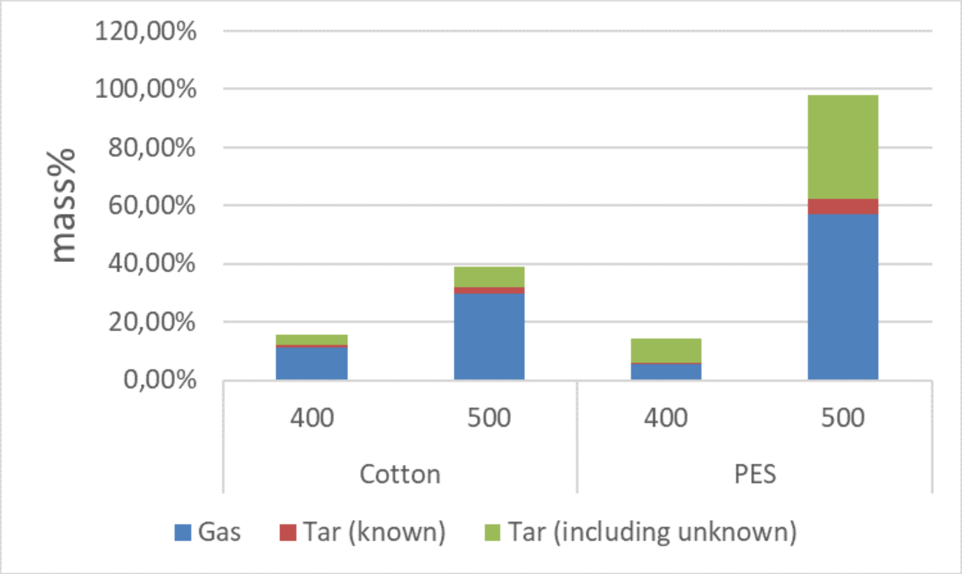


Figure 5.8: Yield of gas and tar for the cotton and polyester experiments (mass%)

In order to explain the low yield a balance over the carbon, hydrogen and oxygen in the produced gas and tar was performed. The mass of carbon, hydrogen and oxygen found in the gas and pyrolysis oil was divided by the mass och the three atoms in the fuel. As it it difficult to estimate the amount of oxygen in the unknown tar species, only the gas and known tar species are included. The result can be seen in Table 5.10 below.

		Gas	Tar (known)	Tar (including unknown)	Total yield
Carbon	Cotton 400	8.62	1.29	6.73	16.64
	Cotton 500	23.47	4.58	10.36	38.41
	PES 400	2.39	0.73	10.70	13.82
	PES 500	29.69	7.86	41.71	79.27
Hydrogen	Cotton 400	0.55	0.78	3.71	5.04
	Cotton 500	7.01	2.68	5.87	15.57
	PES 400	0.00	0.79	10.93	11.72
	PES 500	6.33	8.86	44.83	60.03
Oxygen	Cotton 400	15.22	0.06	-	15.28
	Cotton 500	38.07	0.17	-	38.24
	PES 400	11.84	0.06	-	11.90
	PES 500	114.54	0.61	-	115.14

Table 5.10: Atom balance over recovered carbon, hydrogen and oxygen in mass %

As can be seen, well below 100% of the carbon, oxygen and hydrogen in the cotton is found in the gas or pyrolysis oil produced in the cotton experiments and in the polyester experiment at 400°C. One reason for this might be that the textile sample was not fully converted when the sampling of tar and gas was finished. For polyester at 500°C the recovery of hydrogen and carbon is significantly higher, and the recovery of oxygen is larger than 100%. One explanation might be that the cotton experiments were performed prior to the polyester experiments, according to the order in Table 2.1. The unconverted cotton might then convert together with the polyester, and cause the high recovery of oxygen.

Another possible explanation for the high oxygen recovery is that moisture in the fuel that is not already accounted for reacts with the gas species. By assuming that all excess oxygen found in the products originates from moisture in the polyester, the steam that has reacted can be estimated. As the total number of moles of oxygen in the polyester is known, as well as the number of moles of oxygen in the obtained gas and tar, the steam that has reacted can be calculated, see the equations below:

$$n_{O,H_2O} = n_{O,products} - n_{O,polyester} \tag{5.4}$$

$$n_{O,H_2O} = n_{H_2O} \tag{5.5}$$

$$m_{H_2O} = n_{H_2O} \cdot M_{H_2O} \tag{5.6}$$

By using these equations it was calculated that 0.057 kg steam was converted for every kg of polyester, i.e. 5.7%. This is higher than the moisture content reported in literature, which was 0.27% [32]. As mentioned previously the oxygen content in the unknown tars was difficult to estimate, and is therefore not considered i these calculations. There is also a possibility that steam is formed in the pyrolysis process. As the analysis system used for the gas does not detect steam, this hydrogen and oxygen is not accounted for, and the yield of of these might be slightly higher than calculated.

Some of the carbon that is not obtained in the gas and tar might be in the reactor in the form of char. From literature it is known that the fixed carbon (FC) in cotton and polyester is 8.33% and 8.47% respectively[32]. The mass of char can now be estimated using the following equation:

$$m_c = FC \cdot \alpha_{c,fuel} \tag{5.7}$$

$\alpha_{c,fuel}$ is the mass% of carbon in cotton and polyester; 44.4% and 62.5% respectively. As the recovery of carbon is low, it is assumed that the char has not reacted in any way, and therefore remains in the reactor. With the estimated char included the new carbon balance can be seen in Table 5.11.

	Gas	Tar (known)	Tar (including unknown)	Char	Total yield
Cotton 400	8.62	1.29	6.73	3.70	20.34
Cotton 500	23.47	4.58	10.36	3.70	42.11
PES 400	2.39	0.73	10.70	5.29	19.11
PES 500	29.69	7.86	41.71	5.29	84.56

Table 5.11: Carbon balance when the estimated char is included

An additional reason for the low yield, especially tar, might be that the analysis method is not optimal for the species being analyzed. As mentioned in Chapter 2, the response factor for many hydrocarbons with substituent groups is low. This results in a measured yield that is lower than the actual, and will therefore affect the results. The analysis method applied might also be unable to detect certain compounds, meaning they could not be identified or quantified.

5.3 Limitations and Future Work

As mentioned, the focus in this thesis was pyrolysis of cotton and polyester, as these are the two most common fiber types. However, it is of interest to examine the pyrolysis of more fiber types, especially MMC and polyamide. An investigation of the share of different fiber types in the MSW is also required, as it must not necessarily have the same composition of the consumed textiles.

In the literature reviewed, as well as in the new experiments performed, no consideration was taken into possible additives in the fabric. In order to have a good understanding of the course of the textile pyrolysis and which products to expect, one needs to have knowledge regarding the chemical composition of common dyes and flame retardants, and how they behave in the pyrolysis. These compounds might inhibit the reactions or decompose and react with the textiles.

One limitation of the new experiments performed and analyzed in this thesis is the analysis method. As previously described, many aromatic compounds could not be detected at all or could not be specified. It is therefore difficult to draw conclusions regarding which valuable compounds that can be recovered and in what quantity. If performing new experiments, an analysis method that can detect organic acids and alcohols should be used, as these types compounds are expected to be found in the tar from cotton and polyester pyrolysis. By knowing the retention time of the desired species, these might be detectable with GC-FID. Another option is to chose an additional analysis method, to detect a broader variety of species.

Apart from many technical obstacles that have to be investigated and solved, many changes have to be done on a societal level before textile waste can be recycled by pyrolysis. Firstly, there needs to be a system to collects textiles separately.There might also be difficult to motivate this option, as it may be more costly compared to sending the textile waste to incineration, especially for retailers and textile factories, as they have to compensate incineration facilities in order for them to handle the waste. One solution that is being discussed is introducing a tax on incineration of fossil based waste. In addition, it might be more difficult to motivate recycling over the traditional waste handling method in Sweden compared to other countries. In Sweden, all waste goes to incineration with heat recovery, which is of course a batter option compared to incineration without heat recovery or landfilling. The environmental benefits is therefore smaller compared to in many other countries, where the waste is not utilized in any manner.

6

Conclusion

The currently existing recycling methods, mechanical and chemical recycling faces many challenges. Most mechanical recycling methods are down-cycling methods, meaning the end-product from the process has a lower value and quality compared to the original product. Chemical recycling methods can only handle very homogeneous streams consisting of one fiber type and no additives. These methods are therefore unable to scale up while delivering end-products of a high value, and it is necessary to investigate new recycling methods.

The expected composition of the gas and liquid from textile gasification was investigated, and it was concluded that the content of CO_2 is high due to the relative high content of oxygen in cotton and polyester. This lowers the quality of the syngas and makes it less suitable for fuel production and heat and power applications. The focus of the thesis was therefore to extract chemicals from the liquid product obtained in pyrolysis. As the temperature in pyrolysis typically is lower compared to in gasification, the aromatic structures found in textile waste will not be degraded to the same extent.

Five existing experimental studies on cotton and polyester pyrolysis were reviewed and the information regarding yield and composition of the liquid product were compiled, the five most common mono-aromatic compounds found in the pyrolysis oil; phenol, furan, levoglucosan, benzoic acid and terephthalic acid, were chosen for further investigation. The maximum yield of pyrolysis oil was obtained at a temperature between 400-600°C, between 30 mass% and 60 mass% oil was obtained in this interval. The yield of the five species investigated was lower; between 10-35%. This might be due to the fact that many components in the pyrolysis oil was not included in these calculations. The efficiency of the recovery was between 10-55% and these numbers could possibly be increased by considering more compounds to be recovered.

In the new experiments performed the gas and liquid yield was measured. Many components found in the literature could not be detected with the analysis method applied, and additional analysis methods should therefore be considered if reproducing the experiments. A balance over the oxygen, hydrogen and carbon in the gas and liquid showed that well below 100% of these atom was recovered in the cotton experiments and for polyester at 400°C. One reason for this might be that the samples was not fully converted, and a longer residence time for the cotton might be required. An additional explanation is that the analysis method used is not ideal for measuring the desired compounds, and another method should therefore be considered. In order to implement the proposed recycling method on a larger scale, several changes has to be done on a society level. There needs to be a system to collect textile waste, both from private consumers, but also retailers and textile factories. To motivate recycling it might be of interest to introduce a tax on incineration of fossil based waste. This would make it more costly to let incineration facilities handle the waste, and therefore favor recycling.

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