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Process analysis and concepts for thermal treatment of waste

Master's thesis in Sustainable energy systems

SIMON HAINDL

Department of Energy and Environment
Chalmers University of Technology
Gothenburg, Sweden 2016

MASTER'S THESIS 2016

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Abstract

In order to make a reasonable process proposal regarding the thermo-chemical treatment of waste-streams provided by the STENA Metall, a detailed literature review of different processes and state of art reactors was done. The CHEMKIN PRO simulation tool was used in order to estimate the behaviour of product formation from processing plastic in a thermo-chemical reactor with respect to temperature and the reactor atmosphere. For the process determination, optimal process conditions of pyrolysis and gasification processes are investigated to recover valuable organic and inorganic materials. Different reactors like circulating fluidized beds (CFB) and rotary kilns are examined to prove their technical and economical feasibility. Various waste-streams like SLF and WEEE are assessed by their amount of valuable metals, but also their hazardous elements. Within the CHEMKIN PRO simulation the highest yield of different chemicals and fuels is investigated. The chemicals with the highest mole-fractions are hydrogen, methane, ethylene, ethane, propene and benzene. High temperatures increase the formation of hydrogen, methane and benzene, whereas low temperatures increase the formation of ethylene, ethane and propene. High ratios of steam in the reaction atmosphere increase the production of hydrogen, methane and benzene, whereas low ratios of steam increase the production of ethylene, ethane and propane. After investigations of the influence of different parameter with the CHEMKIN PRO simulation and the evaluation of different process parameter a process layout for selected waste-streams is proposed.

Keywords: pyrolysis, gasification, waste-streams, metal recovery, fuel recovery, simulations, rotary kiln, circulating fluidized bed

Acknowledgements

Studying abroad tares down borders between countries. Since Sweden and Germany are very alike in mentality and culture the borders are not very high, however it is nice to experience similar interests. Waste treatment and the recovery of valuable materials to save natural sources for a sustainable future connects and motivates people working together. This work makes it clear that waste treatment is a global challenge and cannot be done only by one country, one company or a single person, but many helping hands are needed. To make this project possible many hands have been working together, which I am thankful for. In this stage I want to thank the company STENA Metall, especially Marianne Gyllenhammar, Henrik Jilvero and Björn Hall for their cooperation and making this work possible. Further, I would like to thank my supervisor Thomas Ekvall and my examiner Klas Andersson for the supporting in this work and the Chalmers University which provided the facility and the simulation software I could use in this work. I also want to thank Stefan Heyne and Matteo Morandin for their cooperation and quick information update about their findings from their PECREST project. Last but not least I want to thank my family and my friends which supported me mentally and for their prayer during this work.

Simon Haindl, Gothenburg, June 2016

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List of Abbreviation

Abbreviation	Explanation
ASR	Automotive Shredded Residue
BFB	Bubbling Fluidized Bed
CFB	Circulating Fluidized Bed
ECSR	Electric Cable Shredded Residue
ELV	End of Live Vehicles
HFFR	Halogen Free Flame Retardant
IW	Industrial Waste
KTH	Royal Institute of Technology
LHV	Lower Heating Value
MSW	Municipal Solid Waste
OXO	Hydroformylation
PCB	Printed Circuit Bord
PE	Polyethylen
PFO	Processed Fuel Oil
POX	Partial Oxidation
PP	Polypropylene
PUR	Polyurethane
PVC	Polyvenylchloride
ROI	Return Of Investment
SVZ	Sekundaerrohstoff Verwertungs Zentrum
SCWO	Super Critical Wet Oxidation
SLF	Shredded Light Fractions
SNG	Synthetic Natural Gas
TH	Thermal Hydrolysis
UNEP	United Nations Environment Program
WEEE	Waste Electric and Electronic Equipment
WO	Wet Oxidation
XLPE	Cross Linked Polyethylene

1. Introduction

The global rising demand of consumer goods has turned the treatment of waste into a growing challenge. The increasing waste-streams and the expansion of landfills is becoming a big issue, which is tried to be solved by building more and more waste-treatment plants. In this work waste-treatment considers the thermo-chemical treatment methods to recover valuable organic and inorganic material. In 2004 for example the DGE Engineering GmbH from Germany was involved in building one of the largest waste-treatment plants in the world with a capacity of 555 t/day for the JFE holding in Kurashiki (Japan) [1]. In 2012 the waste-streams in the EU were destined in average to 35 % landfill, 25% incineration and 40% recycling. However the EU target for recycling is placed much higher towards 70 % [2]. One possible thermo-chemical treatment method for municipal solid waste (MSW) is the gasification process to produce syngas, which can be reused in the chemical industry [3]. As a result of the growing production of electronic devices, which are based on conductors like copper and gold, but also include rare earth elements it can be an option for waste recovery companies to recover metals from the waste [4]. However, waste is not an average resource, it can contain valuable metals like gold, silver or platinum, as well as hazardous elements like arsenic, mercury or cadmium [5]. The treatment of waste becomes a huge technical challenge due to both, the diversity in composition and the fact that the composition is changing over time as new materials and products are brought into the society. For example, in order to destroy pathogens in waste sludge, water based thermo-chemical treatment methods like thermal hydrolysis, wet oxidation, or super critical wet oxidation are favourable [6]. Since waste treatment requires higher investment and high-tech devices, the recovery of waste is not favourable everywhere on the planet, why a lot of valuable material and resources end up in landfills with no further usage. Globally, the use of plastics in electronics and electrical equipment is growing very rapidly, which leads to an increasing volume of Electrical and Electronical Waste Equipment (WEEE). Today, the share of WEEE accounts for more than 20 % of the waste-streams produced in the EU and shows a steady increase in share [4]. Like WEEE, other waste fractions like Automotive Shredded Residues (ASR) coming from End of Live Vehicles (ELV) are based on plastic and metal fractions. Since in the EU only 15 - 18 % of the plastic waste is recycled, it is common to incinerate the waste leaving no option for (chemical) resource recovery [7]. In figure 1.1 common waste fractions of ELV and WEEE are illustrated. It can be observed, that both charts display a high fraction of steel and iron, but also other metals and plastics.

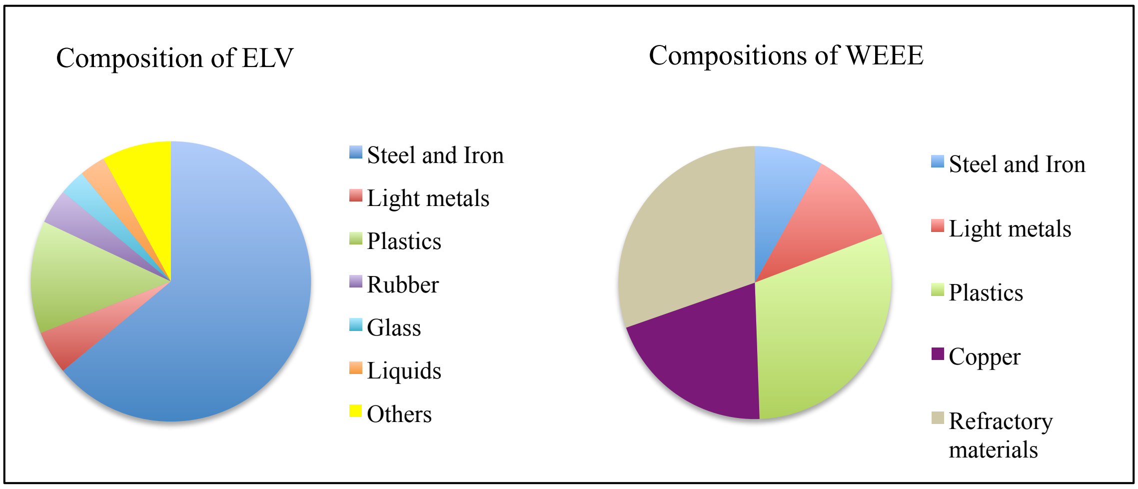

Figure 1.1.: The composition of ELV and WEEE [8], [9]

With the waste volumes that are produced today, there is a huge potential to recover materials, chemicals and energy. Therefore, it is interesting to evaluate the potential for such a recovery from different waste streams. This work will focus on a couple of waste streams from STENA Metall which are interested in terms of recovering metals, but also different chemicals and energy for their own processes or for production of commercial products. This work will evaluate the possibility of utilizing different thermo-chemical processes, especially pyrolysis and gasification which are able to transform waste into useful chemicals, fuels, energy as well as the possibility to recover valuable metals. The different waste-streams from STENA Metall will be evaluated based on their content of hydrocarbons and metals. In addition, a literature review on thermal treatment processes together with simulations will help finding a suitable process for the investigated waste-streams.

2. Methodology

The aim of this work is to propose a process possibility to efficiently transform selected waste-streams from STENA Metall into desired products. Therefore, different thermo-chemical processes, reactors and waste-streams are analyzed together with their possible products. The consideration of certain selection parameters will lead to a process suggestion. This section will point out the method in more detail.

2.1. Literature review

A detailed literature review of different processes and the state of the art reactors is performed to make a reasonable decision regarding which kind of processes that are relevant for thermal treatment of plastic based waste treatment. Investigations of different waste-streams can be found in literature and are used in this work together with chemical composition data provided by STENA Metall and were used to evaluate different waste-process combinations. Information regarding which chemicals that can be of interest and possibly produced, either primary or secondary were found in a report from the PECREST project and were used in the overall evaluation in this work. The PECREST is a collaboration between Chalmers University of Technology, Borealis AB, and Stena Recycling International AB and was done to assess concepts for the chemical recycling of waste streams to produce chemical intermediates.

2.2. Simulation

The software CHEMKIN PRO is a simulation tool which allows the user to simulate gas phase chemistry. The software uses a mechanism containing all the reactions to be considered, this mechanism is specified by the user. Especially, the transformation behaviour of plastic components at different temperatures can be assessed with the software in order to estimate the fuel and raw material production from the introduced waste-streams. This work focuses on long-chained hydrocarbons, which are important components in plastic materials. Since plastic consists of polymer material which is composed of many hydrocarbons, long-chained hydrocarbons were investigated.

The mechanism

In thermo-chemical processes, the chemical reactions can be quite complex. In order to process complex chemical structures, such as long-chained hydrocarbons which are the basis of plastic substances, CHEMIKN PRO needs a mechanism which offers enough chemical reaction possibilities and includes different species. In this work a detailed kinetic mechanism including 451 species and 17848 reactions are used. The kinetic scheme was introduced by Ranzi et al. and has later been used by e.g. Calonaci et al. to study fast pyrolysis of biomass at the particle level, with a predetermined residence time for the secondary pyrolysis [10]. Due to the large number of reactions, the computational time is relatively high. Before this work started, a compression was performed between the model set up used in this work and a work done by P. Mellin et al. [11]. In their work, a simplified version of the mechanism was used in combination with computational fluid dynamic simulations. The result of the comparison show satisfactory agreement between the two models. The results and a detailed model description can be found Appendix A.

The set-up

The model used in this work is based on a plug flow reactor (PFR) which is connected to a reactor input and a reactor outlet. Figure 2.1 illustrates the reactor layout for the CHEMKIN PRO simulation. In the reactor inlet, the input material is specified (the investigated hydrocarbon together with the reactor atmosphere). The plug flow reactor is set to have a residence time of 3 s operating at atmospheric pressure and isothermal temperature conditions. After activating the simulation, the chemicals, which were produced from the thermo-chemical treatment processes can be investigated in the reactor outlet.

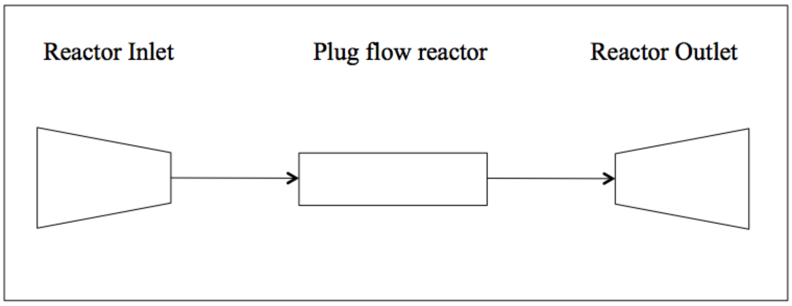

Figure 2.1.: Reactor layout for the CHEMKIN PRO process

By using the mechanism from the CRECK Modeling group, the influence of operating temperature and atmosphere composition has been investigated. Since the mechanism does not contain any actual plastic species another long chained hydrocarbon had to be used to represent the characteristics of the waste-streams investigated. In this work $NC_{16}H_{33}$ was used. Due to the uncertainty that occurs due to the choice of hydrocarbon and the fact that the material in a real waste stream does not vary in composition a sensitivity analysis has been performed. In this analysis the change in product formation due to the input chemical composition has been investigated. The influence of ingoing long-chained hydrocarbons is individually investigated in the outlet composition, when either $NC_{16}H_{33}$, $NC_{10}H_{20}$, NC_7H_{14} or C_5H_8 is fed to the plug flow reactor. During the investigations, the molar flow of hydrocarbons and atmosphere in to the reactor is kept constant at a ratio of one to one. The flow is adjusted to keep a constant residence time for all cases of 3 s. The operating temperature of the isothermal PFR is varied from 500 °C to 1000 °C. Four different atmospheres were investigated, pure nitrogen and pure CO_2, as well as to atmospheres where nitrogen and steam was mixed. In the later case the amount of steam is set by a steam-hydrocarbon mass ratio of 2.02 and 0.63 respectively and nitrogen added by difference. These two atmospheres are also used in two separate works by J.X. Zhu et al. [12] and C. Pfiefer et al. [13] respectively. Together with the steam, nitrogen is added by difference of the plastic component, which was also used from Jonathan C. Acomb et al., who investigated the pyrolysis - gasification of waste plastics for improved production of hydrogen [14]. It should be mentioned that $NC_{16}H_{33}$ was the only hydrocarbon used for the evaluation of different atmospheres and also that the the evaluation of different hydrocarbons fed to the reactor was limited to the temperatures between 600 °C and 900 °C. The settings for the different investigations are summarized in table 2.1.

Table 2.1.: Summary of the investigations

Parameter	Temperature	Hydrocarbons	Atmosphere
Length of hydrocarbons	600 °C	$NC_{16}H_{33}$	N_2
	700 °C	$NC_{10}H_{20}$	
	800 °C	NC_7H_{14}	
	900 °C	C_5H_8	
Temperature	500 °C	$NC_{16}H_{33}$	$H_2O/CxHy = 0.63$
	600 °C		$H_2O/CxHy = 2.02$
	700 °C		
	800 °C		
	900 °C		
	1000 °C		
Atmosphere	600 °C	$NC_{16}H_{33}$	N_2
	700 °C		CO_2
	800 °C		$H_2O/CxHy = 0.63$
	900 °C		$H_2O/CxHy = 2.02$

2.3. Evaluation criteria

In order to make a process proposal, the data investigated from the literature review together with the PECREST project and the results from the CHEMKIN PRO simulation were evaluated. Three main criteria are chosen for the overall process:

- high metal recovery
- good formation of valuable fuels or chemicals
- low oxidation of metals and chemicals

More detailed criteria are chosen for the different parts, reactor, material and product. Each category is presented separately below.

Reactor evaluation criteria

In order to reprocess different plastic materials, an adequate thermo-chemical reactor is necessary. Hereby, several technical and economical requirements are demanded which are presented in the following. One of the technical requirements is a large temperature range to produce different possible chemicals and fuels. A fast and homogeneous heat-transfer as well as a large particle size distribution are also examples for technical process criteria. Economical requirements are low costs and a high return of investment, so that the thermo-chemical treatment allows a lucrative procedure. To complete the list of evaluation criteria, the following listing points out the most important criteria for the selection of a reactor:

- high temperature range Δ T = 300 °C
- good temperature distribution
- low residence time possible (sec. - min.)
- good feedstock-flexibility
- good scale-up possibility
- low costs
- high return of investment (> 20 %)

Waste-stream evaluation criteria

In order to select waste-streams which can be beneficial for the thermo-chemical treatment, certain evaluation criteria were determined with focus on the net profit for STENA. First, it is necessary to have a sufficient amount of waste from the selected fraction to utilize the capacity of a thermo-chemical treatment plant. The main benefits from the thermo-chemical treatment should be considered, which are the revenue from metal recovery and the production of useful fuels and raw material. The fraction of valuable metals in this work are Al, Cu and Fe, since these metals are considered to be technically easy to extract by thermo-chemical processes. Another criteria based on the composition is the concentration of problematic substances which were chosen to be Cl and Br, since they are considered to be technically challenging to treat in thermo-chemical facilities. Another advantage is a lower demand for waste land filling today. Therefore, a lower heating value is important to eliminate a higher fraction of waste in a more efficient way. For the evaluation of the fuels, following parameter were analyzed:

- high waste-production rate (t/yr)
- large amount of valuable metals (Al, Cu, Fe)
- low concentration of problematic substances (Cl, Br)
- low heating value (MJ/kg)

Regarding technical and economical feasibility,the variety of waste-streams is limited and chosen to be restricted by two different waste-types.

Product evaluation criteria

Besides valuable metals, the production of chemicals and fuels is an important factor. Thereby, the chemicals formed in a thermo-chemical reactor should be easily transformed into fuels or chemicals useful in industries. Some of the most relevant fuels and chemicals are:

- hydrogen
- methane
- ethylene
- benzene

In order to produce such chemicals, a variety of different secondary processes can be used. Some of these processes will be described in the following chapter.

3. Thermo-chemical treatment methods

In this chapter, different thermo-chemical treatment methods are presented which are considered as the most promising technologies to recover valuable resources from different waste-streams. The following two thermo-chemical concepts are included in the investigation:

- Pyrolysis
- Gasification

In the following, the different thermo-chemical processes shall be analysed and assessed. Thereby, important process criteria are efficiency, technical experience, energy and material recovery and capacity. Figure 3.1 illustrates some possible process routes to transform waste into chemicals, fuels and energy.

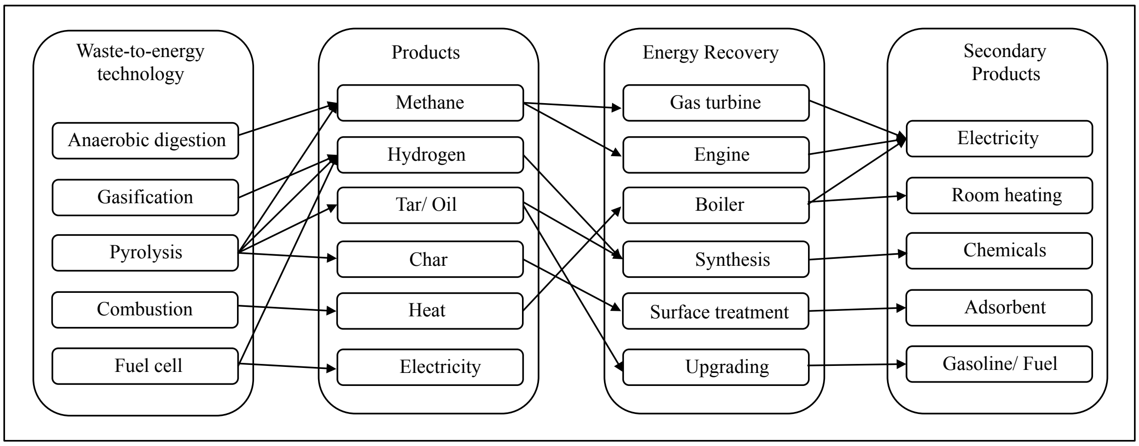

Figure 3.1.: Process routes to transform waste into chemicals, fuels and energy [15]

3.1. Pyrolysis

Pyrolysis is a thermal degradation and carbonization process working with indirect heating under a controlled atmosphere [16]. During the pyrolysis process, long polymeric chains from the input material are cut into smaller molecules [17]. The processes operates at temperatures above 300 °C in the absence of oxygen, so that the organic material decomposes into either gas, liquid or solid species [18]. The state of matter, which can have more than one aggregate phase at a certain stage depends on the heating rate, temperature and pressure. The heat transfer into the particle determines the state of carbonisation which is demonstrated in table 3.1. Slow pyrolysis shows relatively slow heating rates (100 - 300 K/min) to maximize the outcome of solid fuels (charcoal). Globally, **rotary kilns** are employed for slow pyrolysis processes. Often, they are equipped with external heating facilities like natural gas burners. Minerals and metals are easily separated from the char via dry screening or wet elutriation. In condensers, different fractions of hydrocarbons are recovered from the pyrolytic gases. In rotary kilns, different waste streams such as petroleum residues, car shredded parts and MSW can be deployed. Other techniques to realize slow pyrolysis are **moving-bed furnaces**, which are heated by electrical heating systems, molten salt heating systems or heat from the combustion of pyrolytic gases [18]. Fast pyrolysis includes high heating rates (1000 K/min) to reduce char formation and to increase the gas production. Thereby, fast quenching of the gases can increase the amount of liquid carbonisation yield [4]. Due to the high heating rates required fine grinding of the particles is necessary for a fast and homogeneous heat distribution. To realize fast or flash pyrolysis, the **vortex ablative technology** or more often the **fluidized-bed technology** is used [19]. The fluidized-bed technology includes the two reactor types bubbling fluidized-bed (BFB) and the circulating fluidized-bed (CFB) [20].

Table 3.1.: Pyrolysis processes [18]

Process	Slow carboning	Slow pyrolysis	Fast pyrolysis	Flash pyrolysis
Feed size	large	< 200 mm	< 1 mm	< 1 mm
Moisture	-	< 15 %	< 10 %	< 10 %
Heating rate	very low	<100 K/min	<1000 K/s	<10000 K/s
Res. time	days	10-60 min	0.5-5 s	< 1 s
Temp. (°C)	450-600	450-600	550-650	450-900
Pressure	atm.	atm.	atm.	atm.
Products	charcoal	gas, oil, char	gas, oil	gas, oil

3.1.1. Pyrolysis technologies

The following reactors demonstrate examples for industrial waste pyrolysis. Focusing on the most promising reactors for effective waste processing, following techniques are observed: The rotary kiln, moving-bed furnace, the fluidized-bed, the vortex pyrolysis and the rotating cone pyrolysis [21].

Rotary kiln

One of the most promising techniques for the slow pyrolysis of solid waste is the rotary kiln. Solid waste varying in shape, size and heating value can be introduced in batches or continuously. In order to reach a high heating value from the produced gas, an externally heated kiln is used [22]. Usually, the operating temperature for rotary kilns is between 500 - 800 °C, where the exact temperature can be used to set different yields as well as product characteristics. State of the art rotary kilns are known for continuous processing and long-life operation and are usually equipped with an automatic feeding system [23]. An example is the rotary kiln from the DGEngineering in Limassol (CY), which processes scrap tyres with a throughput of 800 kg/h in 2009. However, today the capacity for scrap tyre pyrolysis reaches up to 5600 kg/h. Due to new developed multi-zone electric heating systems, higher yields with less energy requirement can be achieved [23]. A process schematic of a rotary kiln is illustrated in figure 3.2.

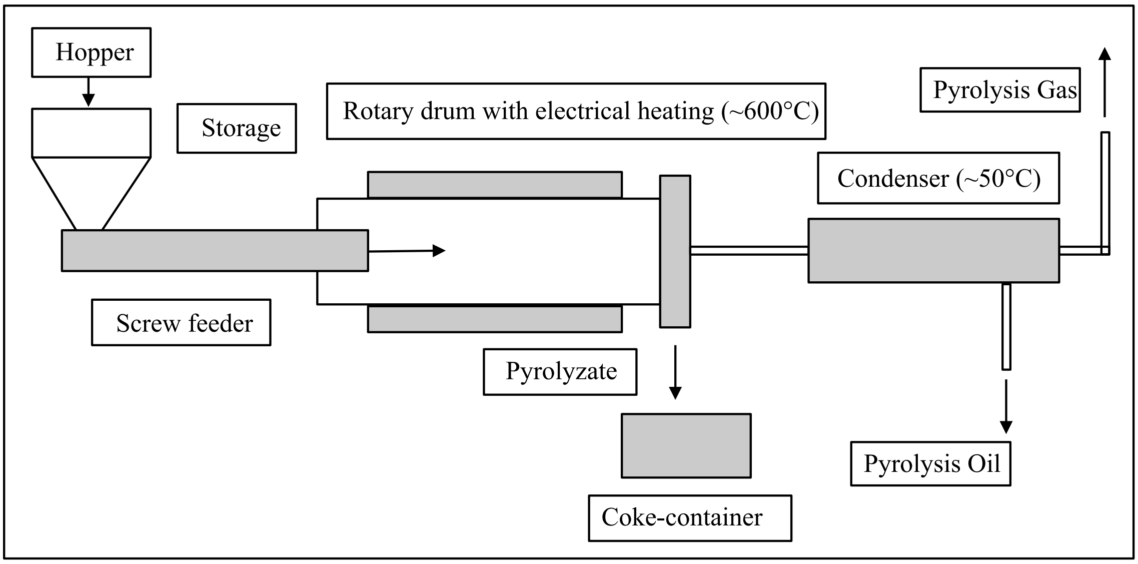

Figure 3.2.: Process schematic of a rotary kiln [23]

Moving-bed

The moving-bed technology is used for slow pyrolysis processes. A moving-bed with a fixed vertical cylindrical furnace including rotating moving blades was developed from Okadora in Japan. The process includes a completely sealed structure with a wrap-around jacket in which hot air is supplied at 600 °C. Before entering the process shell, chlorides are separated and removed from the input material. Inside of the shell, a specially designed fin is attached to the shaft and centred in the shell. By rotating the fin, the material is pushed against the heated wall by centrifugal force. Forming a thin film, the material is carbonized within 40 to 60 minutes. Afterwards carbon char and organic gases, like hydrogen and benzene are collected. A common reactor capacity for plastic waste is about 5000 kg/daily [24]. A schematic of the moving-bed furnace process is shown in figure 3.3.

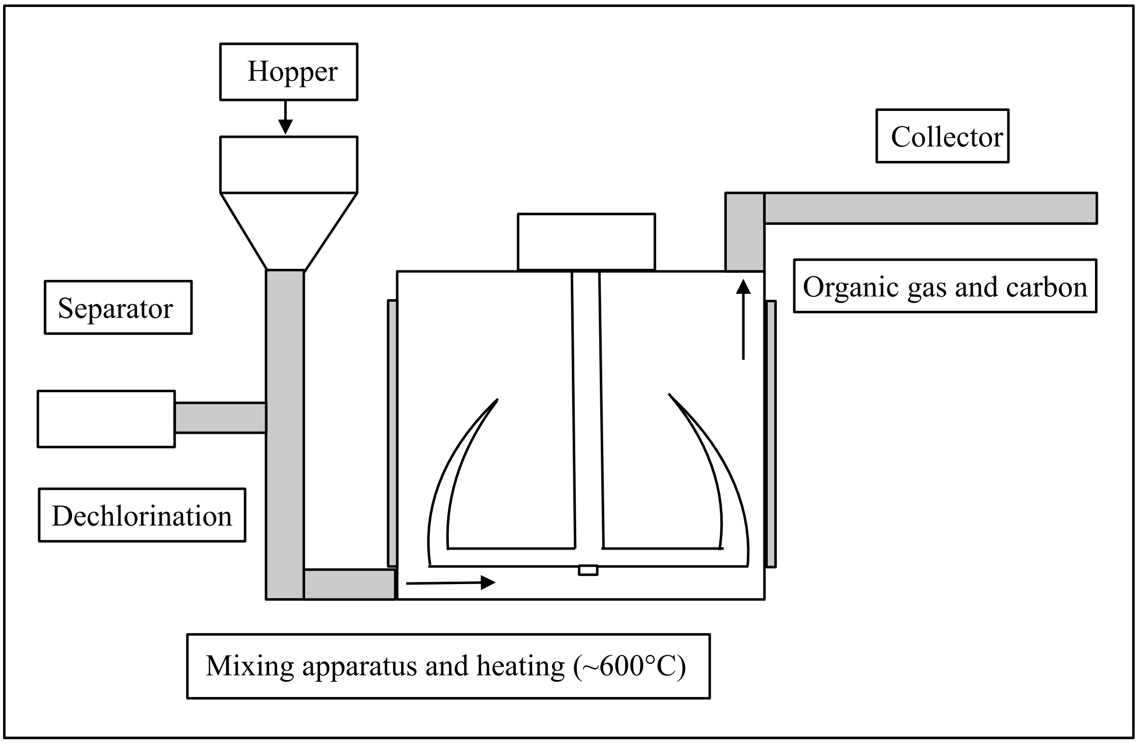

Figure 3.3.: Process schematic of a moving-bed furnace [24]

Bubbling fluidized-bed (BFB)

Due to an experience of over 50 years in the field of petroleum and chemical processing, bubbling fluidized-bed (BFB) reactors have the reputation to be a reliable and mature technology. The reactor type is applied in fast pyrolysis processes and characterized by a high heat transfer and a homogeneous temperature distribution. Depending on the size and density of the bed material different fluid flows are required to maintain the fluidization. Usually resulting in a residence time between 0.5 and 2.0 seconds [20].The fuel size is also important for the fluidization. If the fuel is not sized properly accumulations of char can cause problems why the feed in particles need to be smaller than 2 - 3 mm. Experience shows that the highest liquid yield is gained at operating temperatures of 500 - 550 °C and residence times of about 0.5 seconds. The required temperature depends on the different properties of input material. The largest reactor units are located in Spain operated by Union Fernosa (200 kg/h) and in Canada operated by DynaMotiva (400 kg/h). It needs to be considered that processed char can appear like a catalyst to enforce vapour cracking reactions. Therefore, it needs to be removed from the bed as soon as possible [25]. A schematic of the BFB reactor is illustrated in figure 3.4.

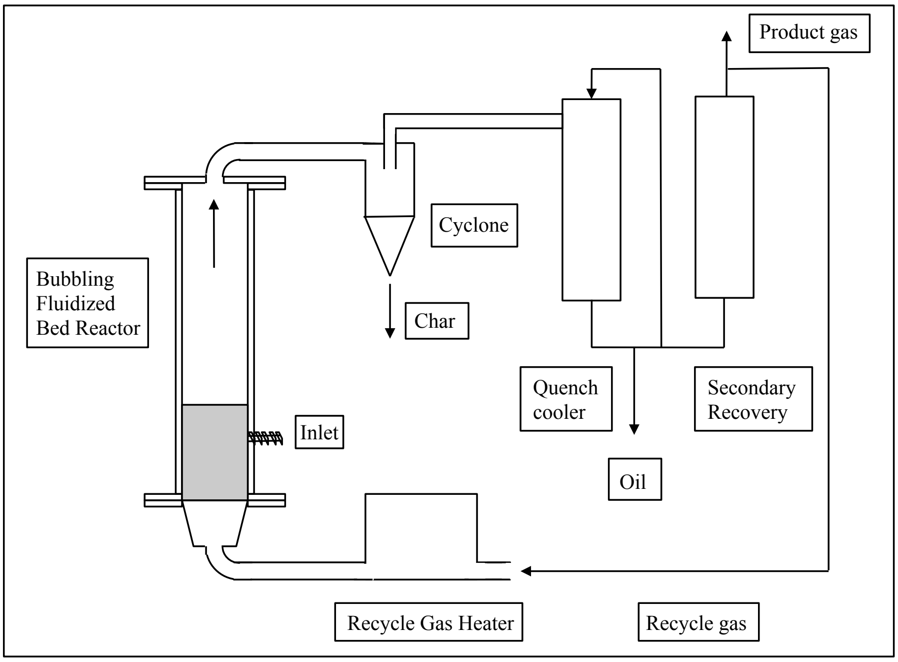

Figure 3.4.: Process schematic of a bubbling fluidized-bed reactor [25]

Circulating fluidized-bed (CFB)

Fast pyrolysis can also be achieved using a circulating fluidized-bed (CFB) reactor which also demonstrates high heat transfer rates and short vapour residence times. Although the technique is more complex and more energy intensive than the BFB reactor, the CFB technology is widely spread and can be found for example in Greece (CRES) and the Nederlands (BTG). In the CFB the flow-rate of sand is about 10 - 20 times higher than the feed-rate of input material [20]. Enabling the constant sand-flow expenses in equipment, maintenance and energy need to be considered. In CFBs, the particle size of the input material must be very small (1 - 2 mm) as the residence time is also very small (0.1 - 1 seconds). For larger particles, this time is not sufficient to transport all heat needed through the particle body. Larger particles which are incompletely pyrolyzed will be separated in the cyclone and burned in a combustor. Therefore, larger input material can lead to a lower oil yield and lower efficiency [20]. An example for the technology is a plant from the company BTG, which has an throughput of biomass of nearly 4000 kg/h and a pyrolysis temperature of 500 °C [25]. A schematic of the CFB reactor is shown in figure 3.5.

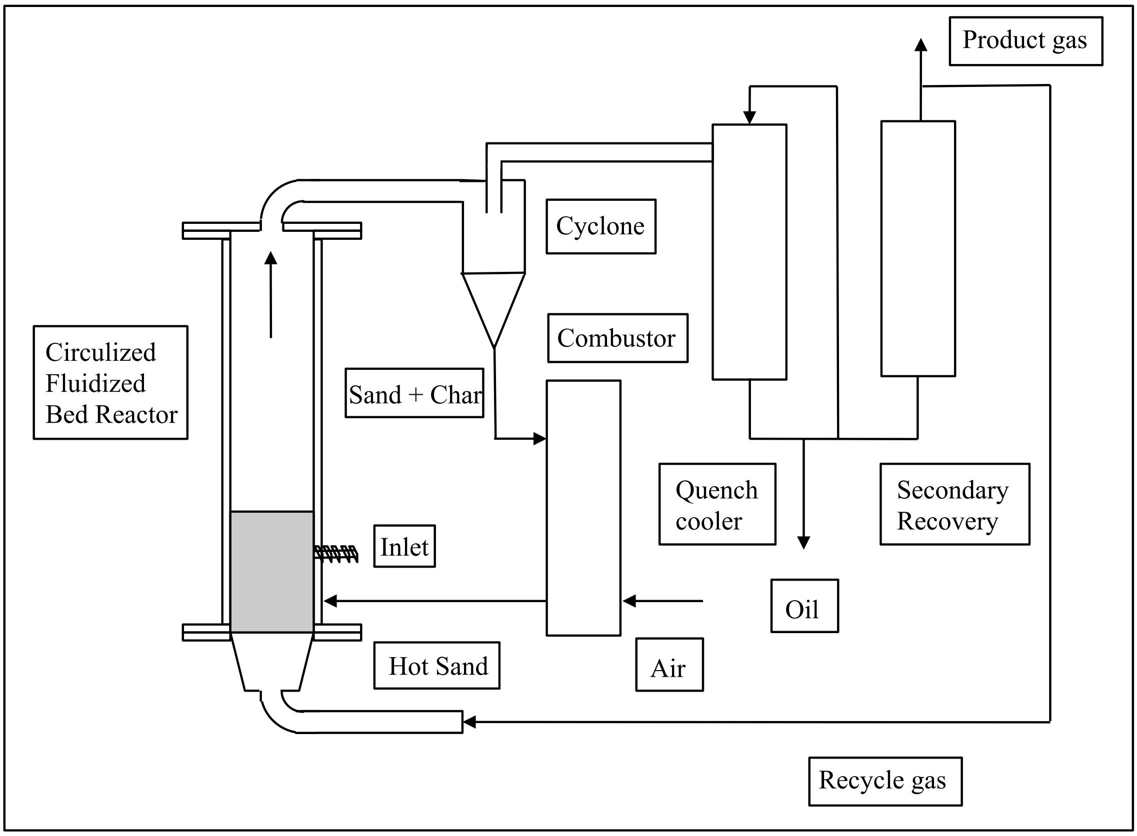

Figure 3.5.: Process schematic of a circulating fluidized bed reactor [25]

Thermoselect

The thermoselect process is a relatively new pyrolysis technology which mainly exists in Japan. During the beginning of the 21st century, high scale plants were build in Yorii, Tokushima, Nagasaki and Kurashiki, whereby each plant processes daily an amount of 300 to 450 tons of waste which consists of MSW and industrial waste. The thermoselect process recovers a synthesis gas in a continuous recycling process by means of high temperature gasification of the organic waste and direct fusion of inorganic components. In comparison with other thermal processes, there is no ash, slag or filter dust which would make secondary treatment necessary. In the first process step, the waste is compressed under high pressure, separating air and liquids. In the second step the temperature is increased and the compressed waste is further dried at the same time as the volatilisation start. The formed gases enter the high temperature reactor afterwards. The remaining solids, now mainly char are gasified under controlled addition of oxygen. Hereby plasma gasification ionize air at high voltage provided by two electrodes. When waste material enters the ionized air O_2 and N_2 atoms recombine and the temperature increases. The formed chlorinated hydrocarbons, dioxins and other organic compounds are destroyed via thermal treatment in a separate step where the gases are heated up to temperatures over 1200 °C for at least 2 seconds. The main components of the produced synthesis gas are small molecules like H_2, CO, CO_2 and H_2O. The inorganic metals and mineral components are melted in the high temperature reactor at up to 2000 °C and stabilized at 1600 °C, before subsequently shock cooled with water, where the metals and minerals are separated and extracted in the form of granulates. The separation of the mineral and metal granulate is done by magnetic separators, where the metals show a very high level of purity [26]. A schematic of the thermoselect reactor is shown in figure 3.6.

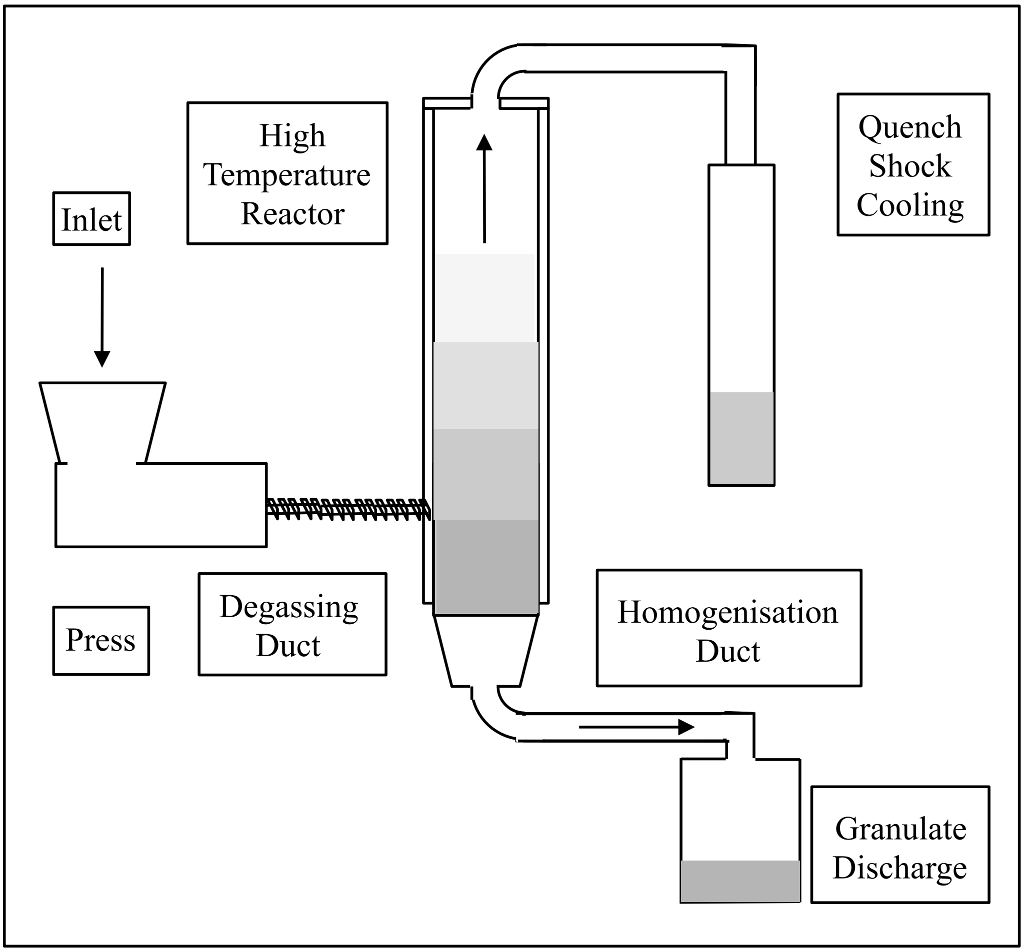

Figure 3.6.: Process schematic of a thermoselect reactor [26]

Rotating Cone pyrolysis

The development of the rotating cone process first started at the University of Twente since 1990^{th}. This fast pyrolysis technique reaches a high gas formation due to rapid heating and a short residence time. Particles fed into the reactor first enter an impeller which is mounted in the base of a heated cone. After leaving the impeller the particles flow outwards over the conical surface and experience a high heat transfer rate due to a small distance to the heated surface [27]. As the solids move over the lip of the cone, the pyrolysis vapours are lead to a condenser. The char and the sand are reheated and introduced to the cone with fresh feed. The advantages of the process are given by the absence of a carrier gas and a reduction of wear problems [28]. The disadvantages are complex design parameters and the uncertainty to scale up the process.

Advantages of fluidized-bed reactors

The following listing summarizes the advantages and emphasizes the benefits of fluidized bed reactors [4]. Table 3.2 lists up the common large scale pyrolysis plants.

- Easy, continuous and reliable operation, through a fast and homogeneous temperature distribution throughout the fluidized-bed.
- Low operating temperature range through an efficient energy allocation.
- High heat and mass transfer between gas and particles, through the liquid like flow of particles.
- Easy possibility to add or to remove high quantities of heat, through the circulation of solids between two fluidized-beds.
- High process flexibility through different fluidizing agents, operating temperatures, gas residence times and optionality of catalytic operation.
- Low maintenance and costs, through the absence of moving parts in hot regions and lower operating temperatures.

Table 3.2.: State of the art pyrolysis plants [29]

Company	Facility	Feed	Product	Reactor	Capacy
Huayin (CHN)	China	Tires	Metal, Oil, Gas	Rotary kiln	1 t/h
VTA (AST)	USA	Plastics	Char, Oil, Gas	Rotary kiln	1 t/h
Pyrocrat (IND)	India	Plastics	Char, Oil, Gas	Rotary kiln	2 t/h
Splainex (NTL)	Europe	MSW	Metal, Oil, Gas	Rotary kiln	3 t/h
RESEM (USA)	USA	Tires	Metal, Oil, Gas	Rotary kiln	3 t/h
BTG (NTL)	Malaisia	Biomass	Bio-oil	CFB	2 t/h
CARE (AUS)	USA	Biomass	Bio-oil	BFB	2 t/h
Ensyn (CAN)	Italy	Biomass	Bio-oil	BFB	6 t/h
Fortum (FIN)	Joensuu	Biomass	Bio-oil	BFB	6 t/h
JFE (JAP)	Nagasaki	MSW	Metal, Syngas	Thermoselect	13 t/h
JFE (JAP)	Chiba	MSW	Metal, Syngas	Thermoselect	13 t/h
JFE (JAP)	Yorii	IW	Metal, Syngas	Thermoselect	19 t/h
JFE (JAP)	Kurashiki	IW	Metal, Syngas	Thermoselect	23 t/h

3.2. Gasification

Gasification is a thermal degradation process working under a controlled atmosphere at temperatures between 800 - 1000 °C [16]. The process involves direct heating, allowing a limited amount of oxygen to react with carbon in order to achieve a partial combustion [4]. Today, there are three different gasification processes available which can also be combined with each other, named oxygen gasification, air gasification and steam gasification. Pure oxygen gasification produces a syngas which generally contains tars, H_2 and carbon monoxide (11 - 13 MJ/m^3) [30]. In the air gasification, also nitrogen is present which restricts the production of high-calorific gasses (4 - 6 MJ/m^3). In the steam gasification a CO and H_2 rich syngas is produced, which contains a higher calorific value (10 - 15 MJ/m^3). Combined steam and oxygen gasification has the advantage of a better process control, as the heat delivered from air gasification (exothermic reaction) can be used to reduce the demand of heat necessary for the steam gasification (endothermic reaction). To realize the gasification of plastic products, following types of gasifiers can be deployed [18]:

- Updraft and downdraft shaft gasifiers (air or oxygen)
- Bubbling- and circulating fluidized-bed gasifiers (air, oxygen or steam)
- Multiple hearth (air) and Rotary kilns (air)

The choice of the technology depends on the input-material and the desired gasification products. Thermal gasification proceeds generally in three major steps. First, the remaining moisture in the material is evaporated, secondly the material is converted into char and condensable gases (water and tars). Finally char is converted into gaseous products and gas phase reactions take place. Some important gasification reactions are listed in the following [31].

$$\text{Biomass} \longrightarrow \text{char} + \text{tars} + CO_2 + H_2O + CH_4 + CO + H_2 + (C_2 + C_5) \tag{3.1}$$

$$\text{Partialoxidation} \qquad C + \frac{1}{2}O_2 \longrightarrow CO \qquad \Delta H_r = -109\frac{kJ}{mol} \tag{3.2}$$

$$\text{ReverseBoudourd} \qquad C + CO_2 \longleftrightarrow 2CO \qquad \Delta H_r = +172\frac{kJ}{mol} \tag{3.3}$$

$$\text{SteamGasification} \qquad C + H_2O \longleftrightarrow CO + H_2 \qquad \Delta H_r = +131\frac{kJ}{mol} \tag{3.4}$$

$$\text{Watergasshift} \qquad CO + H_2O \longleftrightarrow CO_2 + H_2 \qquad \Delta H_r = -42\frac{kJ}{mol} \tag{3.5}$$

Steam gasification

In gasification processes the input material can not only be introduced under an air atmosphere, but also under a steam atmosphere. Compared to technologies such as air and oxygen gasification, the steam gasification shows following benefits [38]: First, the production of a gas with higher heating value second, the decrease of the diluting gas with nitrogen from the air and third, there are economical benefits. The disadvantage of steam gasification are a more complex system and the extra need for heat, which is normally supplied by the partial combustion in air gasification processes [39].

3.2.1. Gasification technologies

As mentioned above, there are several gasification technologies such as two types of fixed-bed reactors (updraft- and downdraft gasification), two types of fluidized-beds (bubbling and circulating), as well as multiple hearth and rotary kiln technologies [18]. Other than the reactors from the pyrolysis process, the reactors from the gasification process allow air in their process, however the reactor layout is the same. Since the fluidized-bed and the rotary kiln technology has been already shown in chapter 3.1, the following section only presents those reactor types which have not been mentioned yet, which are the fixed-bed reactors and the multiple hearth reactor.

Updraft gasification

Updraft and downdraft gasifiers are the most important types of fixed-bed gasifiers. "Updraft" and "Downdraft" are process descriptions, differing in the gas flow pattern. Updraft gasifiers are able to tolerate high moisture contents whereas, downdraft gasifiers need more dry feeds. Updraft gasifiers produce 5 to 20 % volatile tar-oils and are therefore problematic for operating engines for example [32]. In updraft gasifiers, the input-material enters an air seal at the top, where the feed is moving downwards into a counter-currently upward flowing stream of hot gas. In the pyrolysis section, the hot gas transforms the feed into tar-oil, charcoal and gases, which are captured before they reach the hot zone of the furnace. Since there is only a low thermal breakdown, the gases contain much heavy oils and tars [18]. In the reduction zone, the charcoal reacts with the upward flowing gases CO_2 and H_2O, to form CO and H_2. Below the reaction zone incoming air reacts with the charcoal to produce CO_2 and heat. The heat from this exothermic reaction is absorbed from the endothermic reduction of the pyrolysis reaction above [32].

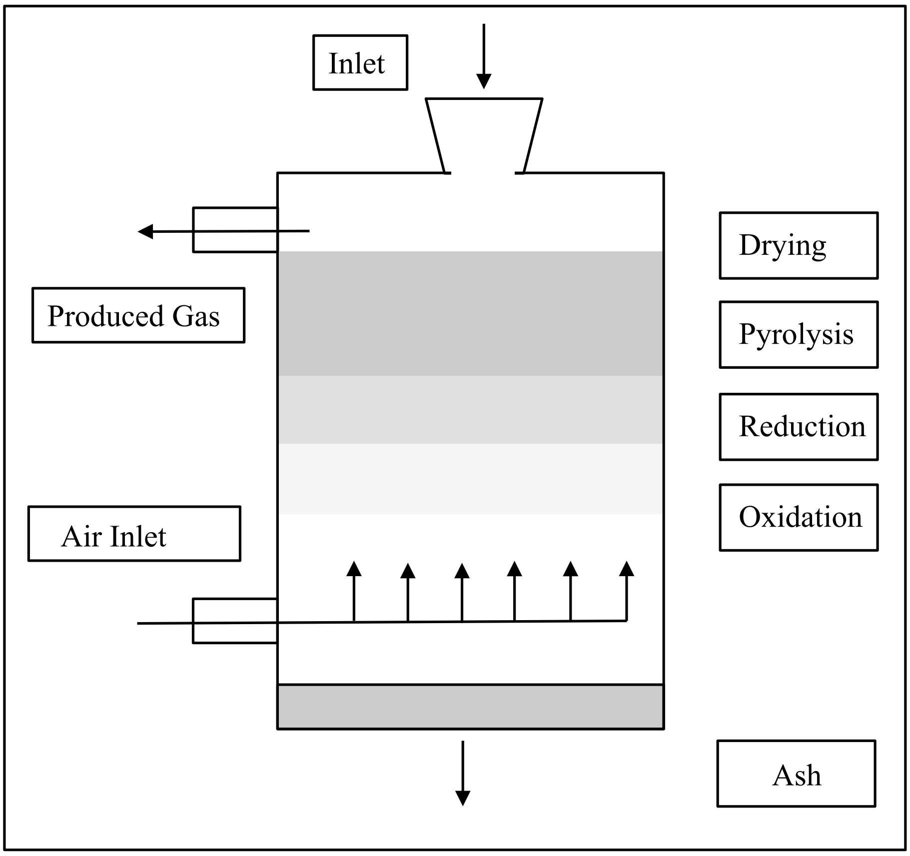

Figure 3.7.: Process schematic of an Updraft gasifier [32]

Downdraft gasification

In the downdraft gasifier, air is co-currently injected within the downwards moving waste-stream. The generated gases, tars and moistures reach the hot furnace zone where the thermal breakdown occurs [18]. When the heat from the burning volatiles (exothermic reaction) maintains the pyrolysis, the limited air supply is rapidly consumed. At the end of the pyrolysis zone, the gases mostly consist of approximately equal parts of CO_2, H_2O, CO and H_2. The so called "flaming pyrolysis" produces combustible gases during downdraft gasification and at the same time consumes 99% of the tars [34]. Important process parameter are the particle size and air velocity. Under high temperature and oxidizing conditions, volatiles and tar are cracked [33]. A process schematic of the downdraft reactor is shown in figure 3.8. In table 3.3 the main difference between fixed bed reactors like the downdraft reactor and the fluidized bed reactors are shown.

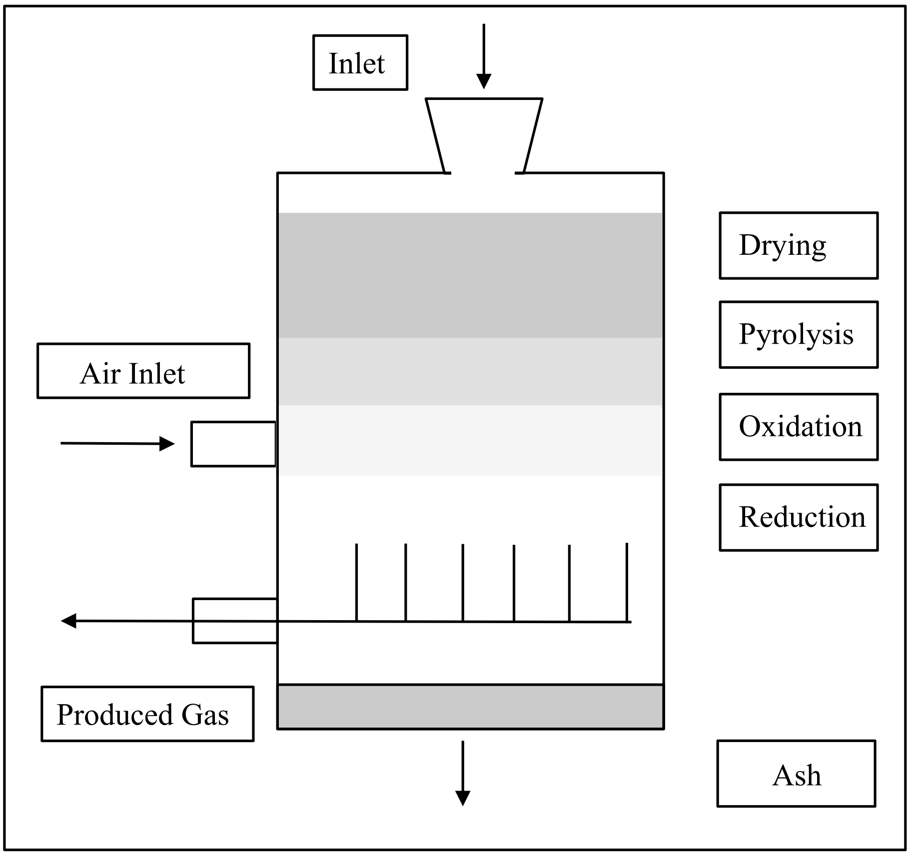

Figure 3.8.: Process schematic of an Downdraft gasifier [34]

Table 3.3.: Main differences between fixed-bed and fluidized bed gasification [37]

Fixed bed with gas	Atmospheric bubbling bed
(+) Large particle size (< 100 mm)	(-) Limited particle size (< 50 mm)
(+) Nearly tar free gas	(-) High tar content in gas (1 g/m^3)
(+) High carbon conversion (90 - 99 %)	(-) Low carbon conversion (90 %)
(+) Possibility of melting ash	(-) High ash and dust content
(-) High investment costs	(+) Lower investment costs
(-) Uniform particle size required	(+) Broad particle size distribution
(-) Lower capacity and slow heat-up	(+) High capacity and fast heat-up

Multiple hearth gasification

In a multiple hearth furnace, the input material is fed at the top and is conveyed to the bottom applying an automatic arm pushing the feed at differently staged hearths. Air flows from the bottom as the flue-gas is mixed with the pyrolytic gases counter-currently flowing upstream heating the waste. Hereby, the ash is extracted at the bottom of the furnace [18]. According to the company CMI group Nesa Solution, the advantages of a multiple hearth furnaces is a high thermal efficiency, a good furnace control, low NO_X emissions and low operational costs [35]. A process schematic of the multiple hearth reactor is shown in figure 3.9. In examining the profitability of the different reactors, one important parameter is the return of investment (ROI). Shown in a study on the pyrolysis of mixed plastics in the Netherlands following results have been assessed. Thereby, a bubbling fluidized bed (BFB) reactor operating at 740 °C showed a ROI of 21.7 %, whereas the ROI of a rotating cone reactor operating at 625 °C was 14.2 % and the ROI of a CFB operating at 840 °C was 29.5 % [50]. Hence the highest economical profitability was achieved by the CFB, which costs 7.8 to 11.2 million USD for a capacity of 50 kt/year [51]. Table 3.4 lists the common large scale gasification plants, which are used in today‘s state of the art gasification plants.

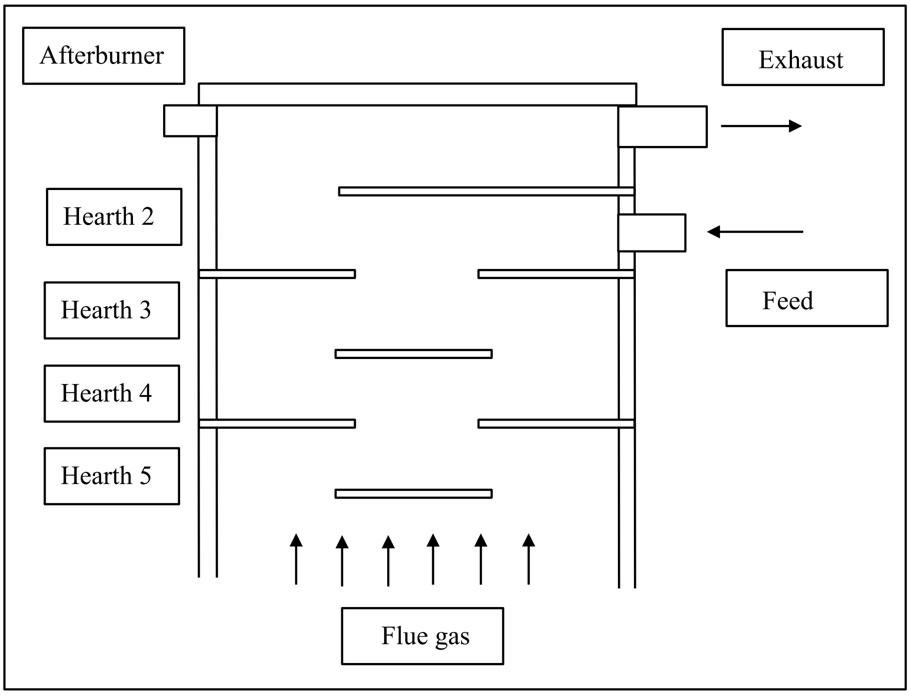

Figure 3.9.: Process schematic of a multiple hearth gasifier [36]

Table 3.4.: State of the art gasification plants [40]

Company	Facility	Feed	Product	Reactor	Capacity
Westinghouse (US)	Mihama	MSW	Syngas	Updraft	1 t/h
ALTER (CAN)	Utashinai	ASR, IW	Syngas	Updraft	7 t/h
Chinook (USA)	UK	ASR, MSW	Syngas	Updraft	11 t/h
InEnTec (USA)	Oregon	ASR	Syngas	Downdraft	1 t/h
SVZ (GER)	Saxony	ASR, MSW	Syngas	Downdraft	21 t/h
Enerkem (USA)	Mississipi	MSW, IW	Ethanol	BFB	11 t/h
Ebara (JPN)	Ube	MSW	Syngas	CFB	7 t/h
Covanta (USA)	Boston	MSW, IW	Syngas	CFB	16 t/h
Lahti (FIN)	Lahti	ASR, MSW	Syngas	CFB	28 t/h
Coskata (USA)	Illinois	Biomass	Ethanol	CFB	60 t/h

Summary of reactors

In table 3.5, four different promising reactor types were characterized by certain technical parameter. Hereby the rotary kiln and the BFB represent promising pyrolysis reactors, whereas the fixed bed and the CFB reactor represent the promising gasification reactors.

Table 3.5.: Characteristics of different reactor types [53]

Property	**Rotary kiln**	**Fixed bed**	**BFB**	**CFB**
Δ T	450 - 800 °C	400 - 800 °C	550 - 850 °C	750 - 850 °C
Heat transfer	Moderate	Poor	Very good	Very good
Particle size	Large	Wide range	Diam: 3 mm	< 10 cm
Res. Time	1-2 hours	-	min / hours	follows recirculation
Conversion	High	High	Poor	High
Feedstock - flexibility	Limited	Poor	Excellent	Excellent
T profile	Large	Large	T constant	Follows mass transfer
w/o Catalyst	Very good with large solid content	Unsuitable	Excellent	Excellent
w Catalyst	-	Slow	Excellent	-
Scale-up	Limited	Poor	Limited	Limited
Cost	Maint. high	High	Moderate	Moderate
ROI	14.2 %	-	21.7 %	29.5 %

4. Material characteristics

This chapter includes the characterisation of different materials with regard to the chemical composition of different waste streams, but also the chemical composition appearing after the thermal treatment of waste. Furthermore, it includes different procedures to treat and transform chemicals.

4.1. Waste characteristics

Some of the most promising waste-streams, which are provided from STENA Metall are listed in table 4.1. This table should give an overview of the main characteristics and the availability of the mentioned waste-fractions. There are some characteristics that are more important than others when it comes to the evaluation if a waste-stream is suitable for thermo-chemical treatment. Such characteristics are, the fraction of valuable metals and problematic components, as well as the energy content and availability. In the following section the characteristics of the waste-streams are explained in more detail.

Table 4.1.: Summary of chemical components from different waste streams *Data from pyrolysis experiments made by the Royal Institute of Technology (KTH)

Waste	Production (t/yr)	Metals	Problematics	LHV (MJ/kg)
Rubber*	TBA	Al 0.25 %, Fe 0.25 %	Cl 0.03 %	32
Cable plastic*	2,500	Al 0.5 %, Cu 0.3 %, Fe 0.01 %	Cl 0.17 %	21-44
PUR*	2,500	Cu 0.1 %	Cl 0.6 %	15
PFO	28,000	Cu 0.002 %	Cl 0.15 %	41
WEEE (landfill)	5,000	Al 4.5 %, Cu 3.0 %, Fe 0.4 %	Cl 4.0 %, Br 0.7 %	20
WEEE (incineration)	5,000	Al 0.35 %, Cu 0.32 %, Fe 0.22 %	Cl 0.24 %, Br 1.5 %	30
SLF	65,000	Al 3.6 %, Cu 2.7 %, Fe 13 %	Cl 1.2 %	16

Cable plastics

Cable plastics are usually provided in a granulate form (2 - 8 mm) and contain different plastic materials like XLPE, PVC and HFFR. The XLPE cable plastics are not contaminated with heavy metals, but include Al and Cl fractions under 0.1 %. PVC cable plastics contain inorganic fillers ($CaCO_3$) and have a Cl content of about 20 %. HFFR cable plastics contain organic fillers ($Al(OH)_3$, $Mg\ (OH)_2$) up to 60 %. The lower heating value (LHV) reaches from 21 to 44 MJ/kg [54].

PUR

The main source of waste containing polyurethane (PUR) comes from freezers and coolers. PUR has relatively high content of nitrogen and oxygen. Today, PUR in waste form is used as an oil-absorbent and sent for incineration. The Cl content in the PUR waste-streams is 0.1 %, whereby the LHV is 15 MJ/kg [54].

PFO (ERC-14)

PFO is the name for a processed fuel-oil made from waste oil fragments. In processing the oil fragments, different solvents together with water and larger particles are removed. It needs to be considered, that PFO is only allowed to be incinerated in facilities that have permits for waste treatment (cement- or waste incineration plants). In the EU these permits are offered by local Environmental Permitting Regulations (EPR). Due to its high heating value (41.4 MJ/kg), it is considered having a high commercial value [54]. In order to determine the different fractions of PFO, the Saybolt laboratory company assessed a sample of PFO (ERC-14) from Stena Metall [55]. Analysing the ash content from the sample, table C4 in the Appendix C shows only little fractions of valuable elements like Cu (0.002 %), Co, Cr, Ni, Tl, Zn and also little health affecting elements like As, Cd, Hg, Sb and V. Analysing the gas content fractions of Cl (0.15 %) and S (0.53%) were observed.

WEEE (incineration)

Observing WEEE, the waste can be divided into material, which is used for incineration purposes and into materials, which is usually stored in landfills. WEEE contains a broad mix of thermoplastics (PE, PS, PP, PC, PVC, ABS) and thermosets like printed circuit boards (PCB) [6]. To extract information of the material elements, the Technical Research Institut of Sweden (SP) analysed a sample of WEEE (incineration) (0.6 kg) from STENA Technoworld [56]. Observing the ash from the sample, table C5 in the Appendix C shows a relatively large fraction of Al (0.35 %), Cu (0.1 %) and Fe (0.22 %), but only little fractions of other valuable elements like Co, Cr, Mo, Ni, Tl, Zn. Analysing the gas from the sample a high fraction of Br (1.5 %), but also fractions of Cl (0.24 %), F (0.15 %) and S (0.02%) were observed. During the analysis a heating value of about 30 MJ/kg was measured.

WEEE (landfill)

WEEE (landfill) is a waste-fraction of WEEE, which is landfilled since it contains a high amount of chlorine. Analysing the elemental fractions of WEEE (landfill), the Technical Research Institut of Sweden (SP) analysed a sample of WEEE (0.7 kg) from STENA Technoworld [57]. The components from the ash of the sample are listed in table C6 in the Appendix C, in which a large amount of valuable elements like Al (4.5 %), Cu (3.0 %), Fe (0.4 %), Ti (0.33 %) and some fractions of Co, Cr, Mn, Mo, Ni, Tl, Zn are observed. However, there are also health affecting elements like As, Ba, Cd, Hg, Pb (0.07 %), Sb (0.2 %) and V. Analysing the gas fractions, Br (0.7 %), Cl (4.5 %), F (0.08 %) and S (0.11%) were observed. It has to be noticed that the content of Cl is quite high and that it is very difficult to treat waste with such a high amount of hazardous substances. During the analysis, a heating value of about 20.3 MJ/kg was measured.

Shredded Light Fractions (SLF)

A sample of the SLF provided by STENA Metall was analyzed by the Swedish Consulting Company WSP. Observing the elemental fractions of the ash content from the sample listed in table C7 in the Appendix C, a large amount of valuable elements like Al (3.6 %), Cu (2.7 %), Fe (13 %), Ti (0.3 %), Cr (0.1%), and some fractions of Co, Mn, Mo, Ni, Tl, Zn is shown. However, some health affecting elements are included like As, Ba (0.4 %), Cd, Hg, Pb (0.1 %), Sb (0.02%) and V. In the gas content from the sample, some fractions of Cl (1.2 %), F (0.2 %) and S (0.5%) were observed. A heating value of about 16 MJ/kg was measured [58].

Rubber

The fraction of rubber is going come from Halmstad, but it is not produced yet. This waste-stream includes mostly rubber and some plastics and is considered a problematic fraction. Unfortunately there are only limited composition estimates, which make the waste characterisation difficult. There are also no specific numbers regarding the yearly production available since the production primarily needs to be estimated [54].

4.2. Thermal treatment of waste

This section presents some of the material characteristics after their thermal treatment. The aim is to assess the aggregate phase of waste material at different temperatures. Another focus is based on the examination of problematic substances which are delivered by breaking up the chemical structures of plastics.

Aggregation conditions of plastic

In the following, the pyrolysis of polyethylene (PE) is used as an example to demonstrate the different aggregate phases in which the initially solid plastic is transformed. To measure the fractions of different products, various techniques are used such as the thermogravimetry (TGA) and the dynamic or isothermal measurement [4]. For the tests, a fluidized-bed (FB) reactor was employed. The measurements include the atmospheric pressure (1 bar), the end temperature and the distribution of the aggregate phase of the sample. In table 4.2 the mass distribution of the particles for different aggregate phases is shown for carbonizing PE at fast heating rates [21].

Table 4.2.: Demonstration of the mass distribution of PE with fast pyrolysis in a fluidized bed reactor (gas G, liquid L, solid S) [18]

Conditions		Mass balance			
Reactor type	p (atm)	T (°C)	G (%)	L (%)	S (%)
FB	1	515	4.3	89.8	5.9
FB	1	654	17.5	73.5	1.1
FB	1	790	61.5	32.8	0.2

Comparing the mass distribution at the fast pyrolysis at atmospheric pressure and increasing temperature, following effects are noticed. During the pyrolysis a relatively high amount of solids is formed at low temperatures and is decreased with increasing temperature. With an increasing temperature, the fractions of gases and liquids increase, where liquids show the highest share at 654 °C and gases the highest share at 790 °C.

Pyrolysis of cable plastics

Examining the different elements of mixed cable plastics, the Royal Institute of Technology (KTH) in Stockholm assessed a sample (30 g) of Electric Cable Shredded Residues (ESCR), which was separated from the copper-cables inside [59]. In order to prevent HCl formation and to avoid corrosion problems, also the PVC was removed, so that the remaining material was only Polyethylene (PE). Due to the dehydrochlorination it is even possible to catalyze and accelerate the pyrolysis process [60]. The pyrolysis experiments took place at a temperature range between 700 -1050 °C and at an applied flow-rate of 0.5 m^3/h. In order to extract composition data, the cable plastics were investigated at a flow-rate of 0.5 m^3/h at temperatures between 700 -1050 °C. Observing the ash from the pyrolysis process table C1 in the Appendix C shows a reasonable amount of valuable elements like Al (0.5 %), Cu (0.3 %) and Fe (0.01 %), but also health affecting elements like Pb (0.004 %). Analysing the gas content, small fractions of Cl (0.17 %) and S (0.001 %) were observed, measuring a heating value of 32 MJ/kg.

Pyrolysis of PUR

In order to determine the composition of Polyurethan (PUR) waste, the KTH assessed a sample (10 g) of ASR [61]. Thereby, the ASR was separated into fractions rich in rubber and rich in PUR plastics. Each fraction was examined by microwave treatment at a flow-rate of 0.65 m^3/h and a temperature of about 900 °C. The pyrolysis experiments took place at a temperature of about 900 °C and a flow-rate of 0.65 m^3/h. Analysing the ash of the sample, table C2 in the Appendix C shows the elemental fractions containing some Cu (0.1 %), but no high shares of other valuable elements like Al, Cr, Ni. Also some health affecting elements like Pb (0.1%) and Cd can be found. Analysing the gas from the sample, fractions of Cl (0.6 %) and S (1.18 %) were observed. During the analysis, a relatively low heating value of about 15 MJ/kg was measured.

Pyrolysis of rubber and SLF

In order to determine different elements of rubber waste, the Royal Institute of Technology in Stockholm assessed a sample (10 g) of SLF. Thereby, the SLF was separated into fractions rich in rubber and rich in PUR plastics. All fractions were treated by microwave pyrolysis, in which the weight of raw SLF was reduced by 50 % and its volume was decreased by 90 %. The pyrolysis experiments took place at temperatures of about 900 °C and a flow-rate of 0.65 m^3/h. Observing the different elements in the ash content of the sample, table C8 in the Appendix shows a relatively large amount of valuable elements like Al (0.25 %) and only little fractions of Cu, Cr and Ni. Analysing the different elements in the gas content of the sample, Cl (0.03 %) and S (1.01%) were observed. During the analysis a heating value of about 32.1 MJ/kg was measured [61].

4.3. Problematic substances

Numbers of substances formed during the pyrolysis and gasification processes are difficult to treat. This section covers only three problematic elements, which commonly demand for cost intensive cleaning steps.

Bromine and Chlorine

Chlorine is a present component in all fractions of plastic waste. Since Chlorine and Bromine are chemically comparable, their reaction behaviour can be considered as similar [62]. During the gasification process, bromine (Br) forms radicals that react to HBr and Br_2, but also metal bromides can be formed [63]. For example, in the case of gasification of PVC the calcium containing filler material reacts by nearly 100 % with HCl and forms $CaCl_2$ [64]. In order to isolate bromine, water can be used to produce aqueous hydrobromic acid or an alkaline sodium or an calcium (hydroxide) solution [65]. A study from the Forschungszentrum Karlsruhe in Germany offered following results considering the co-combustion of WEEE and MSW in a pilot scale plant TAMARA. The amount of bromine was distributed in the grate ash (2 %), fly ash (20 %) and in the flue gas (78 %) [67]. At higher residence times and higher temperatures, more HBr and HCl was found in the fly ash. In gasification or combustion processes limestone ($CaCO_3$) is used to capture HBr, HCl, but also SO_2. However, it is economically very difficult to reprocess the formed salt ($CaBr_2$)to regain the bromine [68].

Antimony

During the gasification process two different formations of the chemical antimony (Sb) appear. At 656 °C the trioxide melts and sublimates at 1550 °C to form Sb_2O_3 and SbO_3. Depending on operating conditions, antimony may be found in the grate, fly ash or in the gas phase. Under reducing conditions, it will be absorbed in the salt form $SbBr_3$, which boils at 280 °C. As the residence time is smaller in the gasification process as in a combustion process not all antimony converts into Sb_2O_3 [66]. During the pyrolysis process, the reducing atmosphere and temperatures between 550 - 850 °C provide conditions for the formation of $SbBr_3$. At lower temperatures, water can be applied to hydrolyse $SbBr_3$ to form trioxide, which can be recovered by filtration [62].

4.4. Production of chemicals

This section deals with the reprocessing possibilities to convert produced chemicals like CO, H and CxHy into more desirable chemicals like methanol, ethanol or benzene. During this work, the PECREST project took place, which is a collaboration between Chalmers University of Technology, Borealis AB, and Stena Recycling AB. PECREST stands for plastics chemical recovery for production of chemical intermediates at a Swedish chemical complex, which should be comparable to the complex in Stenungsund. Within the PECREST project, process concepts for chemical recycling of waste streams for production of chemical intermediates have been assessed [53].

The aim of this project was to develop a layout for an envisioned waste-to-chemical plant, which includes a process for production of ethylene via gasification of plastics and a process for production of syngas for OXO-synthesis applications via pyrolysis of SLF and WEEE. Regarding the metal recovery of these two streams, an efficiency during the pyrolysis process was expected to be at following rate: aluminium 70 %, copper 90 %, iron 70 %. Based on rather optimistic assumptions, it is found that from the Swedish waste-streams about 120 kt of ethylene per year and about 44 kt of syngas can be produced, which correspond to a recycling rate of the waste-input of about 15% and 26%, respectively. The information from the PECREST project were used to make process proposals to maximize the production of certain valuable chemicals in different thermo-chemical processes. There are several routes from "syngas" to other valuable chemicals. This section will list some chemical transformations which were used in the Stenungsund chemical complex. Thereby, "syngas" is commonly understood as a mixture of CO, H_2, which can also include some CO_2, H_2O and other hydrocarbons.

Production of Methanol

The production of methanol via gasification of biomass can reach an efficiency of 45 to 55 % on an energy base [69], but also 60 % are possible on rather advanced gasification processes [70]. The production of methanol via gasification was investigated in the current Skogskemi project [71]. Methanol was synthesized from CO and CO_2 according to following reactions:

$$CO + 2H_2 \longrightarrow CH_3OH \tag{4.1}$$

$$CO_2 + 3H_2 \longrightarrow CH_3OH + H_2O \tag{4.2}$$

Production of Synthetic natural gas (SNG)

At the Stenungsund complex, SNG production was investigated via biomass gasification for a process similar to the process layout of GoBiGas Bio-SNG plant in Gothenborg [31]. Thereby, the conversion from biomass to SNG can reach values between 65 to 70 % on an energy base. SNG can be synthesized from CO and CO_2 according to following reactions:

$$CO + 3H_2 \longrightarrow CH_4 + H_2O \tag{4.3}$$

$$CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O \tag{4.4}$$

Syngas to OXO synthesis

Since natural gas at Stenungsund is used for the production of syngas, the syngas could also be produced directly from biomass without taking the methanation route. Thereby, the OXO synthesis is a possibility to produce syngas directly from biomass. It was found that the direct syngas production can lead to about 5 to 10 percent increase compared to the bio-SNG route on an energy base. In figure 4.1, the different routes for a syngas upgrade are illustrated.

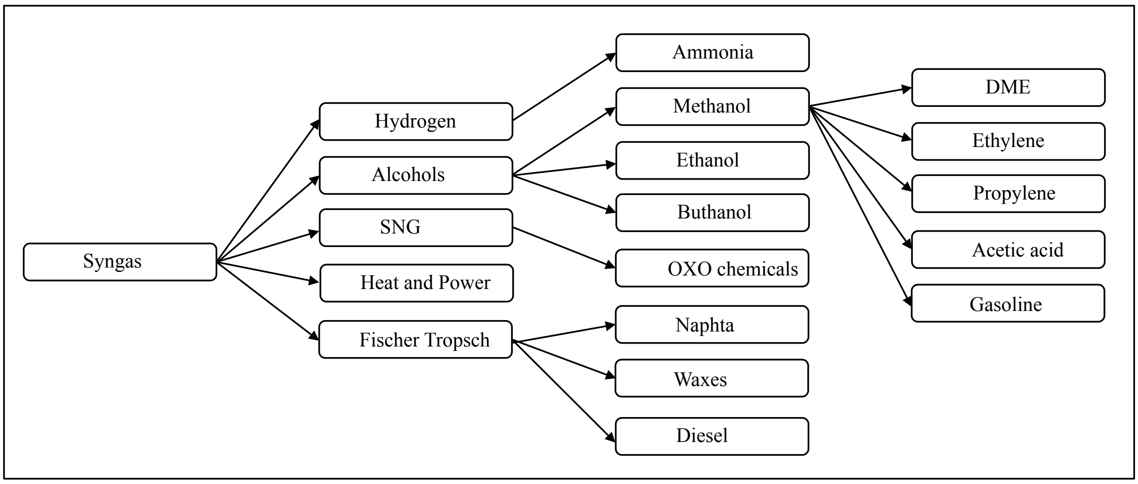

Figure 4.1.: Different synthesis possibilities for syngas upgrading [53]

Partial oxidation (POX)

At the partial oxidation, a fuel-air mixture is partially combusted in a reformer at sub-stoichiometric conditions where a H_2 rich synthesis-gas is formed [72]. Today, two different processes are used, which are Partial Thermal Oxidation (TPOX) and Partial Catalytic Oxidation (CPOX). The reactions at TPOX take place at around 1200 °C depending on the injected air, whereas the reactions at CPOX take place at around 800 - 900 °C depending on the catalytic media. Under a sulphur content of 50 ppm the CPOX can be applied [72].

Steam cracking

Steam cracking is a petro-chemical process which transforms long-chained hydrocarbons (Naphtha, Propane, Ethane) into short-chained hydrocarbons in the presence of steam as a reactive atmosphere [73]. The main products of a typical Naphta process are ethene (29.1 %), benzene (19.6 %) and methane (15.4 %) [74].

Hydroformylation (OXO)

The hydroformylation, known as OXO synthesis, is an industrial process to produce aldehydes from alkenes by using a catalyst [75]. The chemical reaction is based on adding a formyl group (CHO) and a hydrogen atom to a carbon-carbon double bond of an alkene. By hydrogenation the alcohols can be transformed into alcohols that can be converted into plasticizers or detergents [75]. For hydroformylation usually alkene, carbon monoxide and hydrogen react to aldehydes at pressures between 10 to 100 bar and temperatures of 40 to 200 °C [76]. In figure 4.2 a schematic of the hydroformylation is illustrated.

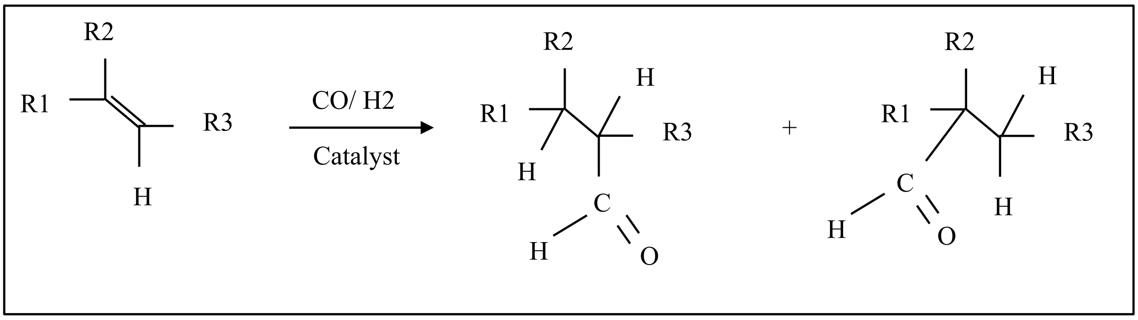

Figure 4.2.: Process schematic of Hydroformylation (OXO-process) [76]

5. Simulation Results

This section presents the results from the CHEMKIN PRO simulation. The aim of the simulations was to show the influence of different parameters on the fractions of products formed in a thermo-chemical reactor. By using several long-chained hydrocarbons, the influence of the temperature and the atmosphere were assessed. Further, it was tested how the length of a hydrocarbon changes the fractions of the produced chemicals.

5.1. The influence of the temperature

In this section, the results of the CHEMKIN PRO simulation are presented testing the influence of the temperature on the fractions of products formed in a thermo-chemical reactor. In figure 5.1, the mole-fractions of the chemical products of $NC_{16}H_{33}$ are presented for a temperature range of 500 to 1000 °C using a H_2O/hydrocarbon atmosphere of 0.63.

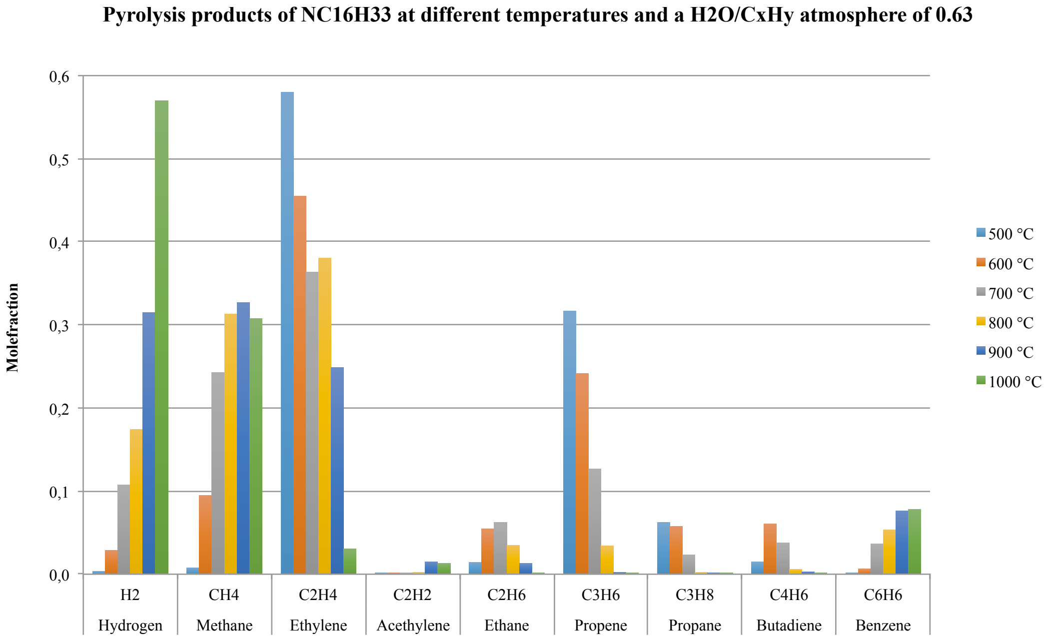

Figure 5.1.: Products after the thermal treatment of $NC_{16}H_{33}$ at a temperature range from 500 to 1000 °C at a H_2O/hydrocarbon atmosphere of 0.63

In the figure above, it can be observed that with increasing temperature the mole-fraction of hydrogen and benzene increases, whereas the mole-fraction of ethylene and propene and propane decreases. It is noticed that there are several temperatures, where the production of a chemical peaks. The mole-fraction of butadiene peaks at 600 °C, whereas ethane peaks at 700 °C. Methane and acethylene showed the highest mole-fraction at 900

°C. The highest ascent can be seen at the mole-fraction of hydrogen between temperatures of 900 °C and 1000 °C, whereas the highest decent can be seen at the mole-fraction of ethylene between the same temperature range. The temperature at which a chemical peaks can be of major importance by selecting the conditions of a thermo-chemical process. Further results with other long-chained hydrocarbons at a temperature range from 600 to 900 °C are illustrated in appendix D.

5.2. The influence of the atmosphere

In this section, the results of the CHEMKIN PRO simulation regarding different atmospheres are presented. The used hydrocarbon ($NC_{16}H_{33}$) was tested at a temperature of 800 °C under different atmospheres (N_2, CO_2, H_2O). Steam was introduced at a ratio of 0.63 ($H_2O/NC_{16}H_{33}$) and 2.02. In figure 5.2, the mole-fractions of the products of $NC_{16}H_{33}$ are shown at a temperature of 800 °C and at different atmospheres which were nitrogen, carbon-dioxide and steam at a ratio of 0.63 ($H_2O/NC_{16}H_{33}$) and 2.02.

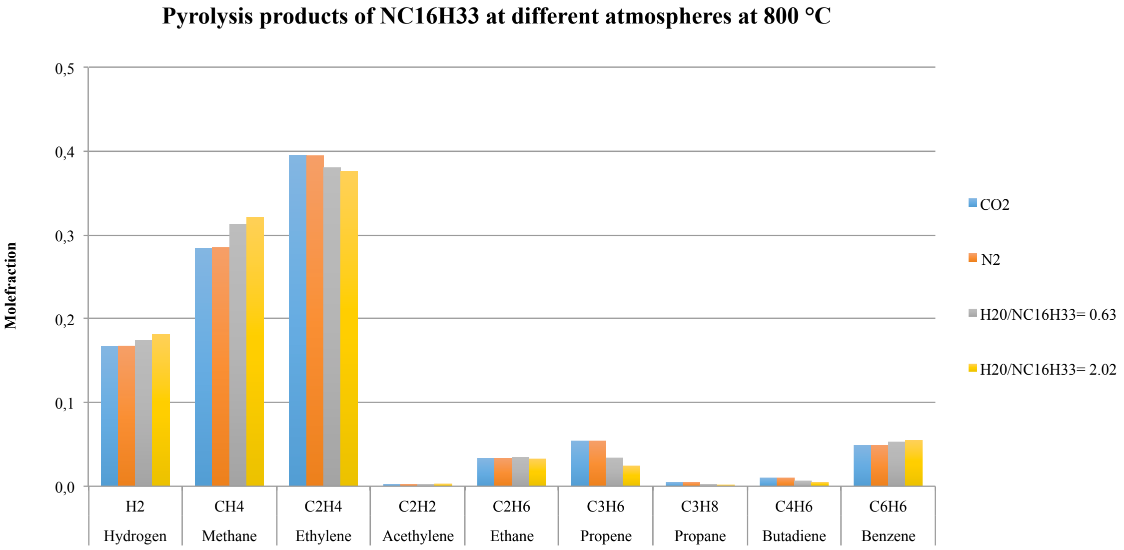

Figure 5.2.: Products after the thermal treatment of $NC_{16}H_{33}$ at different atmospheres at 800 °C

In the figure above, it can be observed that a similar amount of mole-fractions is produced using a carbon-dioxide and a nitrogen atmosphere. Under nitrogen atmosphere, it is observed that the mole-fraction of ethylene, propene, propane and butadiene show the highest mole-fractions. The mole-fraction of hydrogen, methane, ethane and benzene were increasing first with a steam to carbohydrate ratio of 0.63 then with a ratio of 2.02. In general, the differences of the reached mole-fractions at different atmospheres are not very high. It can be investigated, that a higher steam to carbohydrate ratio the amount of hydrogen, methane and benzene is increasing. Further results of $NC_{16}H_{33}$ at a temperature range of 500 to 1000 °C and steam ratios of 0.63 and 2.02 are illustrated in appendix D.

5.3. The influence of the length of hydrocarbons

In this section, the results of the CHEMKIN PRO simulation are presented, testing the influence of the lengths of hydrocarbons in a long-chained hydrocarbon towards the fractions of products formed in a thermo-chemical reactor. The used long-chained hydrocarbon were C_5H_8, NC_7H_{14}, $NC_{10}H_{20}$ and $NC_{16}H_{33}$. In figure 5.3, the mole-fractions of the products with the largest share are shown after the thermal treatment at 800 °C using a nitrogen atmosphere.

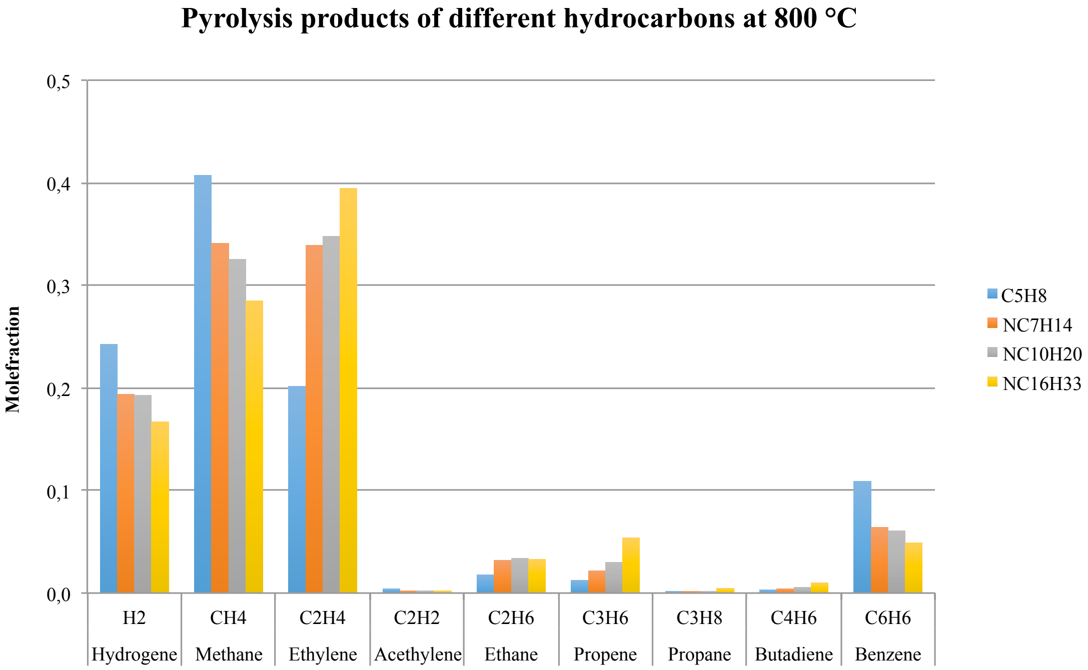

Figure 5.3.: Products after the thermal treatment of different long-chained hydrocarbons at 800 °C at a nitrogen atmosphere.

According to the figure above, it can be observed that the largest mole-fractions of hydrogen, methane and benzene were achieved from the hydrocarbon with the shortest chain C_5H_8. The largest mole-fractions from ethylene, ethane, propene, propene and butadiene were achieved by the hydrocarbon with the longest chain $NC_{16}H_{33}$. By comparing the results it is important to keep in mind that the hydrogen to carbo ratio is not the same for all investigated hydrocarbons. This could be a natural explanation for why there is a higher yield of H_2 in one case compared to another. In addition to that, the molar flow of hydrocarbons is kept constant during the investigation. If the mass flow was kept constant instead that could have some effect on the results. However, both these effects are assumed to be minor in comparison to the difference that has actually been observed. Further results with more temperatures are illustrated in appendix D.

Closing statement

Comparing the CHEMKIN PRO simulation products with real experiments shows, that there is a similar distribution and fraction of formed products. For example, T. William et al. tested 3 g of low density polyethylene (LDPE) in a fluidized bed at 700 °C and under a nitrogen atmosphere and a residence time of 15 s [77]. The products resulting from this experiment were very similar to the CHEMKIN PRO simulations. The small differences in weight-fraction may result from the difference in residence time and the fact that the formation of solids and chars is disregarded in the CHEMKIN simulation The comparison of the CHEMKIN simulation and the experiments from T. William et al. is illustrated in figure 5.4.

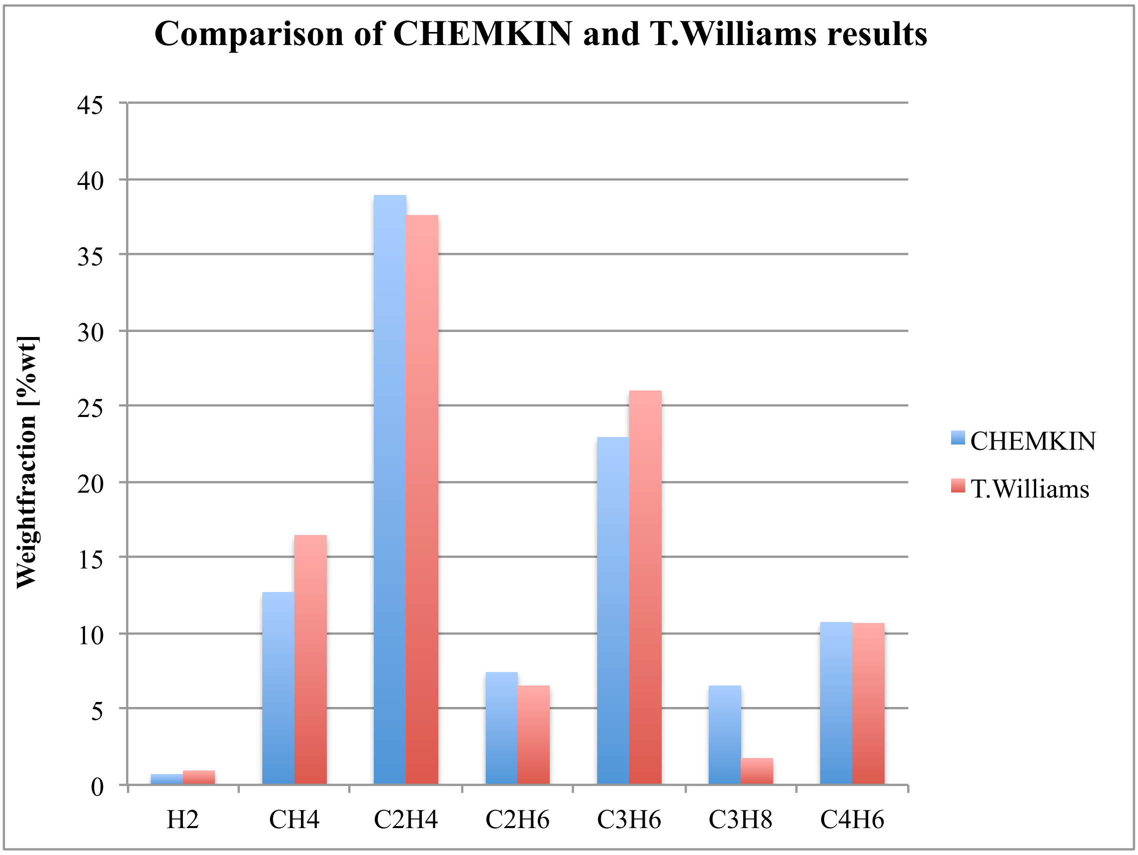

Figure 5.4.: Comparison of the CHEMKIN PRO simulation results and the experiments of T. Williams

6. Discussion

The aim of this chapter is to present an process example, which is based on the previous considerations. This example shall only show hypothetically which kind of processes are possible. Approaching this example different process parameter are evaluated and selected to approach an optimum resource recovery. The consideration include selected processes, reactors and chemical products which can be processed from different waste-sources. The CHEMKIN results, especially the influence of the temperature and the introduced atmosphere shall help making a reasonable process proposal. It needs to be considered that solids and tars are neglected in the process simulation.

6.1. Selection of thermo-chemical processes

In the third chapter, different thermo-chemical treatment methods were presented to process waste-streams. It was found that the pyrolysis process is the best option to recover valuable metals, whereas the gasification process is a good possibility to recover fuels and chemicals, which are interesting in an economic sense. **Pyrolysis and gasification** processes are considered to be a good option to process waste-streams and to recover valuable sources in a profitable way. In order to reprocess different plastic material, an adequate reactor is necessary. Some of the most promising reactors were investigated and evaluated in table 6.1 using several technical and economical requirements. Additionally to the listed reactors there are also other technologies like the thermoselect reactor, which show also promising features, this evaluation however shows only the reactors with a industrial scale implementation and an experience longer than ten years. Some criteria are the energy efficiency, the quality of secondary products, operational experience and profit expectations. For the evaluation credit points, a range of 1 to 3 was selected and the highest points scored best. In table 6.1 it can be noticed, that the **CFB and the Rotary kiln** reached highest score in the evaluating process with different parameter. For the implementation in the two different thermo-chemical treatment methods, the rotary kiln would be a good option for the pyrolysis process , whereas the CFB reactor would be a good option for the gasification process.

Table 6.1.: Evaluation of different reactor types [53]

Property	**Rotary kiln**	**Fixed bed**	**BFB**	**CFB**
Temp range	3	3	2	1
Heat transfer	2	1	3	3
Particle size	3	3	1	2
Res. Time	2	1	2	3
Conversion	3	3	1	3
Feedstock - flexibility	2	1	3	3
Scale-up	2	1	2	2
Cost	2	1	2	2
ROI	2	2	3	3
SUM	21	16	19	22

6.2. Selection of potential waste-streams

In order to select waste-streams which can be lucrative treated in thermo-chemical processes, certain evaluation criteria are determined which focus on the net profit for STENA. Evaluating the waste-streams regarding the selection criteria shows that especially PFO and SLF have a high waste-production rate. The waste-streams of WEEE (incineration and landfill) are quite moderate, whereas the waste-streams of cable plastics and PUR are very low. Since the waste-production rate of rubber is not known, this waste fraction is excluded in the evaluation. Considering the fractions of valuable metals, SLF scores quite high (Al 4 %, Cu 3 %, Fe 13 %), whereas the fraction of aluminium can be even higher in WEEE (landfill), which also contains a large amount of valuable metals (Al 2-7 %, Cu 3 %, Fe 0.4 %). Like cable plastics (Al 0.5 %, Cu 0.3 %, Fe 0.1 %), WEEE (incineration) includes a quite moderate metal fraction (Al 0.35 %, Cu 0.32 %, Fe 0.22 %). PFO contains very few valuable metals (Cu 0.002 %). Even though WEEE (landfill) contains a lot of valuable metals, it also includes a high amount of problematic substances (Cl 4.5 %) whereas, PFO (Cl 0.12 %), cable plastics (Cl 0.17 %), PUR (Cl 0.6 %) and WEEE incineration (Br 1.5 %, Cl 0.17 %) have a low fraction of problematic substances and SLF (Cl 2.1 %) a relatively moderate fraction. In the evaluation, the Cl content was chosen to be lower than 6 %, so that the cost-expensive treatment of problematic substances is limited. To reduce a rather high amount of waste, it is beneficial to burn waste with a low heating value compared to waste with a high one. For example, considering following energy balance: By burning 3 tons of PFO (41 MJ/kg) nearly the same amount of energy is produced as with burning 4 tons of WEEE (30 MJ/kg). Comparing the different waste-streams PFO (41 MJ/kg) scores highest, whereas cable plastics (32 MJ/kg) and WEEE (incineration) (30 MJ/kg) are quite moderate and PUR (15 MJ/kg), WEEE (landfill) (20 MJ/kg) and SLF (16 MJ/kg) have the lowest heating value. In table 6.2 the evaluation of different waste-streams is illustrated using three different evaluation points (3 is best, 2 is moderate, 1 is worst).

Table 6.2.: Evaluation of the different waste-streams from STENA Metall *Data from pyrolysis experiments made by the Royal Institute of Technology (KTH)

Type	**Production**	**Metals**	**Problematics**	**LHV**	**Score**
Rubber*	1	1	2	2	6
Cable plastic*	1	2	2	2	7
PUR*	1	1	2	3	7
PFO	3	1	3	1	8
WEEE (landfill)	2	3	1	3	9
WEEE (incineration)	2	2	3	2	9
SLF	3	3	2	3	11

Evaluating the different waste streams, the waste fraction with the highest score is SLF (11), followed by WEEE (landfill and incineration) (9) and PFO (8). Since an exclusion criteria is a Cl content of a maximum of 4 %, WEEE (landfill) cannot not be selected. Hence, selected waste streams, which will be used to select appropriate thermo-chemical treatment methods are SLF and WEEE (incineration).

6.3. Selection of chemical products

The information from the PECREST project were used to make proposals which kind of processes can be used to maximize the production of certain valuable chemicals in different thermo-chemical processes. **Ethylene** is one of the most promising chemicals used in companies like Borealis, where ethylene is the basis to produce olefins and polyethylene formed by hydrocarbon steam cracking. Ethylene is also the main chemical intermediate for polymers, alcohols ethylene oxide and fundamental chemicals for a large variety of further value-chains. Another valuable chemical resource is synthetic natural gas, which is based on **Methane**, carbon dioxide and small amounts of nitrogen and hydrogen. Synthetic natural gas can not only be used in the energy industry, but also in a feedstock for the production of chemicals, in particular the production of syngas. In the Stenungsund cluster, it is used for hydroformylation (OXO- synthesis) of olefins into aldehydes. Hence, methanol is not only used as an automotive fuel but also as a basis for high value chemicals such as olefins.

6.4. Process example

After evaluating thermo-chemical processes and technologies, two possible process examples have been chosen to treat selected waste-streams. The processes include the most promising pyrolysis and gasification technologies, rotary kiln and CFB to treat the most promising waste-streams SLF and WEEE to create the most promising chemicals and fuels, ethylene and methane, as well as enabling the recovery of metals in the most economical way. The process schematics for two separated paths to reprocess the selected waste-streams are illustrated in figure 6.1.

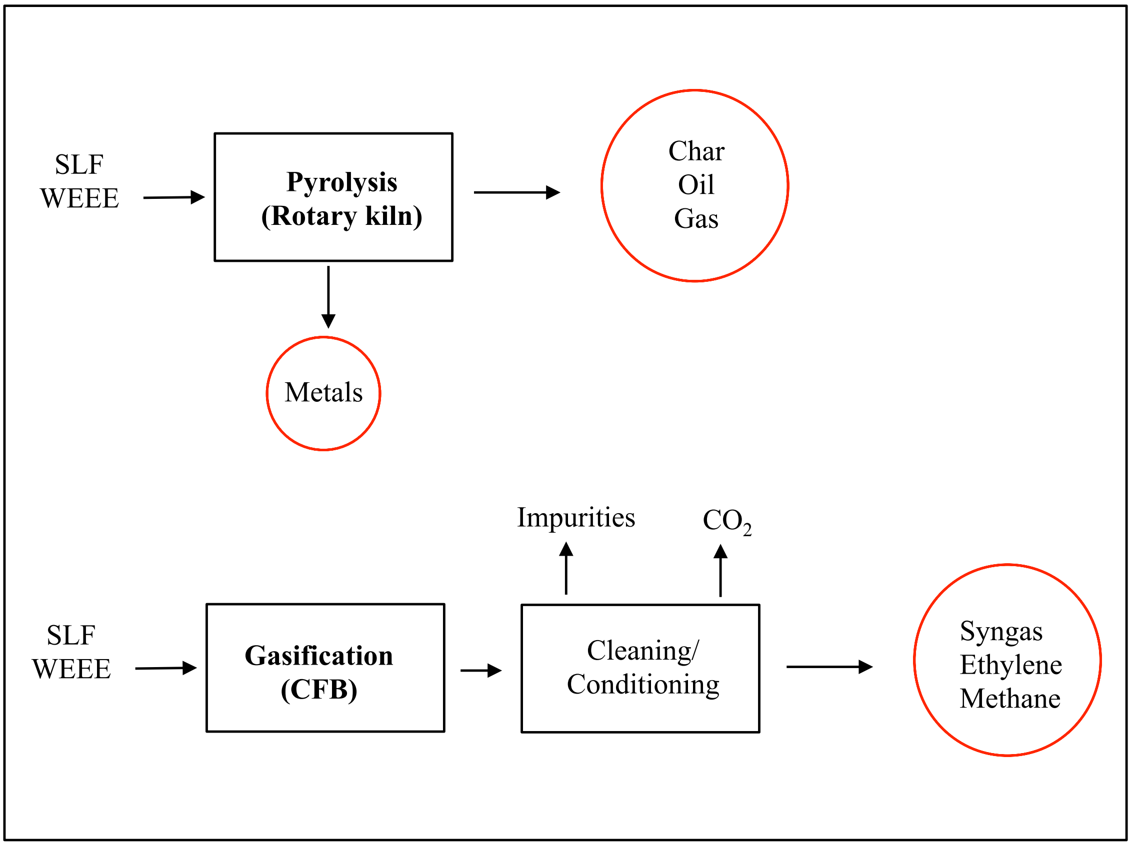

Figure 6.1.: Process scheme of two separated paths to reprocess the waste-streams of WEEE and SLF

It can be seen that metals are recovered in the pyrolysis stage, whereas the secondary products are reprocessed into syngas via partial oxidation (POX) and hydroformylation (OXO). In another process path, the waste streams SLF and WEEE are processed to ethylene using a gasification process connected with a methanol synthesis, ethanol synthesis and ethanol dehydration. The disadvantage of the two separate processes in figure 6.1 is, that it needs to be decided whether metals and syngas, or chemicals and fuels shall be recovered. An own process scheme was drawn, which is illustrated in figure 6.2 to combine both advantages in one process. Further, some other features were included, for example extracting hydroclorine (HCl) in the pyrolysis stage, which ca be used to form PVC. During the pyrolysis stage, valuable metals can be recovered without oxidizing them, whereas hydrogen, ethylene, methane and benzene are formed during the gasification stage. To maximize the output of both ethylene and methane a compromise between temperature and steam atmosphere is recommended. The process parameter can be selected regarding the CHEMKIN simulation results. Regarding the results a temperature of 800 °C and a steam ratio of 0.63 could be used to enhance the formation of hydrogen, ethylene and methane. After the gasification stage, syngas (CO and H_2) could be recovered via partial oxidation. Aldehydes can be formed by combining syngas with alkenes in the OXO synthesis. After various treatment steps methanol, ethylene, DME and ethylene could be formed.

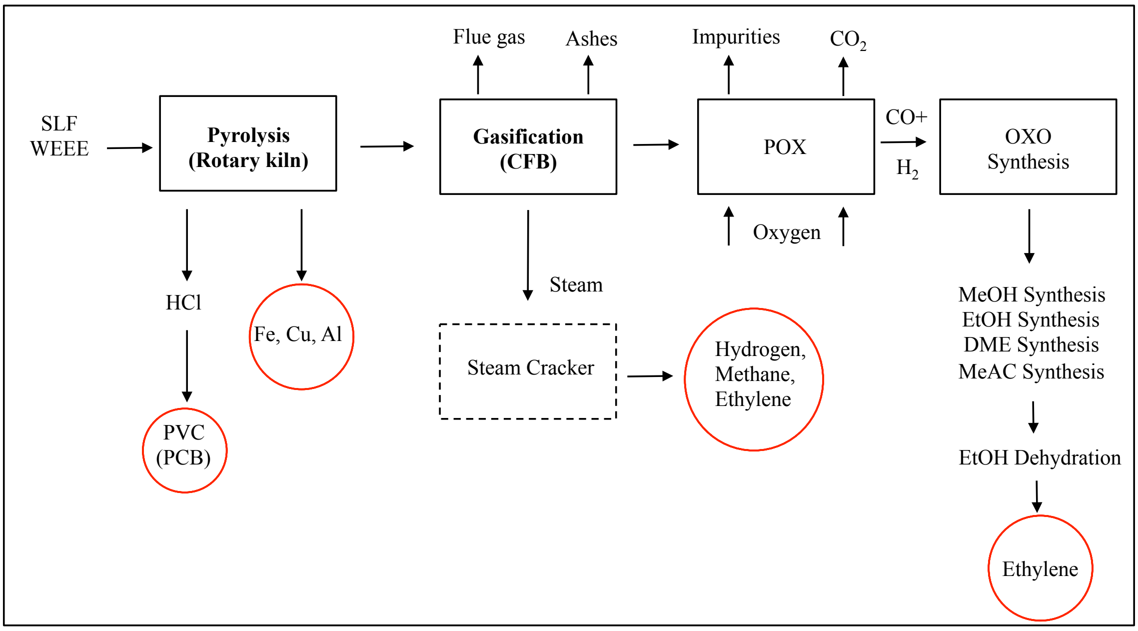

Figure 6.2.: Process scheme of one combined paths to reprocess the waste-streams of WEEE and SLF

7. Conclusions and future prospects

Within this work several thermo-chemical methods for the treatment of different waste-streams have been investigated. This was done in the attempt to find lucrative process technologies to recover valuable resources in certain waste-streams from STENA Metall. Therefore several evaluation criteria were used to select the best possible reactors, waste-streams and chemical products for a possible waste-recovery process. In order to investigate other process conditions, the influences of the temperature and the atmosphere were assessed using the CHEMKIN PRO simulation tool. Analysing the results from the influence of different temperatures, it was observed that with increasing temperature, the mole-fraction of hydrogen and benzene increases, whereas the mole-fraction of ethylene and propene and propane decreases. This can be explained by a higher reactivity of the hydrocarbon to form chemicals with smaller chains, H_2 and CH_4. An important conclusion is that there are certain temperature levels where the production of a chemicals or fuels peak. The mole-fraction of butadiene peaks at 600 °C, whereas ethane peaks at 700 °C. Methane and acethylene showed the highest mole-fraction at 900 °C. Analysing the results from the influence of different atmospheres, it was discovered that the differences of the reached mole-fractions at the different atmospheres are not very high. Especially, the results of a nitrogen or a carbon-dioxide atmosphere are very similar. Under nitrogen atmosphere, it is observed that the mole-fraction of ethylene, propene, propane and butadiene show the highest mole-fractions. It was investigated, that at a higher steam to carbohydrate ratio the amount of hydrogen, methane and benzene is increasing. Since in the process determination a high demand of hydrogen, ethylene and methane is desirable a compromise between temperature and steam atmosphere has to be done. Thereby, it is recommended to introduce the selected waste-streams, SLF and WEEE under a steam atmosphere at a steam to carbohydrate ratio of 0.63 and a temperature of 800 °C. Using the waste-streams an efficient and lucrative process could be realized by using a combination of a pyrolysis or gasification process, implementing first a rotary kiln to recover metals and secondly a CFB reactor to recover chemicals and fuels. Further, the influence of the number of hydrocarbons was assessed to investigate the behaviour of different long-chained polymers on the behaviour of the produced chemicals. It has been observed, that the smaller the length of the hydrocarbon chain the higher the yield of hydrogen, methane and benzene. The investigation showed, that the higher the length of the hydrocarbon chain the higher the yield of ethylene, propene, propane and butadiene. It is important to keep in mind though that the hydrogen to carbon ratio are not the same for all investigated hydrocarbons. This could be a natural explanation for why there is a higher yield of e.g. H_2 in one case compared to another. Future works may also make investigations of plastic pyrolysis and gasification in real testing conditions. It may also be interesting to introduce different kind of species into the CHEMKIN process to observe the behaviour of mixed long and short-chained hydrocarbons. It would also be interesting to look into the thermo-chemical behaviour of long-chained hydrocarbons at temperatures higher than 1000 °C.

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Appendix A.

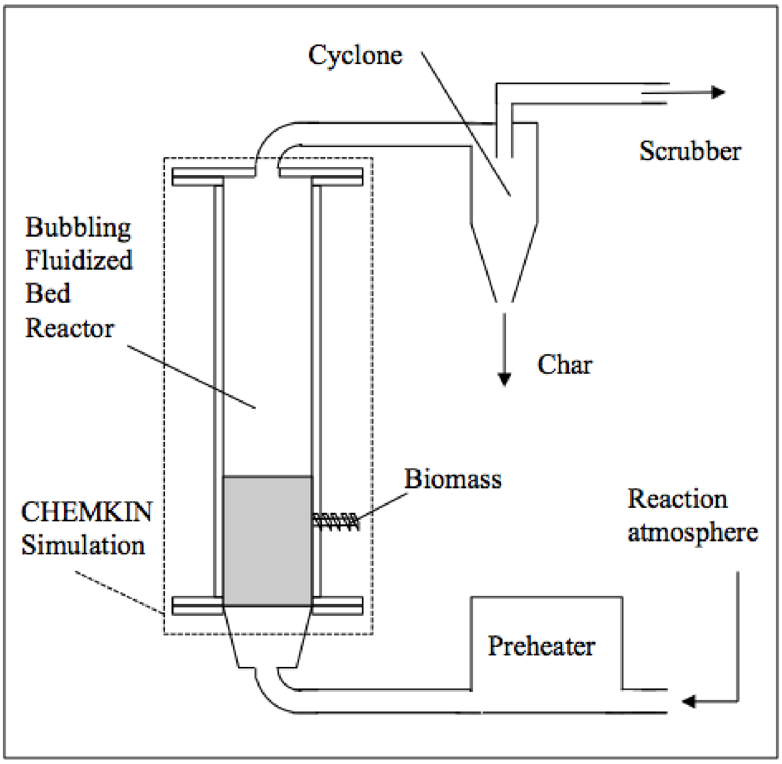
The simulation mechnism

The KTH project investigated a fast pyrolysis of biomass in a fluidized-bed, which were assessed at a temperature of 600 °C, a residence time of 3 s and a "steam to biomass ratio" (S/B) of 0.5 [10]. In the first figure the reactor layout of the CHEMIKN simulation of the KTH is shown. In the following the parameters, which are used for the KTH simulation are calculated. With the reactor dimensions length (0.95 m) and the reactor diameter (0.072 m) the volume is calculated. The volumetric flow of the introduced biomass is achieved by dividing the volume by the residence time (3 s). In the KTH simulation the biomass is introduced by steam whereby the biomass composition is listed in the first table

$$\mathrm{V_{bio}} = \frac{\pi}{4} \cdot D^2 \cdot \mathrm{l} = 0.00387\mathrm{m}^3 \tag{A.1}$$

$$\dot{\mathrm{V}}_{\mathrm{bio}} = \frac{V}{t} = 0.00129\frac{\mathrm{m}^3}{\mathrm{s}} \tag{A.2}$$

Since the mechanism also needs the volumetric flow from the added steam (H2O) the following calculations show how the gravimetric H2O/biomass ratio of 0.5 is transformed to the volumetric ratio. First the molar mass of biomass is calculated by the ideal gas law at a temperature of 600 °C and a pressure of 1 bar. In the table beneath the total molar weight of the biomass is calculated by the product of the molar weight per species weighted with their specific volumetric share. The total molar weight of the biomass can be calculated to 105 g/mole. As only half of the weight from biomass is used for the steam the biomass weight needs to be divided by two. With the molar mass of water the number of mole used for the steam production are calculated. With the ideal gas law the volume of water is calculated. The sum of the H2O volume and the biomass volume is the total volume. The volumetric share of H2O is the H2O volume divided by the total volume. The comparison of the own CHEMKIN PRO results and the KTH results can be seen in the second figure.



Reactor layout for the CHEMKIN PRO simulation from the KTH

$$\mathrm{n_{Bio}} = \frac{p \cdot V}{R \cdot T} = \frac{100000(\mathrm{N/m^2}) \cdot 0.00387(\mathrm{m^3})}{8.315(\mathrm{J/molK}) \cdot 873.15(\mathrm{K})} = 0.0533\mathrm{mol} \tag{A.3}$$

$$\mathrm{m_{Bio}} = \mathrm{n_{Bio}} \cdot 105\frac{\mathrm{g}}{\mathrm{mol}} = 5.598\mathrm{g} \tag{A.4}$$

$$\mathrm{m_{H2O}} = \frac{\mathrm{m_{Bio}}}{2} = 2.799\mathrm{g} \tag{A.5}$$

$$\mathrm{n_{H2O}} = \frac{\mathrm{m_{H2O}}}{18\frac{\mathrm{g}}{\mathrm{mol}}} = 0.155\mathrm{mol} \tag{A.6}$$

$$\mathrm{V_{H2O}} = \frac{\mathrm{n_{H2O}} \cdot R \cdot T}{p} = 0.0113\mathrm{m^3} \tag{A.7}$$

$$\mathrm{V_{tot}} = \mathrm{V_{bio}} + \mathrm{V_{H2O}} = 0.0152\mathrm{m^3} \tag{A.8}$$

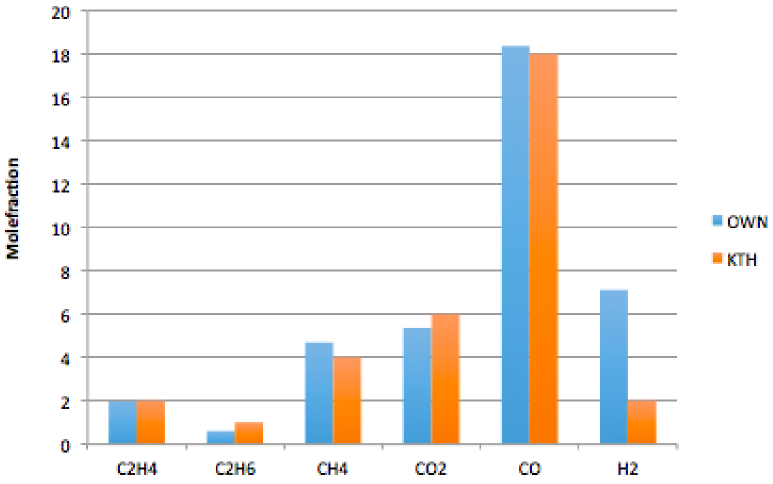
$$\mathrm{S_{VH2O}} = \frac{\mathrm{V_{H2O}}}{\mathrm{V_{tot}}} = 74.55\% \tag{A.9}$$

$$\dot{V}_{tot} = \frac{V_{tot}}{3s} = 0.0051\frac{m^3}{s} \tag{A.10}$$

Proportion of species in the biomass composition [10]

Species	Share [%]	Share (with H2O) [%]	M wt [g/mol]	M frac. [g/mol]
C11H12O4	0.39	0.22	208	0.811
C2H2O2	0.53	0.30	58	0.307
C2H4	2.12	1.21	28	0.594
C2H4O2	2.09	1.20	48	1.003
C2H5OH	0.01	0.01	46	0.005
C3H4O2	0.01	0.01	72	0.007
C3H6O	1.01	0.60	58	0.586
C5H8O4	10.06	5.80	132	13.279
C6H10O5	46.65	26.72	162	75.573
C6H5OH	0.01	0.01	94	0.009
C6H6O3	1.15	0.66	126	1.449
C9H10O2	1.43	0.82	150	2.145
CH2O	2.57	1.47	30	0.771
CH3OH	1.79	1.03	32	0.573
CH4	2.34	1.34	16	0.374
CO	9.81	5.62	28	2.747
CO2	6.15	3.52	48	2.952
H2	0.45	0.26	2	0.009
H2O	11.08	49.10	18	1.994
CH3HCO	0.35	0.20	44	0.154
Sum	1	1		105

For the CHEMKIN PRO simulation a plug-flow reactor with one inlet and one outlet is used. Hereby the dimensions mentioned above and other parameters (T = 600 °C, 1 bar, etc.) were set. The input contains the total volume flow V_{tot} with the species listed in the table above To compare the results with those of the KTH the mole fractions need to be converted into dry mater. Thereby the results need to be divided by 0.645, which equals to 1 - 0.355 (fraction of H2O). The comparison of the own CHEMKIN PRO results and the KTH results can be seen in the figure below The results are quite comparable for most of the products, but diver in the H2 content. The deviation could be explained by the turbulation settings which the KTH introduced by their CFD modulation. Regarding a different kinetic setting of the feeding stream the results seem quite comparable. Verifying the mechanism sets the foundation to the following simulations.



Comparison with the KTH results

Appendix B.

Pyrolysis reactions

Demonstration of the mass distribution of PE with slow pyrolysis [18]

Conditions				Mass balance		
Reactor type	p (atm)	T (°C)	m(g)	G (%)	L (%)	S (%)
TGA	10^{-8}	405	0.1	2.5	86.1	11.4
TGA	10^{-8}	450	0.1	3.1	95.5	1.4
TGA	1	430	0.02	-	-	72
TGA	1	440	0.02	-	-	47
TGA	1	460	0.02	-	-	10
TGA	1	480	0.02	-	-	0

Examples of energy content of pyrolysis products [4]

Waste	Gas + Oils (MJ/kg)	Char (MJ/kg)
Tyres	38	28
Mixed plastics	20	20
ASR	31	10
Paper	23	21
MSW	13	18

State of the art industrial gasification reactors

Gasification is an effective technology in processing plastic waste, since it is an easy way to break down the molecular structure of the plastics in the presence of hydrogen to form CO and H_2 [78]. Following industrial reactors can be mentioned as examples for industrial plastic-waste gasification [79]:

- The **Sekundärrohstoff Verwendungszentrum Scharze Pumpe (SVZ)** is processing coal and waste products with a throughput of shredded residues of 150 kt/a. It contains seven downdraft fixed-bed gasifiers and two entrained flow reactors. One fixed-bed unit gasifies input material with a throughput of 27 - 32 t/h at 1600 °C and 25 bar [80].

- The **Lurgi fixed-bed grate downdraft gasifier (FBG)** works with a mixture of steam and oxygen. Applying a pressure of 24 bar it is processing solid wastes, such as plastics, rubber, MSW and sewage sludge at a flow rate of 8 - 14 t/h and temperatures of 550 - 1000 °C [81].
- The **British Gas/Lurgi downdraft slagging gasifier (BGL)** is able to gasify large amounts of coal and MSW and thereby processes inorganic substances via vitrification. The gasifier reaches temperatures over 2000 °C processing 500 t/day [82].
- The **Lurgi multi-purpose entrained-flow gasifier (MPG)** is processing liquid wastes (solvents, emulsions, tars, oils and slurries) at a high thermal efficiency with a feed capacity of up to 120 kt/yr (500 kg/h). In this "updraft gasifier" minerals in the slag are transformed into synthetic gas or fuel gas at atmospheric or increased pressure (100 bar) at temperatures of 550 - 1000 °C [83].
- The **Texaco Pernis downdraft gasification plant** processes waste with oxygen and/or steam. Thereby it can transform plastic waste, coal, petroleum coke, heavy oils and mixed plastics to hydrogen, ammonia, methanol or energy depending on the selected input-material [84]. Texaco also considered the gasification of plastic within an entrained-bed gasifier to sell syngas to chemical industries. About 45 kt/yr (62 t/h at 75 bar [85]) plastic waste streams are depolymerized within a liquefication process and transformed into synthetic heavy oil, condensable and non-condensable gases [86]. The oil and the condensable gases are transformed into syngas (CO and H_2) with small amounts of methane, CO_2 and water at temperatures of 1300 - 1400 °C [87].
- The **Noell entrained-flow gasifiers** are focusing on the combination of pyrolysis and gasification to to produce solid, liquid and gaseous fuels [88]. The reprocessing coal and waste oil feed can be designed in a size of 6.6 t/h within a temperature range of 800 - 1400 °C [89].
- The Waste Gas Technology UK Limited (WGT) processes different kinds of waste, which are dried, mechanically pre-treated and granulated. In the process HCV gas is produced at 700 - 900 °C .
- The **Lathi gasification plant Kymijärvi II** is a successful gasification small-scale plant, which uses plastics and oil based waste to convert it into fuels. The circulating fluidized-bed gasifiers work at atmospheric pressure, whereby the sand is heated up from natural gas and can reach temperatures up to 850 - 900 °C [90]. The throughput of solid wastes, such as plastics, woods and MSW is 28 t/h [91].
- The **KITech bubling fluidized-bed gasifier** in Japan is processing wood pellets at a throughput of 1 t/day to extract biomass and biodiesel . The cold gas efficiency reaches higher than 60 % and the syngas relation between H_2 and CO is higher than 1 within a temperature range of 650 - 800 °C [92].

Appendix C.

Composition of different waste fractions

C1: Composition of cable plastics, investigations from the KTH [59]

Elemental gas analysis	**Dry (wt %)**
C	67.64
H	9.48
S	0.001
N	0.07
Cl	0.17
O	21.75
Ash content (of dry fuel)	13.98
Moisture content (of submitted fuel)	0.24
Heating value (MJ/kg)	32.0
Ash analysis	**(mg/kg dry fuel)**
Al (aluminium)	5171
Cd (cadmium)	not detected
Cr (chromium)	10.7
Cu (copper)	2564
Fe (iron)	925
Mn (manganese)	44.5
Ni (nickel)	7.2
Pb (lead)	35.9
Zn (zinc)	99.2

C2: Composition of PUR, investigations from the KTH [61]

Elemental gas analysis	**Dry (wt %**
C	38.76
H	2.67
S	1.18
N	3.58
Cl	0.6
O	3.00
Ash content (of dry fuel)	49.74
Moisture content (of submitted fuel)	2.34
Heating value (MJ/kg)	14.98
Ash analysis	**(mg/kg dry fuel)**
Al (aluminium)	14
Cd (cadmium)	19
Cr (chromium)	605
Cu (copper)	1199
Fe (iron)	92
Mn (manganese)	1491
Ni (nickel)	292
Pb (lead)	1253
Zn (zinc)	9508

C3: Product yield from the pyrolysis of mixed plastic [4]

Feed	Reactor	Temperature (°C)	Gas (wt %)	Oil (wt %)	Char (wt %)
Plastic mix	Vacuum	520	6.3	91.8	1.3
Plastic mix	Fixed-bed	700	9.6	75.1	2.9
Plastic mix	Fluidized-bed	600	44.7	43.2	7.6
Plastic mix	Fixed-bed	500	85.2	12.5	3.0
MSW plastic	Fluidized-bed	787	43.6	26.4	25.4
MSW plastic	Fixed-bed	430	25	59	16

C4: Composition of PFO [55]

Elemental gas analysis	**Dry (wt%)**
S	0.53
Cl	0.15
Ash content	0.784
Moisture content	0.41
Heating value (MJ/kg)	41.4
Ash analysis	**(mg/kg dry fuel)**
As (arsenic)	<1
Cd (cadmium)	<1
Co (cobalt)	2
Cr (chromium)	12
Cu (copper)	20
Hg (mercury)	<0.1
Mn (manganese)	29
Ni (nickel)	13
Pb (lead)	9
Sb (antimony)	1
Tl (thallium)	<1
V (vanadium)	17
Zn (zinc)	100

C5: Composition of WEEE (incineration) [56]

Elemental gas analysis	**Dry (wt %)**
C (dry ash-free fuel)	72.2
H (dry ash-free fuel)	6.3
S (dry ash-free fuel)	0.02
N (dry ash-free fuel)	1.6
Cl (dry ash-free fuel)	0.7
Br (dry ash-free fuel)	1.5
F (dry ash-free fuel)	0.15
O (dry ash-free fuel)	14
Ash content (of dry fuel)	5.9
Moisture content (of submitted fuel)	12.4
Calorific value (MJ/kg with constant volume)	31.4
Heating value (MJ/kg with constant pressure)	30.1
Ash analysis	**(mg/kg dry fuel)**
Al (aluminium)	3500
As (arsenic)	4
Cd (cadmium)	4
Co (cobalt)	14
Cr (chromium)	16
Cu (copper)	3200
Fe (iron)	2200
Hg (mercury)	0.4
Mo (molybdenum)	0.7
Ni (nickel)	40
Pb (lead)	81
Sb (antimony)	3200
Se (selenium)	<5
Sn (tin)	93
Tl (thallium)	<5
V (vanadium)	2
Zn (zinc)	360

C6: Composition of WEEE (landfill) [57]

Elemental gas analysis	**Dry (wt %)**
C (dry ash-free fuel)	49.5
H (dry ash-free fuel)	5.4
S (dry ash-free fuel)	0.11
N (dry ash-free fuel)	2.2
Cl (dry ash-free fuel)	5.6
Br (dry ash-free fuel)	0.7
F (dry ash-free fuel)	0.08
O (dry ash-free fuel)	12
Ash content (of dry fuel)	24.3
Moisture content (of submitted fuel)	3.4
Calorific value (MJ/kg with constant volume)	21.5
Heating value (MJ/kg with constant pressure)	20.3
Ash analysis	**(mg/kg dry fuel)**
Al (aluminium)	20000
As (arsenic)	31
Ba (barium)	1400
Ca (calcium)	46000
Cd (cadmium)	8
Co (cobalt)	9
Cr (chromium)	70
Cu (copper)	30000
Fe (iron)	4000
Hg (mercury)	0.3
K (potassium)	700
Mg (magnesium)	6200
Mn (manganese)	100
Mo (molybdenum)	4
Na (sodium)	1600
Ni (nickel)	64
P (phosphorus)	1500
Pb (lead)	740
Sb (antimony)	2500
Se (selenium)	<10
Si (silicone)	30000
Sn (tin)	186
Ti (titanium)	3300
Tl (thallium)	<10
V (vanadium)	6
Zn (zinc)	1700

C7: Composition of SLF [58]

Elemental gas analysis	**Dry, ash- free (wt%)**	**Dry (wt%)**
C (dry ash-free fuel)	63.8	35.3
H (dry ash-free fuel)	8	4.5
S (dry ash-free fuel)	0.5	0.3
N (dry ash-free fuel)	1.7	0.9
Cl (dry ash-free fuel)	2.1	1.2
F (dry ash-free fuel)	0.2	0.1
O (dry ash-free fuel)	23.7	12.9
F (of dry fuel)	0.1	0.1
O (of dry fuel)	12.9	12.9
Ash content (of dry fuel)	-	44.9
Moisture content (of submitted fuel)	11.3	11.3
Ash analysis		**(mg/kg dry fuel)**
Al (aluminium)		35950
As (arsenic)		22.5
Ba (barium)		4000
Ca (calcium)		24550
Cd (cadmium)		16.5
Co (cobalt)		30.5
Cr (chromium)		1177.5
Cu (copper)		26975
Fe (iron)		130000
Hg (mercury)		2
K (potassium)		5175
Mg (magnesium)		5750
Mn (manganese)		1325
Mo (molybdenum)		96.5
Na (sodium)		7350
Ni (nickel)		605
P (phosphorus)		1425
Pb (lead)		1410
Sb (antimony)		197.5
Se (selenium)		<10
Si (silicon)		59700
Sn (tin)		104.25
Ti (titanium)		3675
Tl (thallium)		<10
V (vanadium)		51.25
Zn (zinc)		12625

C8: Thermal value of SLF [58]

Thermal value of SLF	**Dry, ash-free**	**Dry**
Heating value const. pressure (MJ/kg)	29.7	16.4
Calorific value (MJ/kg)	31.4	17.4
Heating value const. volume (MJ/kg fuel)	14.3	14.3
Calorific value (MJ/kg fuel)	15.4	15.4

C9: Composition of Rubber [61]

Elemental gas analysis	**(wt %)**
C	84.58
H	2.82
S	1.01
N	0.12
Cl	0.03
O	2.33
Ash content (of dry fuel)	9.11
Moisture content (of submitted fuel)	0.80
Heating value (MJ/kg)	32.12
Ash analysis	**(mg/kg dry fuel)**
Al (aluminium)	2516
Cd (cadmium)	nd
Cr (chromium)	17
Cu (copper)	76
Fe (iron)	2524
Mn (manganese)	66
Ni (nickel)	20
Pb (lead)	50
Zn (zinc)	11

Selected waste-streams for the thermo-chemical treatment

Waste-stream	valuable metals	problematic substances	heating value
SLF	Al (4 %) Cu (3 %) Fe (13 %)	Cl (2.1 %)	16.4 (MJ/kg)
WEEE (incineration)	Al (0.35 %) Cu (0.32 %) Fe (0.22 %)	Br (1.5 %), Cl (0.24 %)	30.1(MJ/kg)
Waiting list			
WEEE (landfill)	Al (2-7 %) Cu (3 %) Fe (0.4 %)	Cl (6.7 %)	20.3 (MJ/kg)

Typical Swedish plastic waste-streams [53]

Plastics	**Residential waste from packaging (t/y)**	**Other residential waste (t/y)**	**Bulky waste (t/y)**	**Total (t/y)**
HDPE	24250	900	5400	30550
LDPE	47260	4500	5400	57160
PP	29550	16500	18000	64050
PVC	1590	1200	1800	4590
PS	21800	3900	1800	27500
PET	13250	300	1800	15350
PUR	-	540	-	540
ABS	-	540	-	540
PC	-	540	-	540
PMMA	-	540	-	540
PA	25300	540	1800	27640
TOTAL	163000	30000	36000	230000

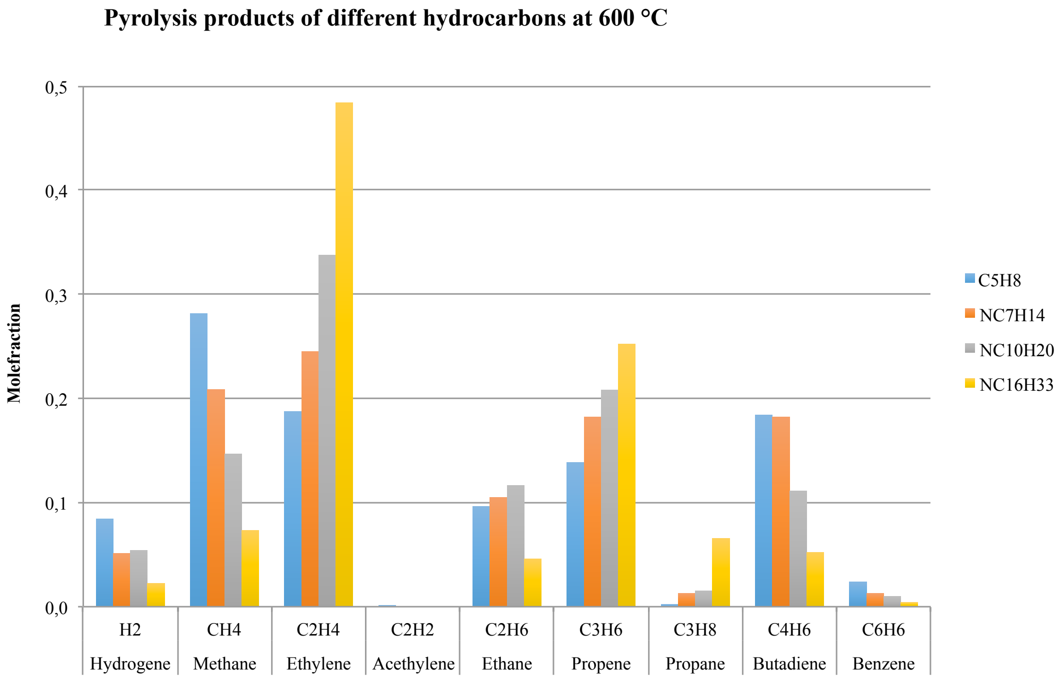
Appendix D.

Further simulation results

This section presents the results from the CHEMKIN PRO simulation. The aim of the simulations was to show the influence of different parameter towards the amount and ratio of products formed a thermo-chemical reactor. The parameter are the number of hydrocarbons , the temperature and the used atmosphere in a thermo-chemical process.

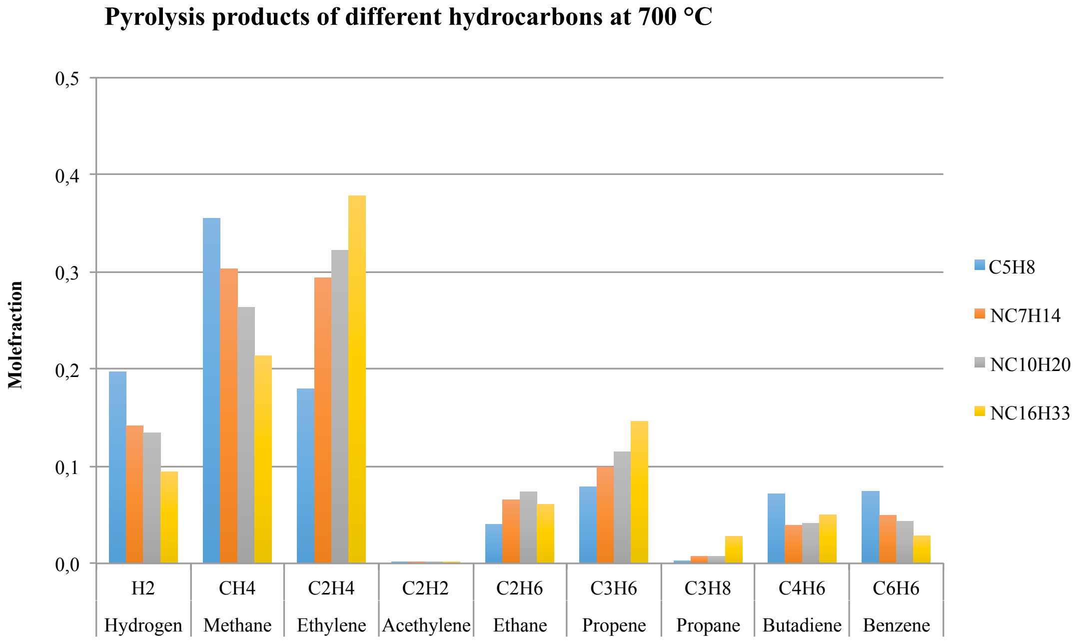
The influence of the length of hydrocarbons

In this section the results of the CHEMKIN PRO simulation are presented testing the influence of the number of hydrocarbons, which are present in a long-chained hydrocarbon. The used long-chained hydrocarbons were C5H8, NC7H14, NC10H20 and NC16H33, which were tested at a temperature range of 600 to 900 °C and at a nitrogen atmosphere. In the following figure, each figure shows the molefractions of formed products at a certain temperature.



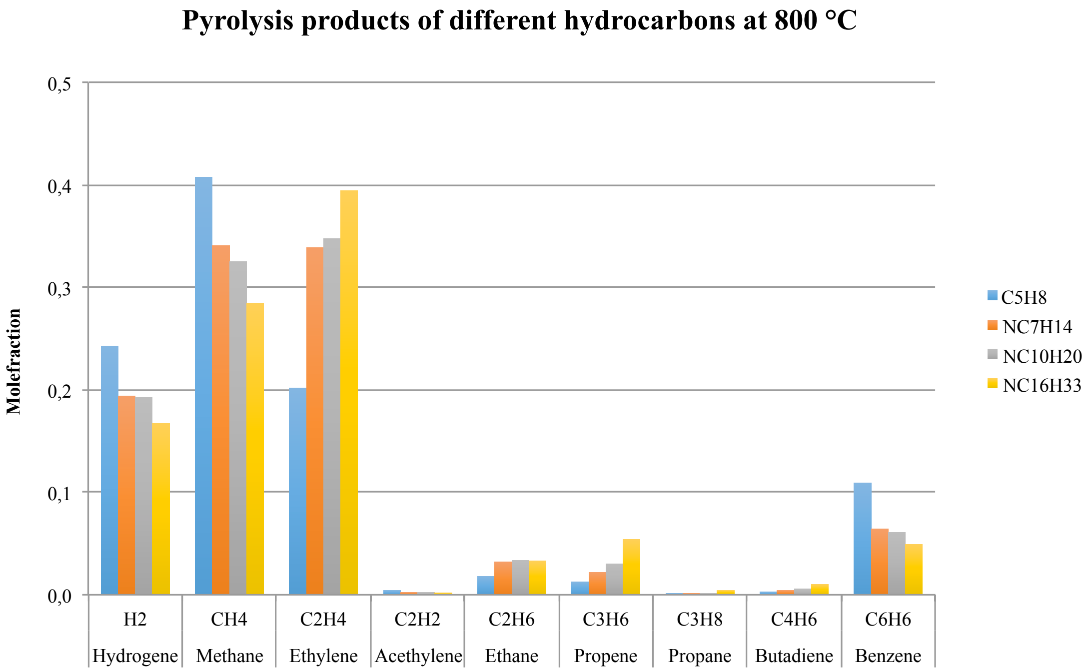
Products of different long-chained hydrocarbons after pyrolysis at 600 °C

In the figure above it can be observed that the largest mole-fractions of hydrogen, methane, butadiene and benzene were achieved from the hydrocarbon with the shortest chain C_5H_8. The largest mole-fractions from ethylene, propene, propene and butadiene were achieved by the hydrocarbon with the longest chain $NC_{16}H_{33}$. Ethane showed a peak at the hydrocarbon $NC_{10}H_{20}$.



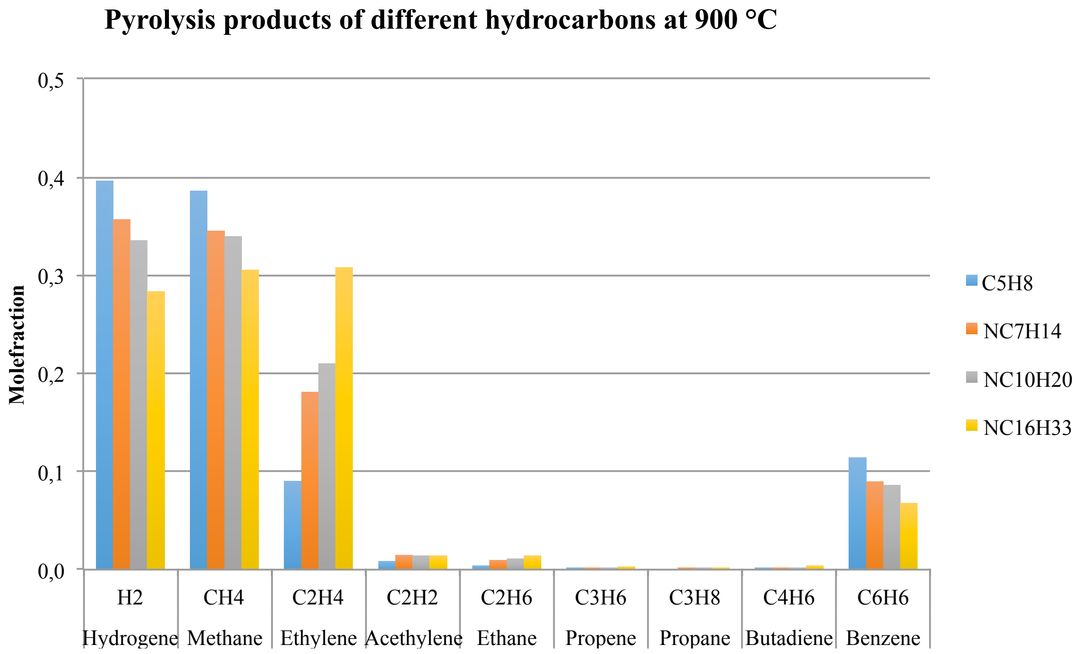
Products of different long-chained hydrocarbons after pyrolysis at 700 °C

In the figure above it can be observed that the largest mole-fractions of hydrogen, methane, butadiene and benzene were achieved from the hydrocarbon with the shortest chain C_5H_8. This is alike the last results. The largest mole-fractions from ethylene, propene, propene and butadiene were achieved by the hydrocarbon with the longest chain $NC_{16}H_{33}$. Ethane showed a peak at the hydrocarbon $NC_{10}H_{20}$.



Products of different long-chained hydrocarbons after pyrolysis at 800 °C

In the figure above it can be observed that the largest mole-fractions of hydrogen, methane, butadiene and benzene were achieved from the hydrocarbon with the shortest chain C_5H_8. This is alike with the last results. The largest mole-fractions from ethylene, propene, propene and butadiene were achieved by the hydrocarbon with the longest chain $NC_{16}H_{33}$. Ethane showed a peak at the hydrocarbon $NC_{10}H_{20}$. Methane and Ethylene show similar production rates at all different hydrocarbons.



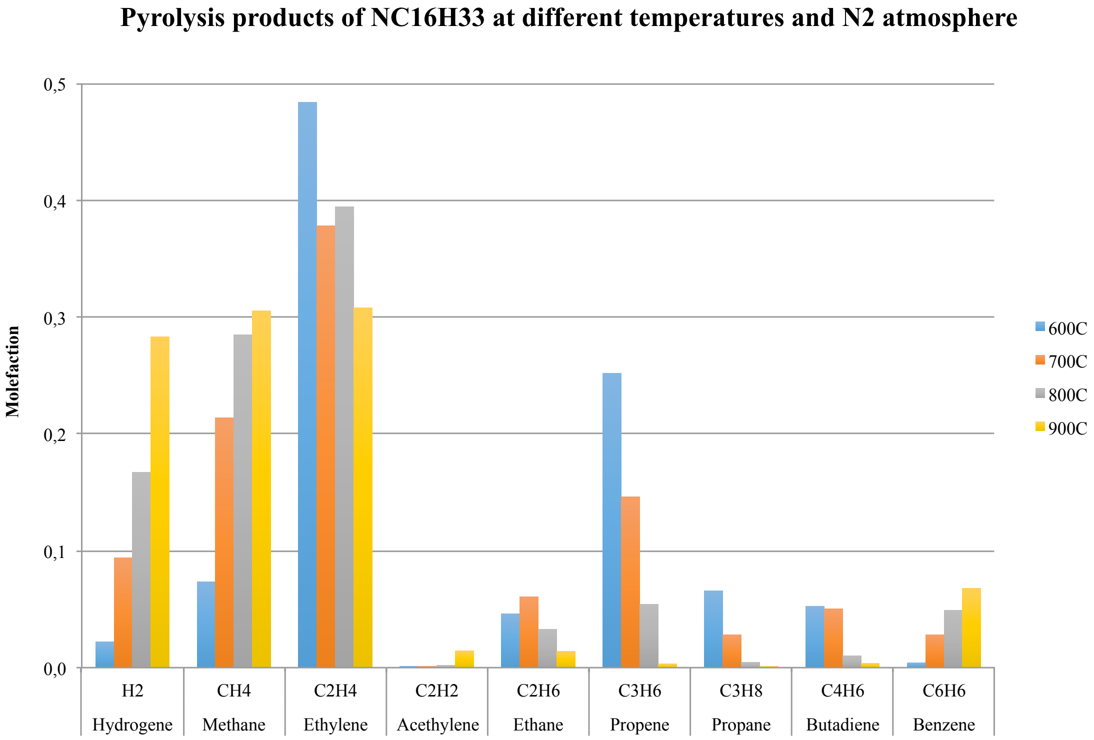
Products of different long-chained hydrocarbons after pyrolysis at 900 °C

In the figure above it can be observed that the largest mole-fractions of hydrogen, methane and benzene were achieved from the hydrocarbon with the shortest chain C_5H_8. This is alike with the last results. The largest mole-fractions from ethylene, were achieved by the hydrocarbon with the longest chain $NC_{16}H_{33}$. The mole-fractions of propene, propene, ethane and butadiene are very small, so that no certain statement can be made. Hydrogen, methane and ethylene show similar production rates at all different hydrocarbons.

Closing statement Applying different temperatures results in a changing fraction of certain products. Thereby it can be observed, that at lower temperatures (600 and 700 °C) the mole-fraction of ethylene, propene and butadiene is high, whereas the mole-fraction of hydrogen, methane and benzene is low. At higher temperatures (800 and 900 °C) it can be observed, that the mole-fraction of ethylene, propene and butadiene is low, whereas the mole-fraction of hydrogen, methane and benzene is high.

The influence of different temperatures

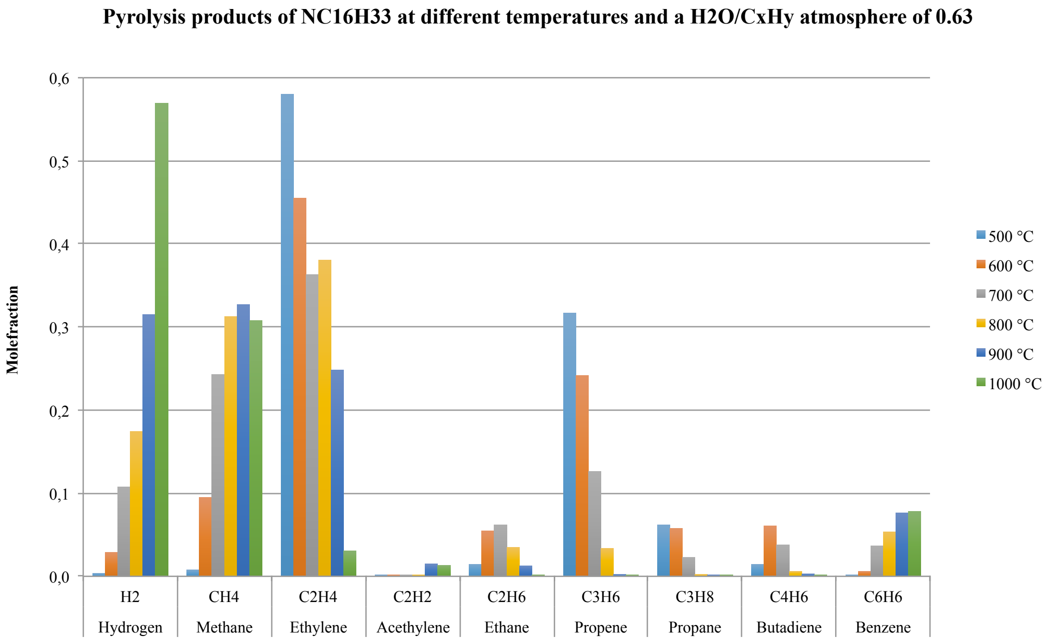
In this section the results of the CHEMKIN PRO simulation testing the influence of different temperatures and are presented. The used hydrocarbon was $NC_{16}H_{33}$ at a temperature range of 600 to 900 °C under a nitrogen atmosphere and at a temperature range of 500 to 1000 °C under a steam atmosphere. The following figure shows the mole-fractions of formed products at different temperatures.



Products after the pyrolysis of NC16H33 at different temperatures and a nitrogen atmosphere

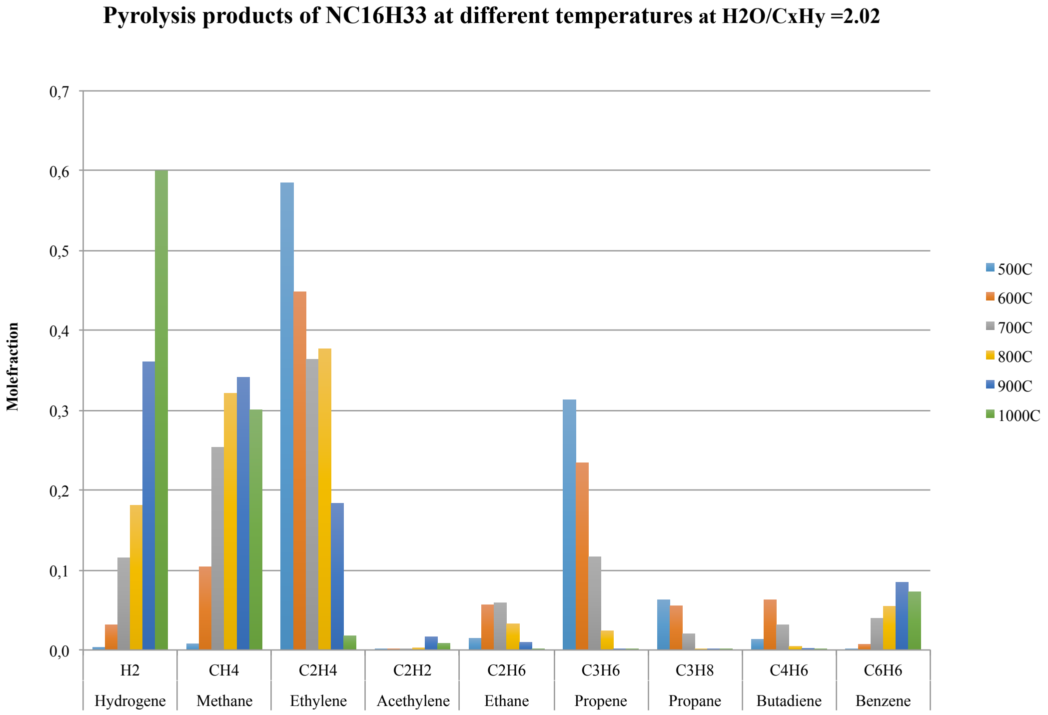
In the figure above the mole-fractions of the products of $NC_{16}H_{33}$ are shown using a nitrogen atmosphere. It can be observed that with increasing temperature the mole-fraction of hydrogen, methane and benzene is increasing, whereas the mole-fraction of ethylene, propene, propane and butadiene is decreasing. It can noticed, that the mole-fraction of ethane peaks at 700 °C,

In this section the results of the CHEMKIN PRO simulation regarding different atmospheres are presented. Each figure compares the different products of the used hydrocarbon $NC_{16}H_{33}$ at a temperature interval from 500 to 1000 °C. After introducing the $H_2O/NC_{16}H_{33}/N_2$ mixture in the plug-flow reactor certain chemical reactions take place, so that different products can be observed in the output. Since the number of formed chemical products is quite large only the products with the largest molefractions are shown.



Products of the steam-pyrolysis of NC16H33 at different temperatures and a steam/NC16H33 ratio of 0.63

In the figure above the mole-fractions of the pyrolysis products of $NC_{16}H_{33}$ at a steam/$NC_{16}H_{33}$ ratio of of 0.63 are shown. Iit can be observed that with increasing temperature the mole-fraction of hydrogen and benzene is increasing, whereas the mole-fraction of ethylene, propene and propane is decreasing. It can be noticed, that there are several temperatures, where the production of a chemical peaks. The mole-fraction of methane and acethylene peaks at 900 °C, whereas the mole-fraction of ethane peaks at 700 °C and the mole-fraction of butadiene peaks at 600 °C.



Products of the steam-pyrolysis of NC16H33 at different temperatures and a steam/NC16H33 ratio of 2.02

In the figure above the mole-fractions of the pyrolysis products of $NC_{16}H_{33}$ at a steam/$NC_{16}H_{33}$ ratio of of 2.02 are shown. It can be observed that with increasing temperature the mole-fraction of hydrogen and benzene is increasing, whereas the mole-fraction of ethylene, propene and propane is decreasing. It can be noticed, that there are several temperatures, where the production of a chemical peaks. The mole-fraction of methane and acethylene peaks at 900 °C, whereas the mole-fraction of ethane peaks at 700 °C and the mole-fraction of butadiene peaks at 600 °C.

Closing statement Applying different temperatures results in a changing fraction of certain products. It can be observed, that at lower temperatures (500, 600 and 700 °C) the mole-fraction of ethylene, propene and butadiene is high, whereas the mole-fraction of hydrogen, methane and benzene is low. At higher temperatures (800, 900 and 1000 °C) it can be observed, that the mole-fraction of ethylene, propene and butadiene is low, whereas the mole-fraction of hydrogen, methane and benzene is high.