



# **Experimental pyrolysis of polyethylene in order to produce ethanol**

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Examensarbete / Degree Thesis  
Utbildningsprogram / Degree Programme  
2020

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DEGREE THESIS	
Arcada UAS	
Degree Programme:	Materials Processing Technology
Identification number:	18954
Author:	Lev Lebedev
Title:	Experimental pyrolysis of polyethylene in order to produce ethanol
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Commissioned by:	
Abstract:	
<p>The goal of this thesis work was to build a system where it would be possible to convert polyethylene into alcohol (ethanol) by performing first pyrolysis (to crack down polyethylene into ethylene) and then force ethylene to hydrate in the presence of water, forming ethanol solution. After completing the experiment, received solids and liquid samples were tested using FTIR spectrometry. Unexpectedly, it was found out that the ethylene generated by pyrolysis did not react with water to produce measurable quantities of ethanol. On the contrary, it reacted with oxygen, forming oxidized ethylene, also known as polyethylene wax.</p>	
Keywords:	Plastic, waste, recycling, fuel, polyethylene, pyrolysis, polymerisation, alcohol, ethylene, polyethylene wax
Number of pages:	56
Language:	English
Date of acceptance:	

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## **FOREWORD**

I would like to forward my deepest appreciation to the all the employees of the Department of Energy and Materials Technology of Arcada University of Applied Sciences, where I had a pleasure to study, do practical training and write my thesis eventually. Their positive and helpful attitude combining with a great amount of knowledge and desire to share it made my studies unforgettable.

Concerning my thesis works, I would like to thank my classmates and other students, who helped me with the equipment's usage in the laboratory, gave bits of advice and supported me through my work. I would like to thank personally Alex Clark, who changed lamps in the UV spectrometer, Harri Anukka, Arcada's laboratory engineer, who helped me with fixing and ordering various equipment for the experiment and Silas Gebrehiwot, Degree Programme Director, Senior Lecturer in Mechanical Engineering, who helped me with MasterCAM software.

Finally, I would like to forward my limitless acknowledgement, gratefulness and thankfulness to Stewart Makkonen-Craig, Vice Head of Department of Energy and Materials Technology, Senior Lecturer in Materials Science and my Thesis Supervisor, who was always there for me whether I had a question to be answered or a fire to be extinguished.

## **1. INTRODUCTION**

This chapter provides basic information about the thesis – motivation of the author and the structure of the text. Also, it includes a comparison of what was planned to be done with the eventual results.

### **1.1. Motivation**

The motivation stands behind the following thesis work could be divided into two main constituents. First one is the author's strong desire to make a bit of a contribution to solve the global problem of recycling plastic waste on Earth. The second one is to research ways of plastic recycling that differ from those that are widely used nowadays – burning waste with further production of heat and electricity or reusing it as a raw material for new plastic production. Although both of the methods listed above have proven to be efficient and helpful to the global environment, it was believed that new approaches must be investigated. The diversity of methods and ideas is one of the main drivers of progress.

Alcohol is known for its immense range of properties that allow its usage in numerous industries and various field of applications. Perfumes and toilet waters, food-, healthcare- and pharmaceutical industries, cleaning chemicals, chemicals solvents and fuel. These are only a small bit of fields of applications where alcohol could be successfully implemented.

There are billions of pieces of plastic waste lay on the ground or floating around the oceans nowadays. What if all of it is carefully collected and recycled into alcohol, that is used after for various purposes?

### **1.2. Objectives**

The aim of the research was to test alternative ways of polyethylene recycling to get substances or materials, that could be used for the various applications afterwards.

It was planned to convert polyethylene into ethylene during the first step of the work by the process known as pyrolysis and hydrate ethylene into ethanol at the second step. The third step of the practical work was to analyse results of the first and the second steps, searching for the further application(s) for the converted substance(s) and/or material(s).

### **1.3. Methodology & structure of the thesis**

The following thesis is divided into two main parts – practical one, that collects all the information about completed experiments and other laboratory works (together with the results) and theoretical one.

At first, the theoretical part includes an overview of global plastic waste management and municipal solid waste management in various countries and regions. Then, a summary of different methods of plastic waste treatment is mentioned, including landfilling, energy recovering, recycling and converting into fuel. Short description of polyethylene production and explanation of pyrolysis and depolymerisation processes are mentioned within the theoretical part as well.

The theoretical part is intended to support the practical one, providing the information which the experiments and researches are based on.

The practical part introduces all the used equipment, then goes through actual experiments and based on them tests. The part is finished by results and conclusions.

All of the experiments were held in Arcada's laboratories according to the Finnish and international safety standards.

## 2. LITERATURE REVIEW

In this chapter facts and statistics of plastic waste treatment around the world are mentioned, as well as information about the main methods of plastic waste disposal is provided. Also, processes important for the understanding of the entire thesis are explained, such as pyrolysis, depolymerisation and polyethylene production. Finally, the articles most pertinent to the experimental work are discussed.

### 2.1. Plastic waste management around the globe

- **Europe**

According to PlasticsEurope Market Research Group, there were 64.4 million tonnes of plastic produced in Europe in 2017, and over 60 million tonnes a year earlier. Europe is producing approximately 18.5% of the world's plastic, that was estimated at 348 million tonnes in 2017 (excluding PET-, PA- and polyacryl-fibres). Almost 40% of European plastic is used for packaging, therefore polypropylene (PP) is the most common type of plastic produced – 10 million tonnes, followed by low-density polyethylene (LDPE) and high-density polyethylene (HDPE) – 9 and 6 million tonnes respectively.

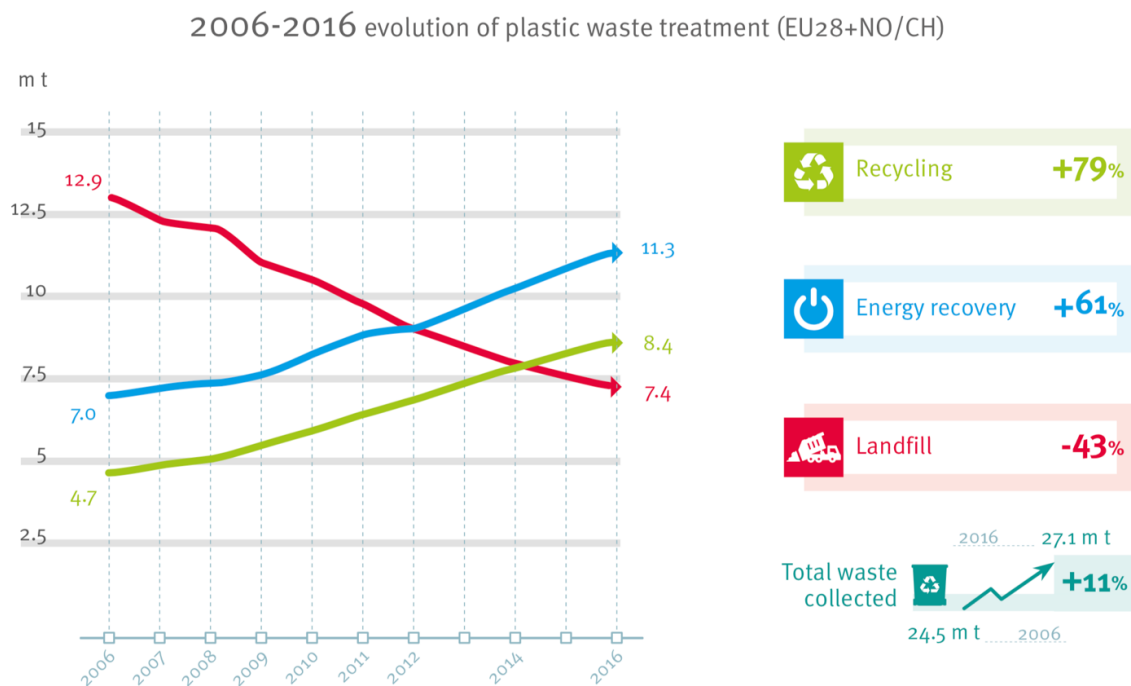


Figure 1. Evolution of plastic waste treatment between 2006-2016,  
Confederation of European Waste-to-Energy Plants (2017).

During ten years from 2006 to 2016 methods of plastic waste treatment in Europe changed significantly. While landfilling was losing its dominant position, the development of technologies increased the popularity of plastic recycling and turning it into energy. As it is visible on Figure 1, in 2015 recycling overtook landfilling followed by even a bigger gap in 2016.

A positive influence driving us towards waste recycling and energy recovering over landfilling were landfilling bans and taxes implemented in European countries. For example, there are neither additional bans (comparing with Directive 1999/31/EC, also called “Landfill Directive”) nor taxes for landfilling municipal solid waste (MSW) applied to Malta – consequently, there only 20% of plastic waste is recycled. The same situation may be observed in Cyprus. Finland, on the contrary, is obligated to pay a tax of 70 euros per tonne and has a ban on organic waste landfilling since 01.01.2016. What is more, another ban on construction and demolition waste was applied on 01.01.2020. Switzerland has a ban on landfilling untreated and combustible waste since the year 2000 – that refers to 100% of waste is recycled or energy recovered nowadays (see Figure 2).

Plastic post-consumer waste rates of recycling, energy recovery and landfill per country in 2016

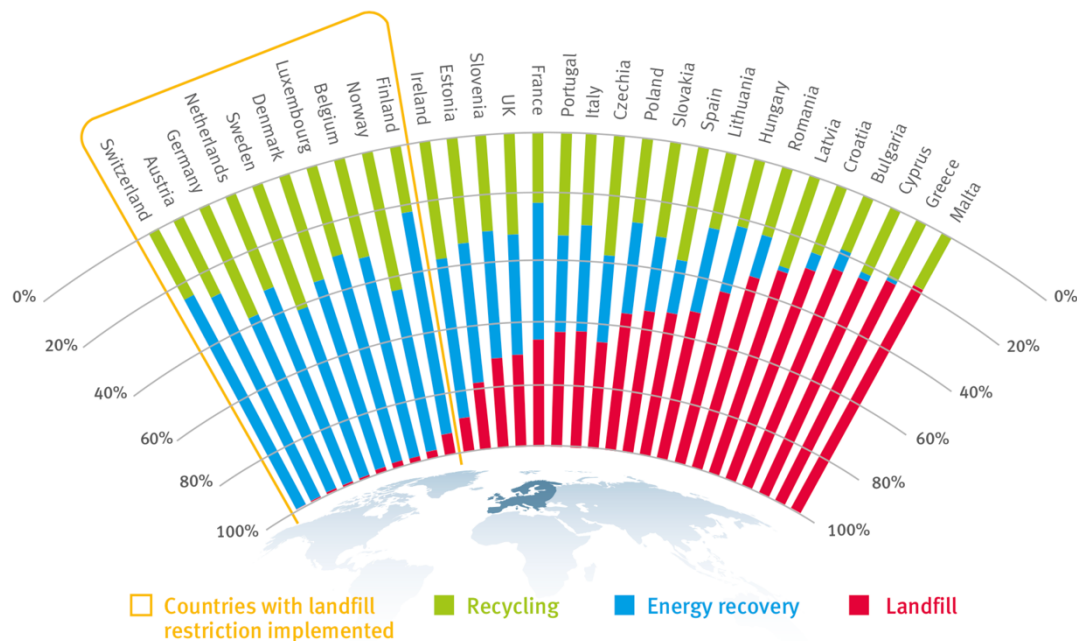


Figure 2. Ways of plastic waste treatment in Europe, Confederation of European Waste-to-Energy Plants (2017).

Different European countries are choosing different methods of plastic waste treatment. Some of them are gaining the most profit by recycling it while others – like Finland – by recovering energy from plastic waste. For example, in 2016<sup>th</sup> 97% of MSW was recovered. Approximately two-thirds

of it was used as a fuel for energy production, while the rest was recycled or composted – in terms of food waste (see Figure 3).

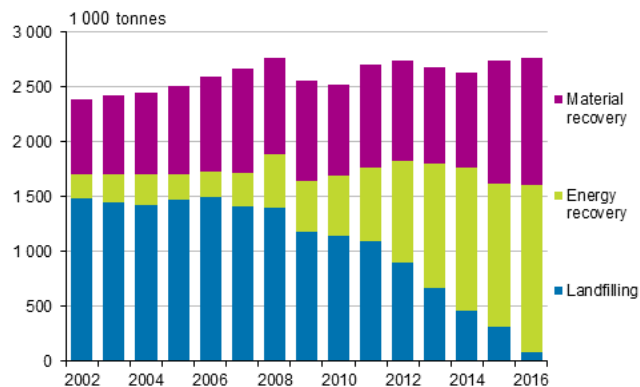


Figure 3. Municipal solid waste treatment in Finland, Espo & Pakarinen (2018).

In general, Europe is moving to the “greener future” faster than it was planned. Having looked at the overview of packaging recycling in Europe in 2016, a noticeable growth is visible. Although, the target of Plastic Packaging Waste Directive of 20 December 1994 was to recycle a minimum of “22.5% by weight for plastics” packaging (EUR-Lex, 2018), in 2016 average recycling rate was already 42.4% (Eurostat, 2018) (see Figure 4).

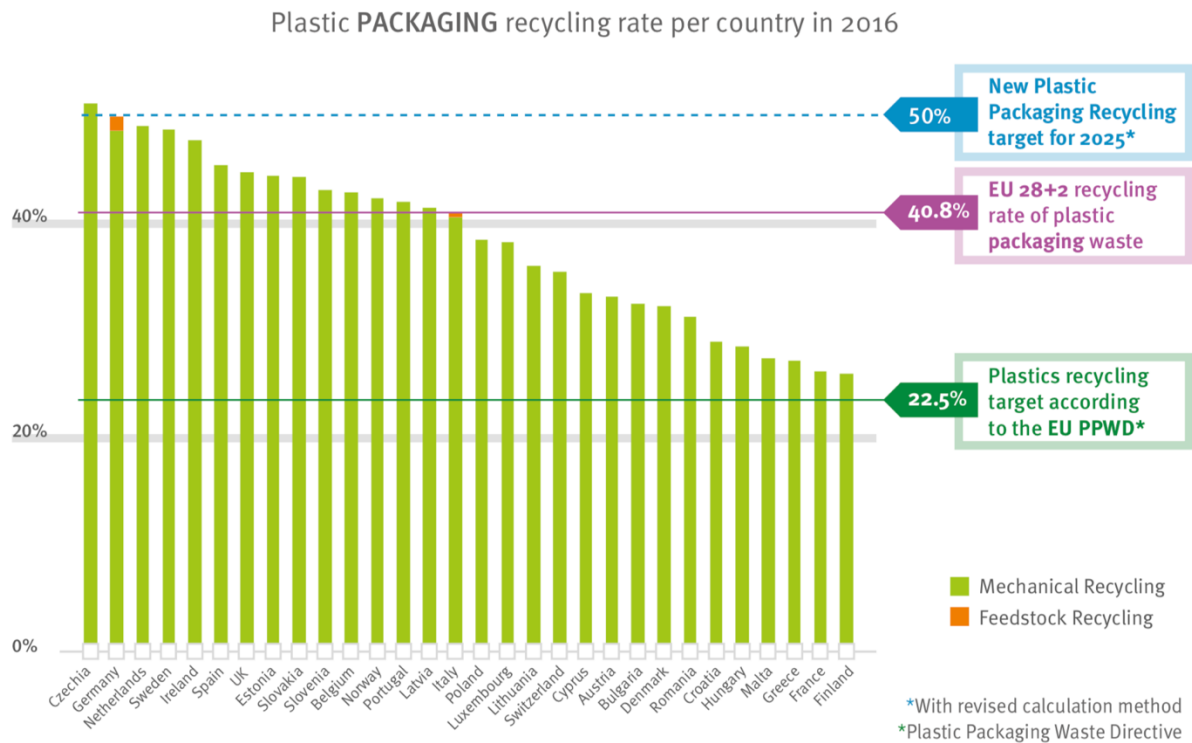
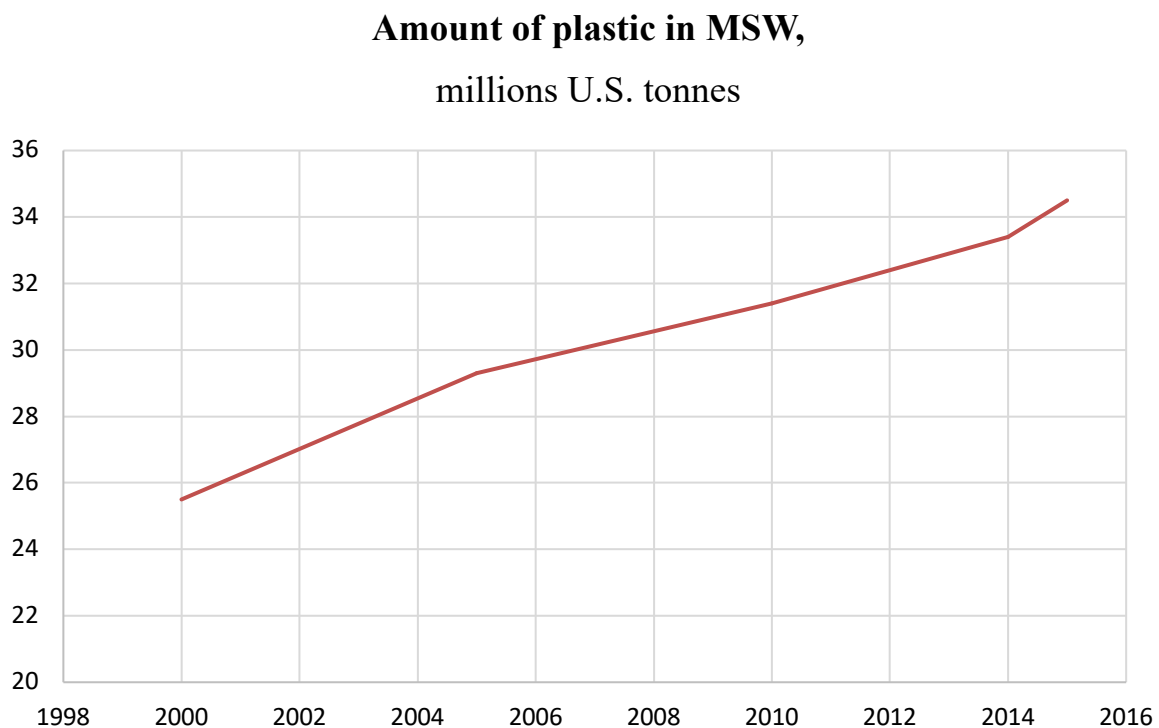


Figure 4. Packaging recycling in Europe, Confederation of European Waste-to-Energy Plants (2017).

- **USA**

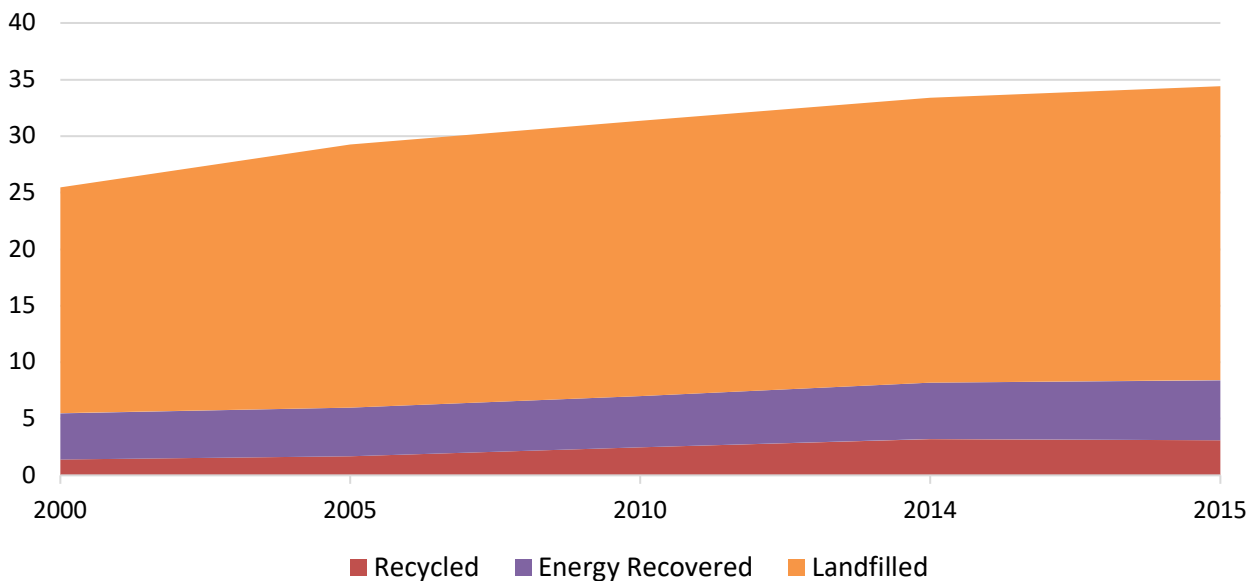
Although, NAFTA countries (Mexico, Canada, United States) produce almost the same amount of plastic as Europe – 17.7% over 18.5% of the world’s plastic production (Confederation of European Waste-to-Energy Plants, 2017), America is taking worse care of plastic waste compare with European countries. In 2015 only 10% (3.1 millions of U.S. tonnes) of all plastic was recycled. Although, some specific types of plastic are claimed to be recycled better. For example, the recycling rate of HDPE and polyethylene terephthalate (PET) bottles was estimated at 30%. During the same year, 5.4 million tonnes of plastic found in MSW was combusted with energy recovery, that makes approximately 16% of all the combusted MSW. At the same time, 26 million tonnes of plastic were landfilled among other MSW, forming 19% of all the MSW landfilled. (U.S. Environmental Protection Agency, 2017).

Despite the fact the amount of plastic waste is increasing yearly (see Figure 5), the amount of its recycling and combusting is either growing slightly or stays the same. This is especially well noticeable while comparing with the amount of plastic sent to landfills (see Figure 6).



*Figure 5. Amount of plastic in municipal solid waste in U.S.,  
U.S. Environmental Protection Agency (2017).*

### Methods of plastic waste treatment in MSW, millions U.S. tonnes



*Figure 6. Ways of plastic waste treatment in municipal solid waste in U.S., U.S. Environmental Protection Agency (2017).*

- **China & Asia**

China is the largest plastic producer in the world with almost 30% of the world's plastic production (Confederation of European Waste-to-Energy Plants, 2017). It was also the largest importer of global plastic waste (see Figure 7). In general, Asia is the most polluted with plastic and the largest pollutant region on the globe. 86% of all the plastic input into the oceans via rivers in 2017 was from Asia (see Figure 8). At the same time, China was the largest country-pollutant of the global ocean with plastic (see Figure 9). For example, among the 20 world's most pollutant with plastic rivers, 6 of them were Chinese, delivering half a million tonnes of plastic annually. (Lebreton et al., 2017).

## How much plastic waste does China import?

Total annual plastic waste to manage in China, differentiated by domestic plastic waste generation and global imports of recycled plastic waste. This is measured in tonnes of plastic per year.

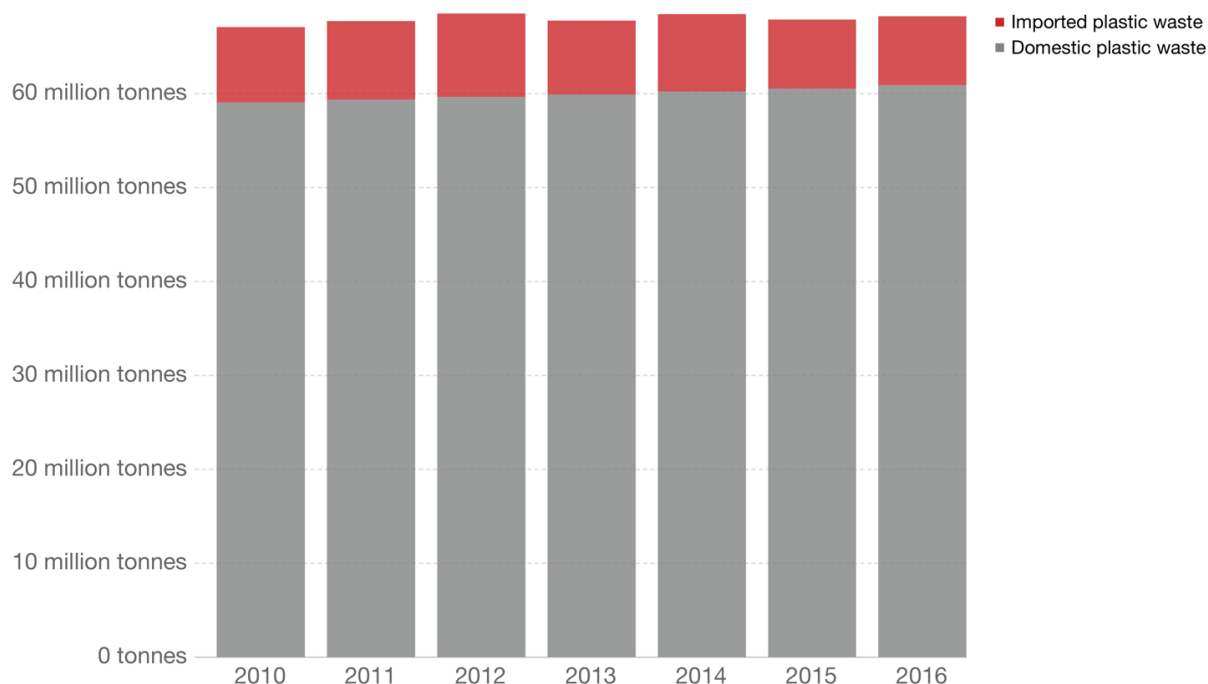


Figure 7. China's plastic import, Brooks et al. (2018).

## Global river plastic input to the ocean by region, 2015

Share of annual global plastic inputs from rivers into the ocean, differentiated by region.

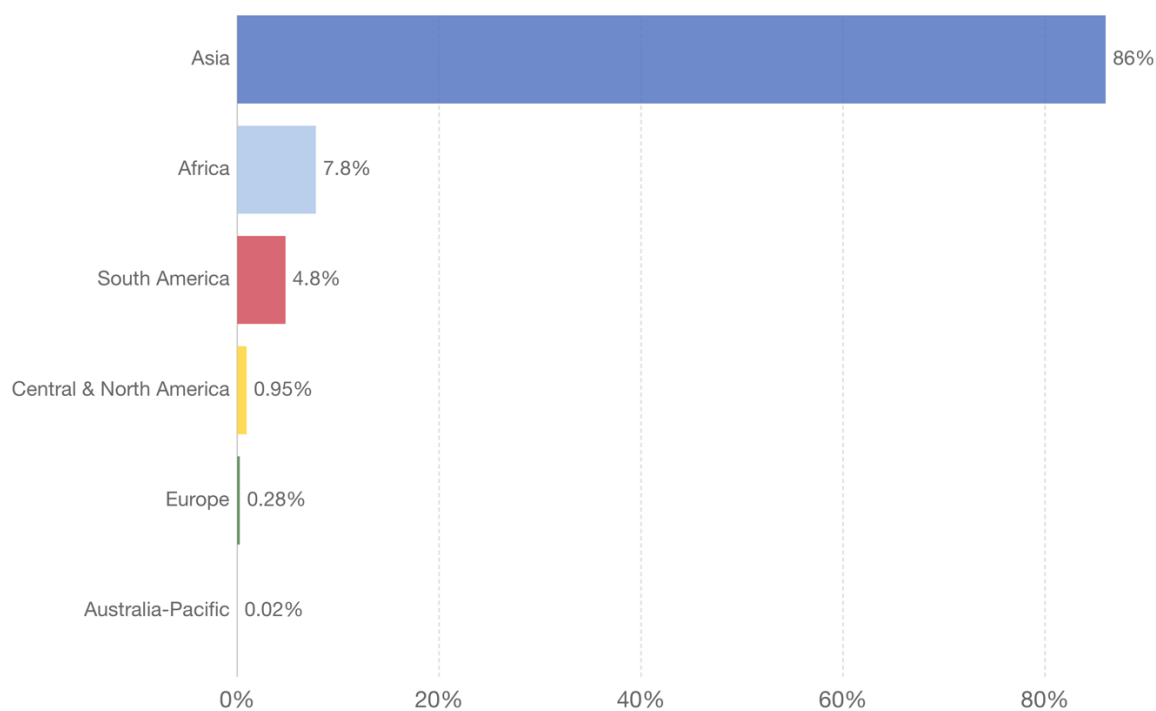
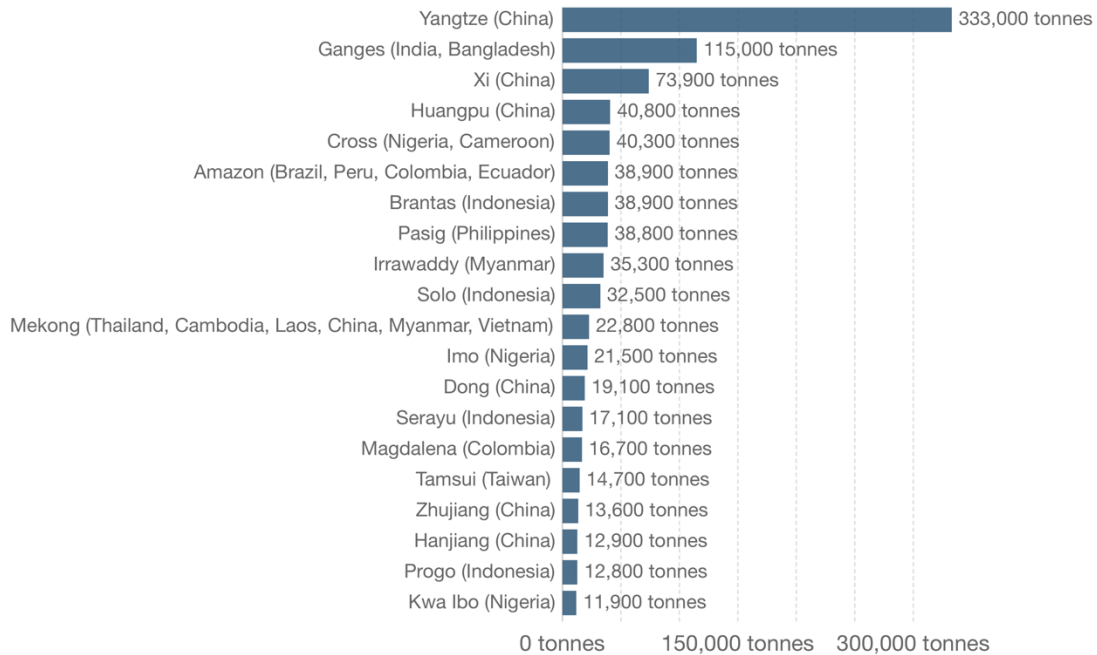


Figure 8. Plastic input to the ocean, Lebreton et al. (2017).

## Plastic ocean input from top 20 rivers, 2015

Plastic input to the ocean from the top 20 polluting rivers across the world. Shown is the given river, its location, and estimated annual input of plastic to the oceans in tonnes.



*Figure 9. Rivers containing the most amount of plastic, Lebreton et al. (2017).*

This is rising a big question of why China keeps importing plastic waste being the largest pollutant on the globe and why other countries keep exporting their waste there. However, everything might change in the nearest future – starting from the year of 2018 China stopped importing other countries plastic waste, claiming it is too dirty, hazardous and therefore environmentally dangerous. A year after the ban, the global plastic waste routes changed significantly, as it is visible in Figure 10. (Reed et al., 2018).

## How the global river of plastic waste changed course in just 12 months

Exports of plastic waste, parings and scrap from G7 countries ('000 tonnes)

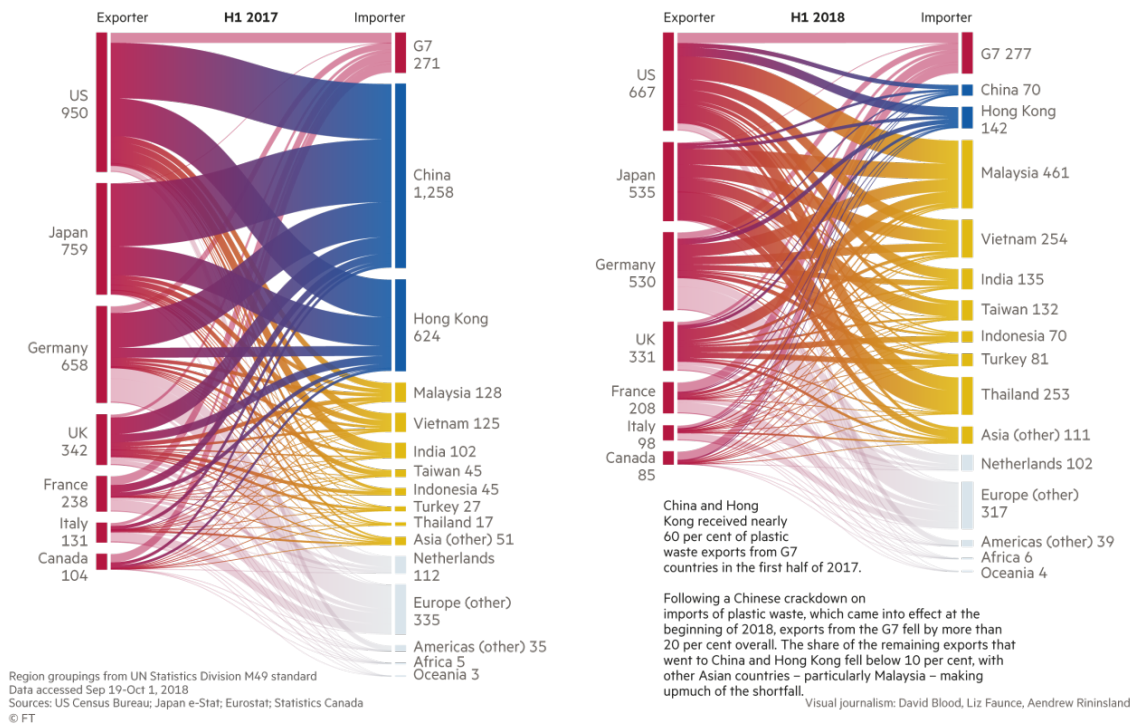
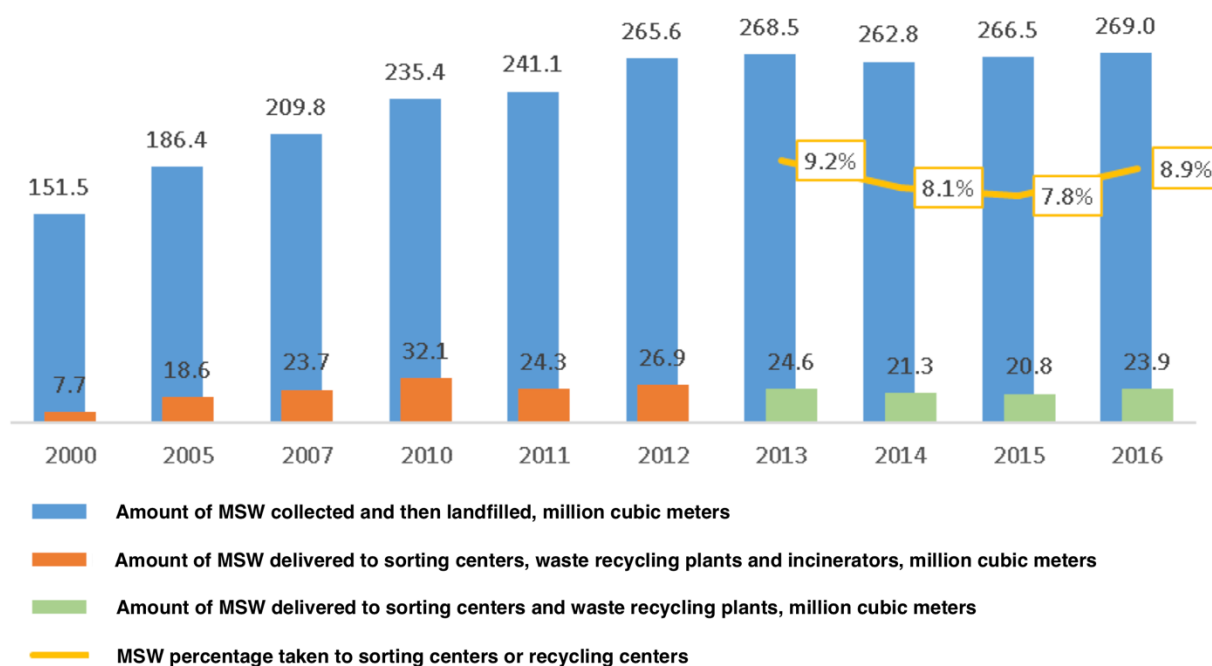


Figure 10. Comparison of global plastic waste import and export between 2017-2018, Reed et al. (2018).

- **Russia**

Russia is going far behind European countries in terms of MSW and plastic waste recycling or energy recovering. Having observed MSW management from 2013 to 2016, it was found that less than 9% of all the MSW was delivered to the sorting and recycling stations (see Figure 11). (Volkova, 2018, p. 17).



*Figure 11. Ways of municipal solid waste treatment in Russia between 2000-2016, Volkova (2018).*

The same statistics might be observed for plastic waste recycling. While most of the plastic waste is generated in MSW – about 60% – there is a problem exist of collecting and sorting it, as not every citizen has access to waste-separated waste containers. Commercial sector generates 34% of plastic waste. The rest 6% are generated by industrial and construction services.

The most common type of plastic waste, the same as in Europe, is various kinds of packaging and films. PET containers are taking only third place in plastic waste production. However, exactly PET is recycled in Russia the most. This is because PET containers require the least effort to be collected and sorted. Unfortunately, the highest recycling rate for PET containers is 20% only. On average, less than 10% of plastic waste is recycled.

Nevertheless, a positive trend is observed even there. Out of all recycled plastic, in 2016 the amount of plastic sorted in the sorting stations increased three times, while manual collection at landfills decreased twice compare with 2012 (see Figures 12, 13). Also, waste separation by households delivered 16 times more plastic in 2016 than in 2012. It is important to notice, however, that this method took only 3.2% of all the recycled plastic. (Volkova, 2018, p. 44).

2012

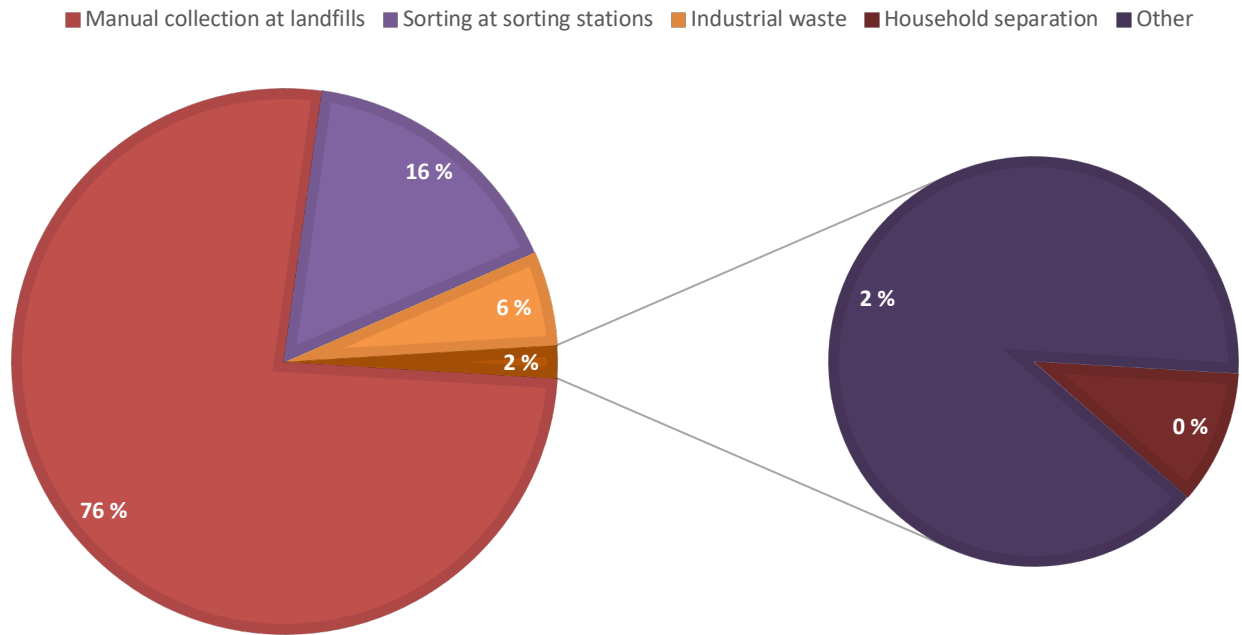


Figure 12. Sources of plastic to be recycled in Russia in 2012, Volkova (2018).

2016

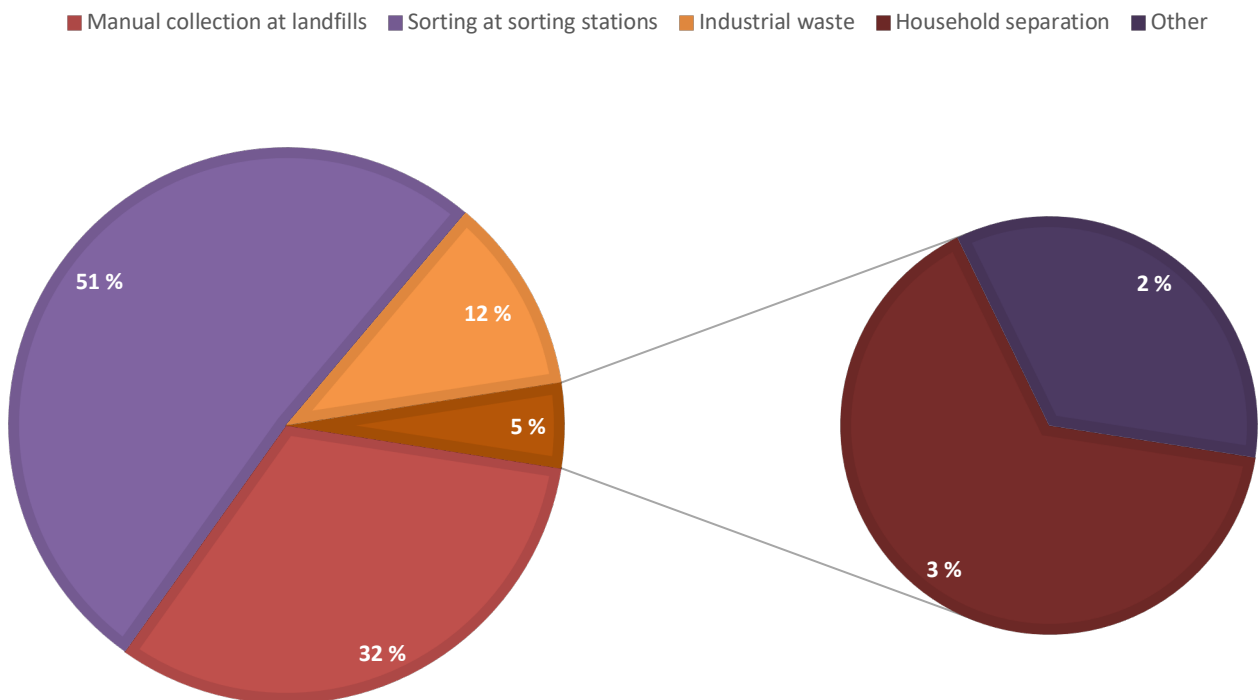


Figure 13. Sources of plastic to be recycled in Russia in 2016, Volkova (2018).

## **2.2. Main plastic waste management methods**

- **Landfilling**

Landfilling is the oldest and most traditional approach to dispose of not only plastic but any type of waste in general. Some materials are able to be decomposed that way within a year, while for plastics it may take from dozens to hundreds of years.

The most common concern lately about landfills is not even an environmental impact, but the amount of space they take. The Earth's population keeps growing and correct space management is becoming an urgent issue.

Correct landfilling requires a lot of attention – groundwater must be protected, landfill gases and soil spoiling must be controlled, layers of waste must be alternating with layers of soil. Landfills can be located only in areas with minimal flood risk to prevent waste from going into rivers and oceans and far from inhabited areas.

For example, among many other requirements, the Finnish government obligate landfilling companies to collect landfill gas and put to use. In case it cannot be used, it should be flared. Otherwise, its migration must be monitored and controlled. Landfills must be fenced and secured. The layer underlying landfill must be at least half a meter thick for non-hazardous waste and at least one meter for hazardous. (Finlex, 2016).

However, this is a standard approach for landfills. It is now clear to many countries that trash actually consists of energy. The energy that could be at least recovered, even when it is complicated to recycle the material itself. In other words, dumping waste to landfills practically means throwing away money and valuable fuel or raw material, that could be successfully implemented elsewhere. What is more, many countries are inputting or increasing taxes for landfilled waste, making this business sector being less profitable for companies and entrepreneurs. (Pandey & Siddiqui, 2013, p. 86).

- **Energy recovering**

Incineration of plastic (and other MSW) is a process which allows to gain energy from materials and use it as a fuel for producing heat and electricity. Here, new waste simply serves as the fuel for flame in the incinerators, meaning no external energy supply is required to keep incinerators working.

Plastic is a great source of energy. As it is shown in Table 1, wood's calorific content is half that of PET and almost one quarter that of HDPE. (LaRiviere, 2007).

Typical Heat Content of Materials in Municipal Solid Waste (MSW)	
Materials	Million Btu per ton
Plastics	
Polyethylene terephthalate (PET)	20.5
High density polyethylene (HDPE)	38.0
Polyvinyl chloride (PVC)	16.5
Low density polyethylene/ Linear low density polyethylene (LDPE/LLDPE)	24.1
Polypropylene (PP)	38.0
Polystyrene (PS)	35.6
Other	20.5
Rubber	26.9
Leather	14.4
Textiles	13.8
Wood	10.0
Food	5.2
Yard trimmings	6.0
Newspaper	16.0
Corrugated Cardboard	16.5
Mixed paper	6.7

*Table 1. Comparison of energy values of different waste, LaRiviere (2007).*

*1 Btu per pound is equal to 2.326 kilojoules per kilogram (Convertunits, 2018). 1 US ton consist of 2000 pounds (Asknumbers, 2015). Therefore, PET's and HDPE's calorific content is 95366 and 176776 kilojoules per kilogram respectively.*

The biggest challenge here is to create a sufficient cleaning system, that would prevent many hazardous substances such as dioxins and polychlorinated-biphenyls leaking into the atmosphere and damaging the natural environment. However, as experience shows, it is not impossible anymore. Modern, high-quality incinerators can filter chimney gas particles by at least 90%. For example, Finnish Vantaan Energia is successfully producing heat and electricity for hundreds of thousands of inhabitants in large municipal areas, reducing the world's carbon dioxide emission into the atmosphere. (Vantaan Energia, 2019).

## - **Recycling**

Plastic recycling is a process of reusing plastic waste as a raw material for new plastic products. It is a very "green" way to go since plastic waste is neither thrown into landfills nor it is burned at incinerators with a probability of chimney gas exhalation into the atmosphere.

Unfortunately, unlike metals or glass, plastic molecules are degrading with every cycle of the recycling process, meaning new portions of raw material must be added to keep the required physical properties of products. However, the main issue of plastic recycling is its complexity. Plastic is cheap

to produce while collecting plastic waste, cleaning it, separating and recycling is more complex and expensive. For example, different plastics cannot be melted together because of the different chemical structures (Fleischman, 2017).

Finally, public awareness is key to the efficiency of plastic recycling. Public infrastructures to make recycling less expensive and more efficient are required, such as waste-separated recycling bins or special trucks for different types of waste.

- **Waste-to-fuel**

Converting polyethylene into fuel is a relatively new method based on the components of plastic and fuel. They all consist of carbon and hydrogen, placed in the different order and forming different structures. During the process, plastics are cracked to smaller molecules which could be then modified by adding water or catalysts, forming fuel-like products, for example, ethanol or diesel.

Synthetic fuels are claimed to be more efficient in terms of burning, therefore engines produce less carbon dioxide, reducing its emission into the atmosphere (Al Jazeera, 2012).

It must be noticed that, more or less, everything consists of carbon, meaning not only plastics may be transformed into fuel but basically any waste. The major issue here is to create a way that would be profitable enough. Nowadays, it is still cheaper to produce fuel in a common way instead of spending money and time for cleaning and converting waste. However, there are companies around the world which are successfully operating industrial-scale biofuel production as well as other products made from plastic and other waste, e.g. Enerkem (Enerkem, 2019).

## **2.3. Key publications on the pyrolysis of polyethylene**

There were a few kinds of research dedicated to polyethylene pyrolysis taken as a base of the future recycling process. First of all, two huge and very important works “Two-steps selective thermal depolymerization of polyethylene” (Della Zassa et al., 2010) and “Characteristics of a new type continuous two-stage pyrolysis of waste polyethylene” (Park et al., 2019) were researched. In both articles similar two-step processes of the pyrolysis of polyethylene were researched. In a two-step pyrolysis two separate heating units generate different temperatures. In their articles, a first unit was meant to preheat polyethylene and start the pyrolysis process with relatively low temperatures, while the second one was meant to crack the pyrolysis products down to the ethylene molecules by using high temperatures and small reaction times. Both articles claimed to receive successful results with, among the other substances, up to 45% of ethylene received from a unit of used polyethylene. Despite

the lack of capacity to implement suggested processes, the articles gave an invaluable insights and ideas to the future working process and were used for understanding the process of polyethylene depolymerization on the industrial scales.

After being familiarized with theoretical and industrial-scales methods of polyethylene pyrolysis, the gained knowledge was supplemented with research laboratory scale setups. Here, great experiments “A comparative study on co-pyrolysis of lignocellulosic biomass with polyethylene terephthalate, polystyrene and polyvinyl chloride: Synergistic effects and product characteristics” (Özsin & Pütün, 2018), “A process study on the pyrolysis of waste polyethylene” (Zeaiter, 2014) and “The effect of slow pyrolysis on the conversion of packaging waste plastics (PE and PP) into fuel” (Das & Tiwari, 2018) were used as the base for some of the experimental work in this project. For instance, all of the key experimental parameters such as heating temperatures, times, gas flow rates and some of the setup ideas were observed from exactly these three pieces of research. As a result of the Zeaiter’s work, a lot of fuel like products, olefins and aromatics were found to be presented in the pyrolysis products.

In all articles mentioned above gas chromatography was used as a main analytical method. Gas chromatography is an ideal method to use when different gaseous products appear during the pyrolysis process and should be analysed precisely.

## **2.4. Polyethylene production**

Polyethylene is the most commonly used plastic in the world. It is a synthetic resin that is made from ethylene by the process known as polymerization, during which small molecules (monomers) are combined, forming large networks or chains of molecules. Therefore, the name “polymer” appears. While polyethylene is made out of ethylene, the last one is produced from ethane – which is a constituent of natural gas. Alternatively (and more often on practice) it could be produced by distillation of petroleum. (Encyclopædia Britannica, 2017).

Polyethylene industry largely depends on the petroleum industry.

## **2.5. Depolymerisation and pyrolysis**

In contrast to the polymerisation process described above, depolymerisation is an action during where chains and networks of polymers are breaking down to monomers. Depolymerisation can be achieved by the process called pyrolysis – chemical decomposition of materials via heat

application. Pyrolysis is performed in the absence of oxygen, since its absence does not allow the material to burn. One of the most common products of pyrolysis is charcoal. (Encyclopædia Britannica, 2018).

The idea of polyethylene pyrolysis is to transform it back into ethylene, which then might be used for ethanol production. During the pyrolysis, polyethylene is breaking into the monomers – molecules of ethylene. Later on, those ethylene molecules undergo the contact with water, that caused hydration – a chemical reaction when substance is combined with water. Hydrated ethylene becomes ethanol.

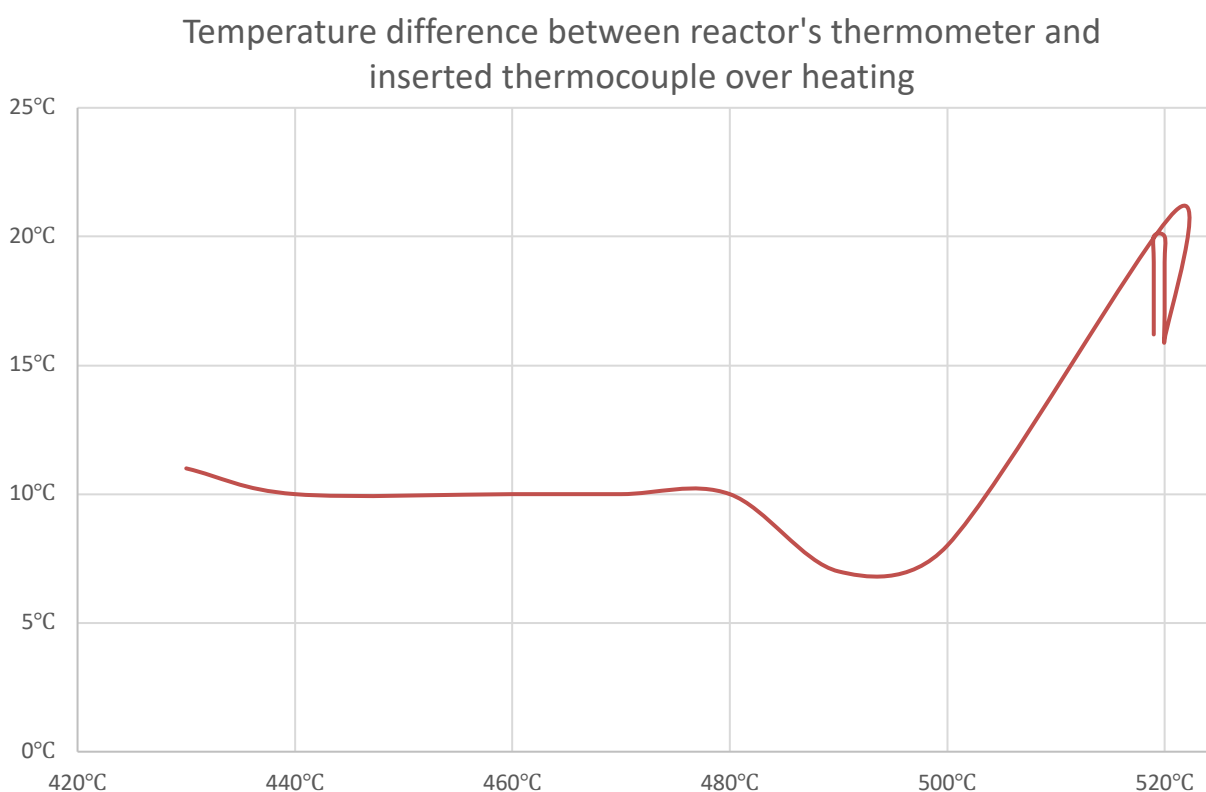
### 3. GENERATION I EXPERIMENTS

This chapter is dedicated for the practical aspect of the thesis – every used equipment, its preparation, every made experiment and performed testing together with the results are represented below.

#### 3.1. List of equipment

To complete the pyrolysis of polyethylene and transform it into alcohol, a few pieces of equipment were used – a furnace, a reactor, two water columns, one nitrogen gas bottle and a few Swagelok pipes, connectors and valves.

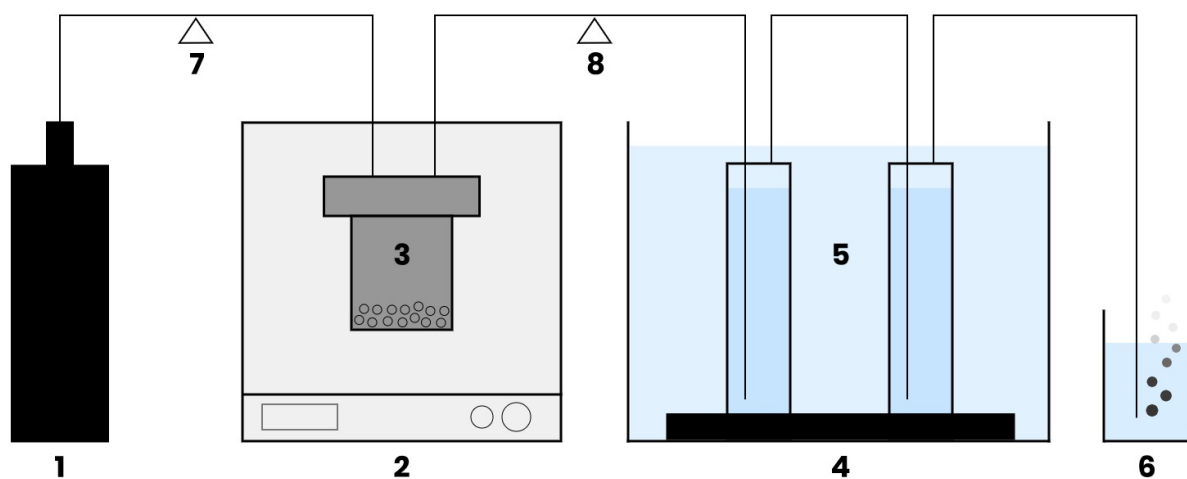
At first, an old furnace was repaired, and its temperature was calibrated by using a separate thermocouple. It was found out that the temperature shown by the furnace's thermometer was incorrect by 20°C (at the pyrolysis temperature, the furnace was 20°C colder than the thermometer showed). Therefore, during further experiments, the furnace's temperature was calculated as shown furnace's temperature +20°C.



*Figure 14. Representation of temperature difference in furnace's and thermometer's data (2019).*

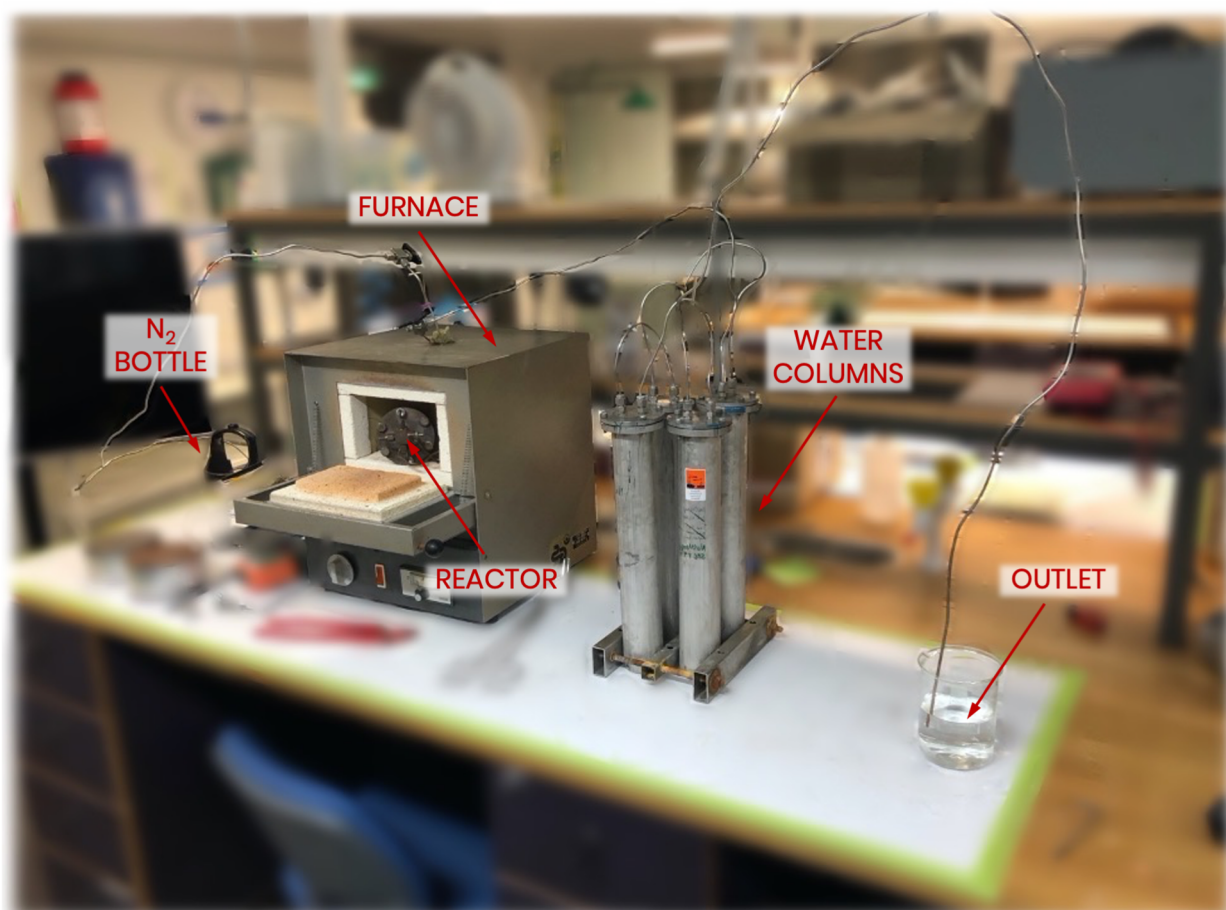
Secondly, the reactor made out of stainless steel was welded better to provide stronger connection between the lid and the body of the reactor (the old weld beads were breaking apart) and adjusted in a way all the currently unused inputs and outputs were blocked by a Swagelok 4-way valve. Then, a two-columns system (each filled with water) was repaired, assembled and connected in a consistent order. Gas from the reactor was supposed to go via each of the column (the input pipes went to the bottom of columns, while output ones remained on the top). A water tank was placed at the very end of the system. It was used to show that the gas flow was stable and was going through the system without any choking or interruptions.

Nitrogen gas was used to carry the generated ethylene gas flow and to provide an inert atmosphere inside the system. Stainless steel pipes connected the nitrogen bottle with the reactor and the reactor with the water-columns system. Two Swagelok 3-way valves were inserted into the setup – one before the reactor and one after – to prevent the water suck-back into the gas bottle and to regulate nitrogen input into the reactor. Water columns were put into the container with cold water to keep as low temperature as possible for better reaction with ethylene (Engineering ToolBox, 2008).



**1** – nitrogen bottle, **2** – furnace, **3** – reactor with polyethylene, **4** – system of 2 water columns, **5** – container with cold water, **6** – water tank, **7,8** – Swagelok connectors

*Figure 15. Schematic drawing of the setup (2019).*



*Figure 16. A picture of the setup during the assebmly (2019).*

### 3.2. Experiments

- **Experiment #1 (i.e. LDPE 1.0)**

The first test of the entire system was attempted on January 30<sup>th</sup>, 2019 at 12.29. The system was assembled, connected and placed inside the fume cupboard. Two additional aluminium seals were inserted between the reactor and its lid to prevent leakages – aluminium is expanding with such a high temperature blocking possible gaps. 6.66 grams of low-density polyethylene (LDPE) were placed into the reactor. 600 millilitres of water were poured into each column. Then, all of the connecting pipes and the reactor itself were filled with nitrogen to ensure an inert atmosphere inside the system. The furnace was heated up by 500°C with a heating rate of 8.9°C per minute. The nitrogen pressure was kept at 1 bar throughout the heating. After the needed temperature was reached, white smoke started to come from the last output of the system indicating the process of pyrolysis had

started. After 20 minutes from the beginning of the reaction, constant nitrogen flow became unstable – something inside the system was preventing proper gas flow. It was decided to increase the pressure of the nitrogen up to 2.5 bars, however, nothing changed. On the 28<sup>th</sup> minute of pyrolysis or 94<sup>th</sup> minute from the beginning, the test was terminated.

After disassembling the water columns, it was found out that the polyethylene decomposition products going out of the reactor had condensed inside the first connecting tube due to the contact with cold water. That caused its solidification and further slow-down of the gas flow. It was observed that the substance formed by the gas solidification was in the form of an inner diameter of the connecting tube, that proved earlier suggestions (see Figure 17). Both the substance and water solutions inside the water columns had a strong smell of petrol oil.

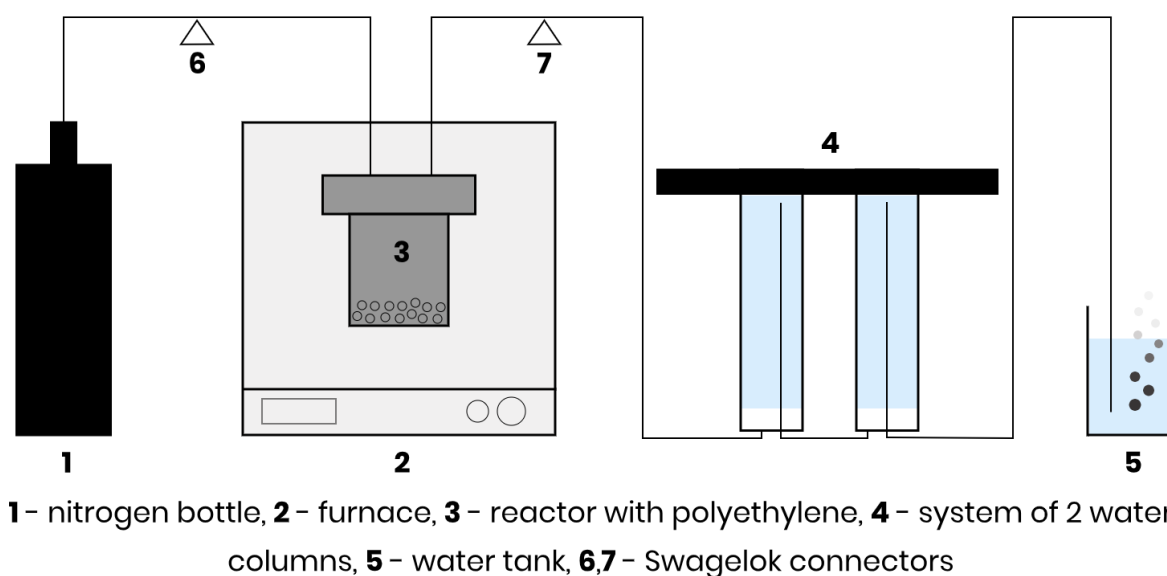
There was no presence of polyethylene found inside the reactor, meaning 28 minutes were enough to decompose 6.66 grams of LDPE.



*Figure 17. Pyrolysis products in the first water column (2019).*

- **Experiment #2 (i.e. HDPE 1.0)**

The second test was held on the next day after the first one. The setup was slightly changed – it was decided to flip water columns upside down to reduce cooling time of the pipe transferring the gas from the reactor. Now, all the inputs were located on the top of the columns, while output tubes started at the bottom of the columns – therefore, gas was released into the water mixing with it while going upward, where the output tube begins.



*Figure 18. Schematic drawing of the new setup (2019).*

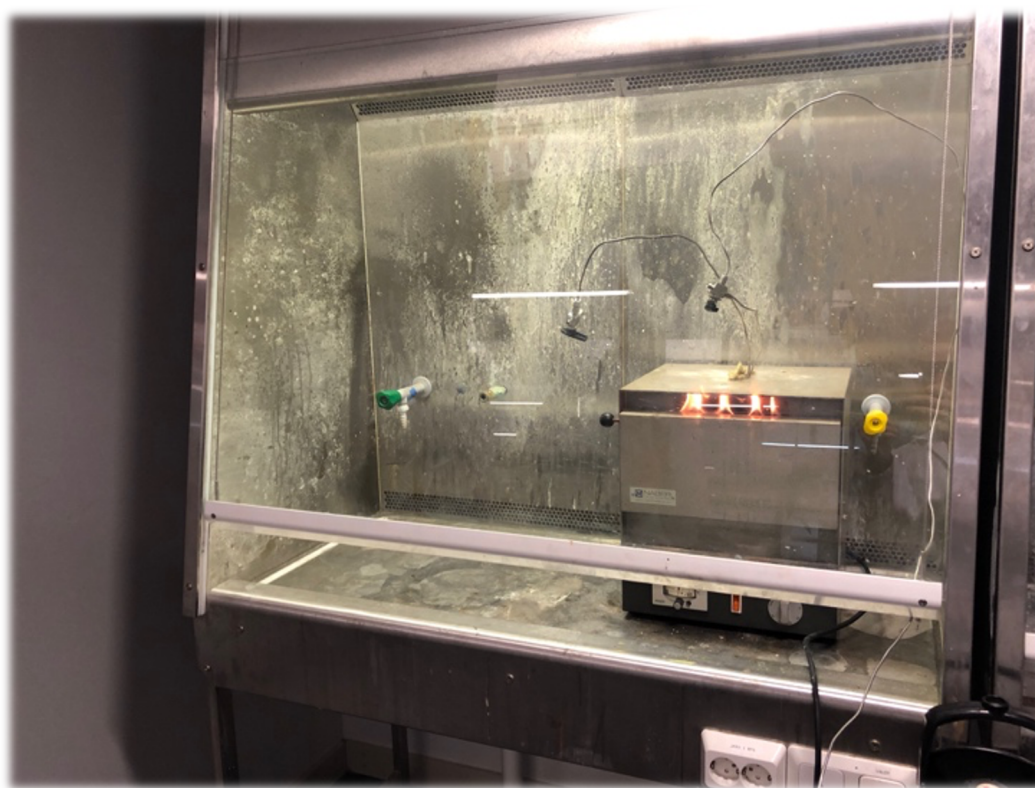
This time, 6.66 grams of high-density polyethylene (HDPE) were put into the reactor. The heating rate was increased by 16.5°C per minute. 25 minutes after the furnace had reached 500°C and the reaction started, the gas flow became unstable again – however, this time the problem was solved by increasing the pressure by 3 and later by 4 bars. After 36 minutes of pyrolysis, the gas flow became even again indicating the end of the reaction – there was no more polyethylene left inside the reactor. Having disassembled the system, same petrol smell came out. The water columns did not have as many solid residues as previously – almost none. It was assumed that changes in the setup helped to dissolve ethylene in water.

- **Experiment #3 (i.e. LDPE 2.0)**

The main purpose of the third experiment was to increase the amount of polyethylene. It was assumed that a concentration of ethanol in the final solution would increase respectively, therefore it would be easier to find the presence of ethanol in the resulting solution during analyses. This time, instead of 6.66 grams of LDPE 66.6 grams were taken. The heating rate was 16°C per minute.

27 minutes after the furnace reached 500°C, ethylene started to leak from the reactor inside the furnace. That caused it's autoignition, that is usually happening at a temperature range between 470°C and 490°C (Inchem, 1996) – mistakenly, before the experiment it was believed the ethylene's autoignition temperature is higher. Immediately after the opened fire was noticed, the furnace was unplugged from the socket, Swagelok #7 (Figure 18) was closed and the nitrogen bottle was disconnected. Afterwards, the supervisor and the laboratory security authorities were called. 67 minutes after the ignition fire was eliminated by inserting water from the top of the furnace. The experiment was terminated.

After being cooled down, the reactor was opened. Inside, a soft, waxy substance was found. Its weight was half that of the initial mass of polyethylene. The water from the water columns was collected for analysis.



*Figure 19. Picture of the burning furnace (2019).*

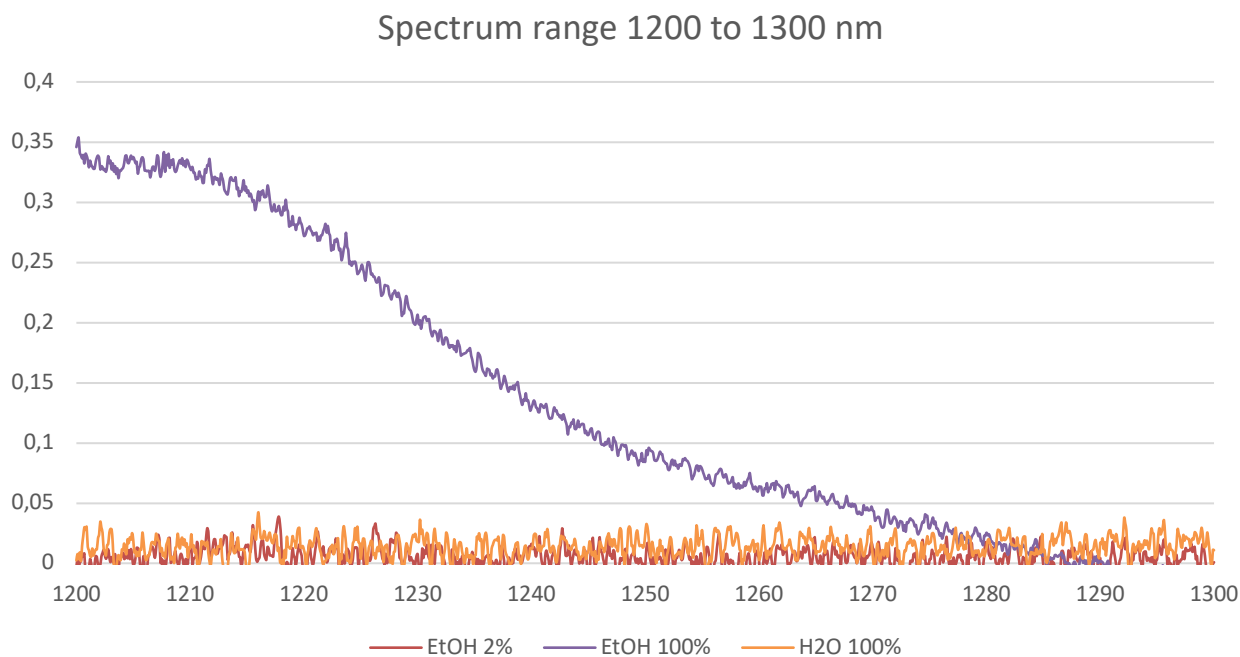


*Figure 20. Picture of the LDPE residues inside reactor (2019).*

### **3.3. Analyses**

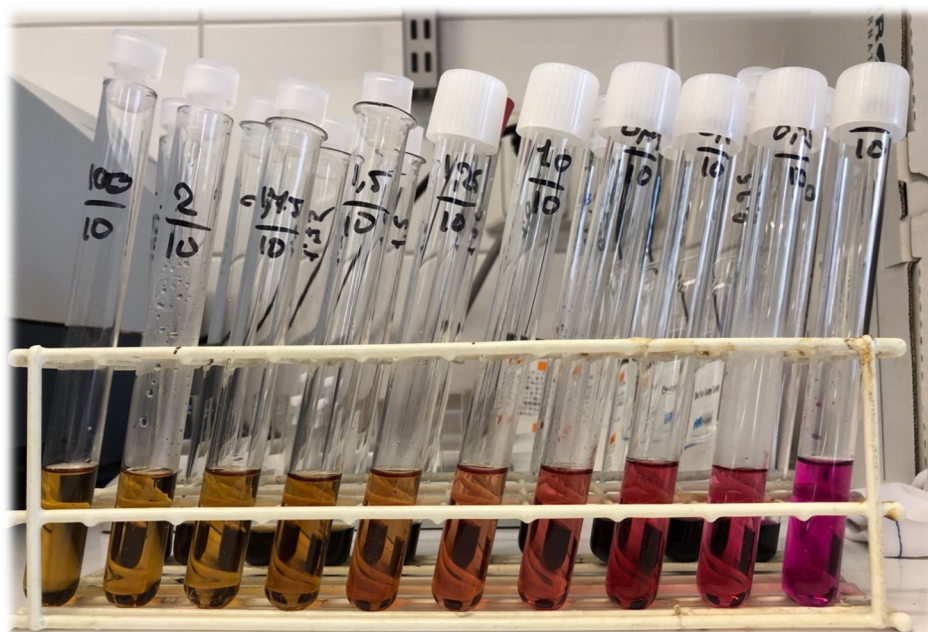
After the accident, it was decided to terminate any further experiments due to the high danger of repeating ethylene autoignition and due to the damage of the apparatus. There were seven different solutions by three performed experiments (two solutions out of two water columns plus one solution from the final water tank for first and second experiments and two solutions from two water columns from the third experiment) that had to be tested.

At first, a UV-vis spectrometry method was decided to be an optimal one. However, measurements using the Jasco V-670 spectrometer indicated all seven solutions were water. It was assumed, that UV lamps are not new enough to detect such small amounts of ethanol. Therefore, the lamps were replaced with new ones and spectrometer was calibrated. To test its performance, eight different solutions of deionized water and ethanol were prepared – from 0.25% to 2% with 0.25% step. After testing them and comparing with pure water and pure alcohol samples it was found that they still looked like water according to Jasco V-670. Thus, a different testing method should have been applied.

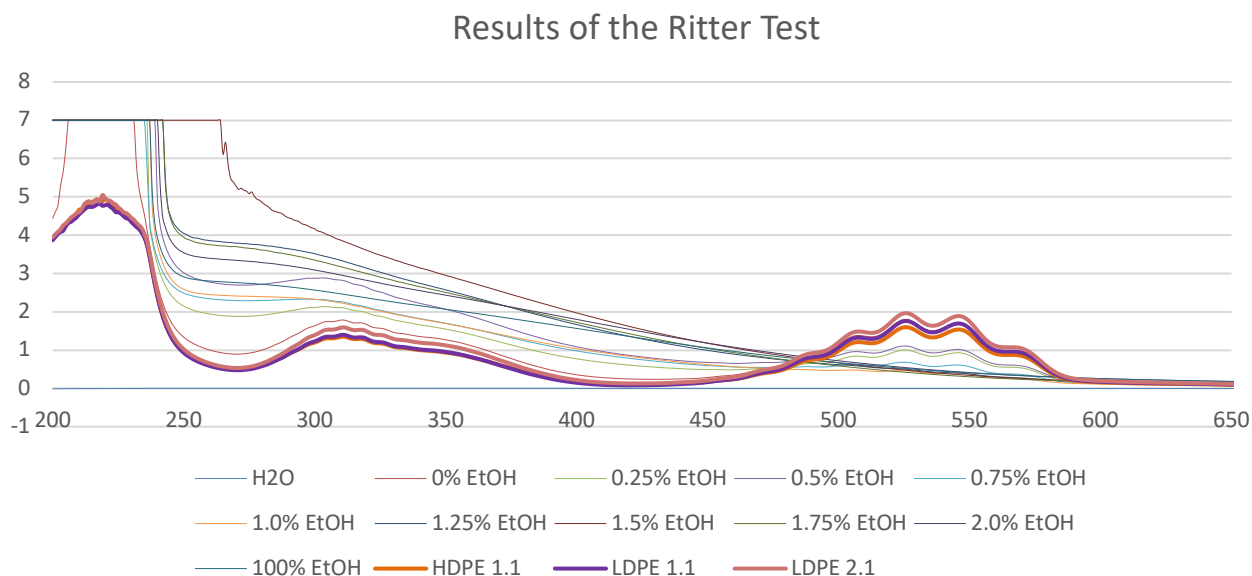


*Figure 21. Analyses of ethanol and water solutions (2019).*

The Ritter Test was implemented. Eight ethanol solutions were mixed with acetic acid, and potassium permanganate in certain proportions – 2 ml of acid, 0.2 ml of alcohol solution and 0.05 ml of concentrated potassium permanganate water solution. After reactions had been completed, each solution was dissolved in water, decreasing its concentration 10 times (to make spectrometer analysis possible). Eventually, 10 solutions were obtained – with 0%, 0.25%, 0.5%, 0.75%, 1.0%, 1.25%, 1.5%, 1.75%, 2.0% and 100% of ethanol concentration.



*Figure 22. Picture of solutions prepared for analyses (2019).*



*Figure 23. UV analyses of Ritter's test's solutions (2019).*

However, after results were received and analysed, no clear relation was found in the behaviour of Ritter's Test's solutions and solutions received during the experiments. It should be noticed, however, that there was a very similar path of the experiment's solutions and 0.25%, 0.5% ethanol solutions between 490 and 590 nanometres wavelength. Other graphs, however, did not make it possible to give any certain judgments. At this point it became clear that either solution had no presence of ethanol (or less than 0.25%) or the analysing method – UV spectrometry – was a wrong one to be chosen. Luckily, at the same time, Arcada bought an FTIR machine for the chemistry lab. It was immediately used as a second method of analysing experiment's solutions.

This time, 7 different ethanol-water solutions were prepared with 1%, 2%, 10%, 50%, 70%, 80% and 90% of ethanol. From the experiment's solutions, only LDPE 1.1 (first water column of the LDPE 1.0 experiment) and HDPE 1.1 (first water column of the HDPE 1.0 experiment) were analysed. The wavenumber limits were put from  $400\text{cm}^{-1}$  to  $4000\text{cm}^{-1}$  and absorbance was recorded.

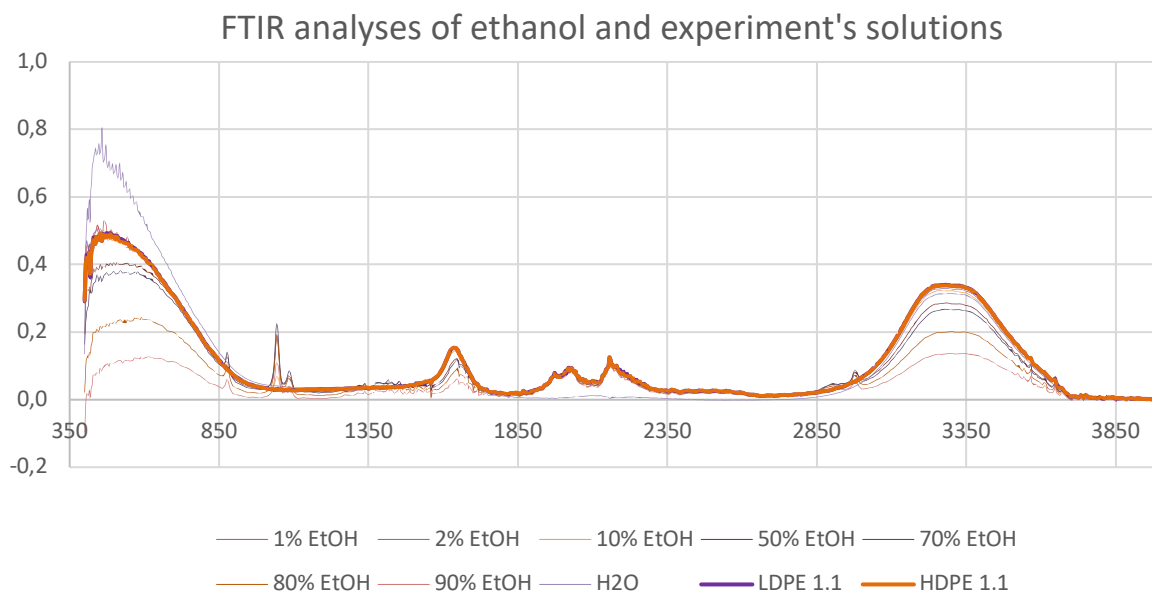


Figure 24. FTIR analyses of ethanol and experiment's solutions (2020).

The results received from the FTIR analyses were much clearer and more useful compare with the UV spectrometry. By analysing the behaviour of the curves, it was noticed that solutions received during the experiments have similarities in behaviour both with the pure water and prepared ethanol solution.

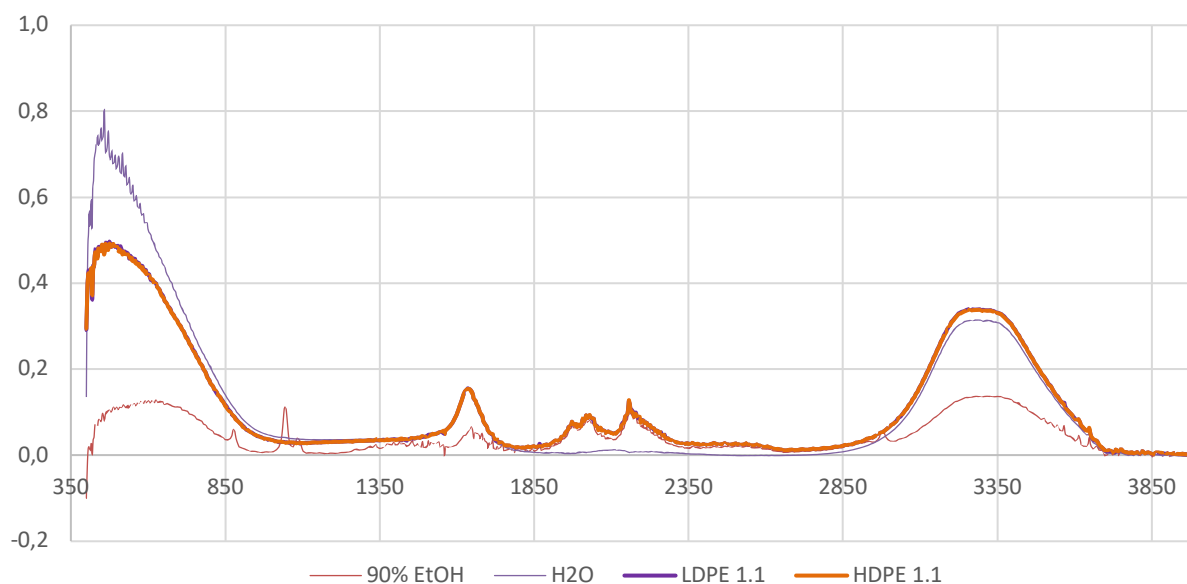


Figure 25. FTIR analyses of 90% ethanol solution, water and experiment's solutions (2020).

On Figure 25, LDPE 1.1 and HDPE 1.1 curves behaved absolutely the same, therefore it was impossible to see them both at the same time. It was clear that all the curves have a stretch between  $3000\text{cm}^{-1}$  and  $3500\text{cm}^{-1}$ , which correspond to O-H bond, presented in ethanol, water and experiment's solutions (Smith, 2017). After it, both LDPE 1.1 and HDPE 1.1 repeat the water's peak at  $1600\text{cm}^{-1}$  but ignore completely typical ethanol's peaks at  $1050\text{--}1350\text{cm}^{-1}$  which relate to the alcohol's C-O bonds (Mudalip et al., 2013, p. 127). The most interesting part of the graph, however, lays between  $1900\text{cm}^{-1}$  and  $2250\text{cm}^{-1}$  length waves, where experiments solutions repeat almost identically 90% ethanol's solution. Those stretches correspond to  $\text{C} \equiv \text{C}$  bonds or  $\text{C} \equiv \text{N}$  bonds. However, it was hard to believe that some triple carbon bonds appeared during the experiments, especially the one including nitrogen. Therefore, after a month of investigation, new analyses were performed. To avoid any possible mistakes, every component – distilled water, two experiment's solutions and three alcohol solutions – was analysed 5 times and an average data for each of them was calculated. Based on this data, the new graph was made. It appeared to be the same one as before with only difference – unknown stretches in the  $1900\text{cm}^{-1} - 2250\text{cm}^{-1}$  region disappeared. It was concluded that they happened to be there initially because of an unknown FTIR spectrometer mistake.

On the new graph, both experiment's solutions (LDPE 1.1 and HDPE 1.1) showed the same behaviour as water. Although, LDPE 1.1 repeated C-H peaks between  $2900\text{cm}^{-1}$  and  $3000\text{cm}^{-1}$ , it was impossible to say whether it indicated the presence of ethanol or polyethylene in the solution.

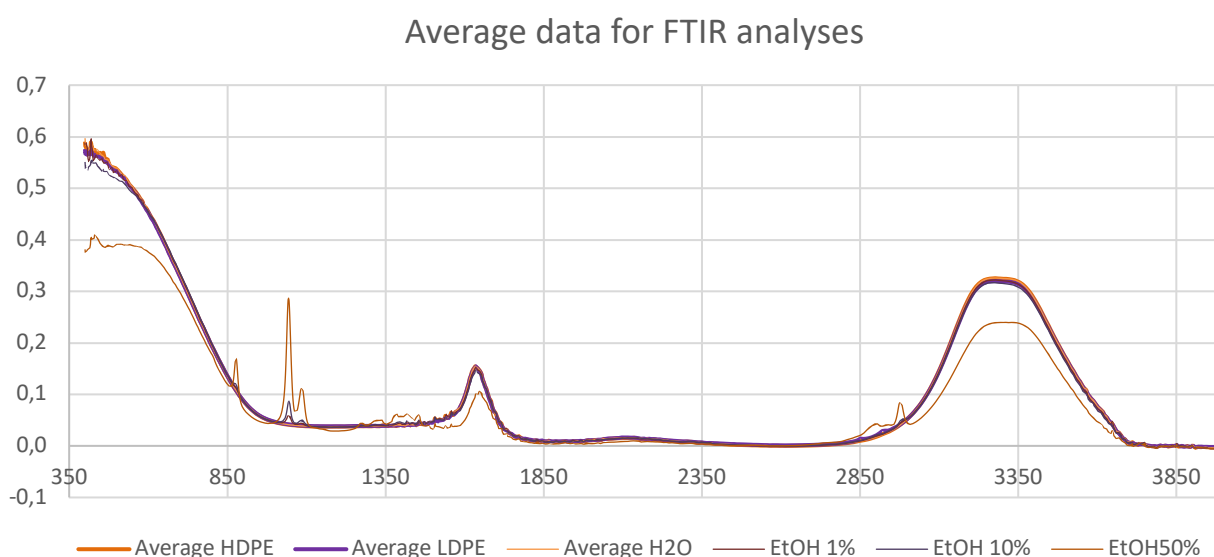


Figure 26. FTIR analyses of ethanol solutions, water and experiment's solutions (2020).

## 4. GENERATION II EXPERIMENTS

Being unable to detect ethanol in the water solutions received during the first three experiments, it was decided to try to repeat experiments with a larger amount of polyethylene presented, assuming it might help to produce more concentrated solutions, which therefore would be easier to analyse on the presence of ethanol. However, after the previous accident with ignited ethylene, it was impossible to use neither old equipment nor the same methods. Therefore, a few other strategies were considered.

- **An attempt to manufacture a new reactor**

At first, an attempt to produce a new reactor with a better design was made. The new reactor was designed using SolidWorks 3D modelling software. It was designed specifically to prevent possible leakages, using customised connectors and special materials, which would be able to expand under a certain temperature, blocking all the possible gaps.

The initial idea was to manufacture all parts using Arcada's milling machine. It requires a G-code which is generated by the MasterCAM software. Therefore, all parts of the reactor were modelled one more time in MasterCAM to determine all tools to be used for milling and their paths. Unfortunately, due to the lack of qualified for milling Arcada's personnel for milling, it was impossible to accomplish the reactor's manufacturing.

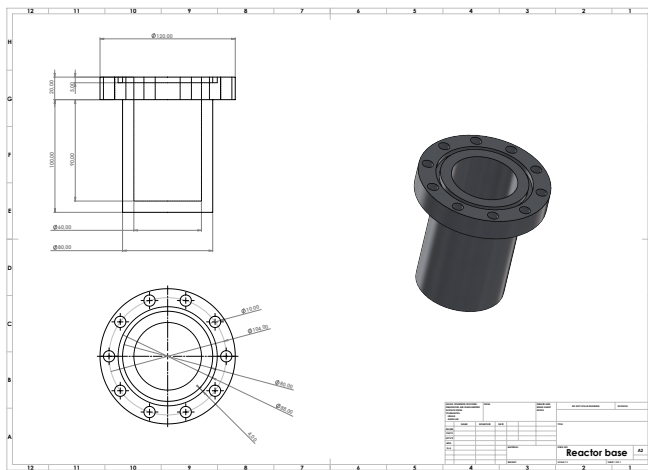


Figure 27. Reactor's base drawing (2020).

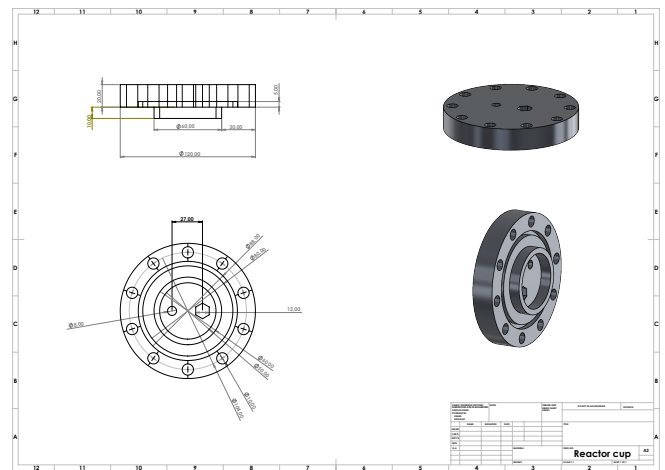


Figure 28. Reactor's cup drawing (2020).

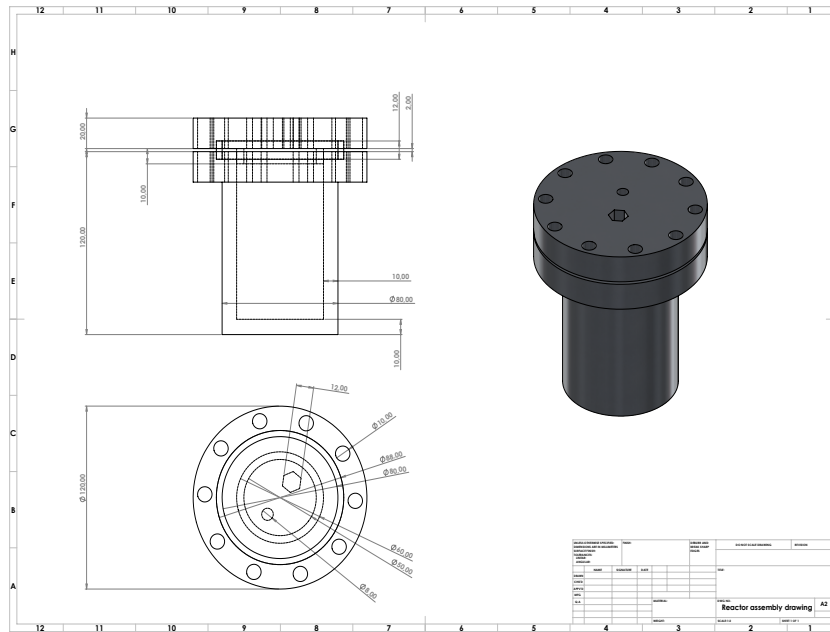


Figure 29. Reactor's assembly drawing (2020).

- **An attempt to improve another reactor and heating element**

After the failure of manufacturing the new reactor, it was decided to use another reactor Arcada already had. However, the other reactor's seal located between the lid and the base of the reactor had to be made, as the original one was made out of plastic and would melt during the heating process. Similar to the original form, a new seal was designed using SolidWorks software and ordered to be produced out of copper from eMachineShop.

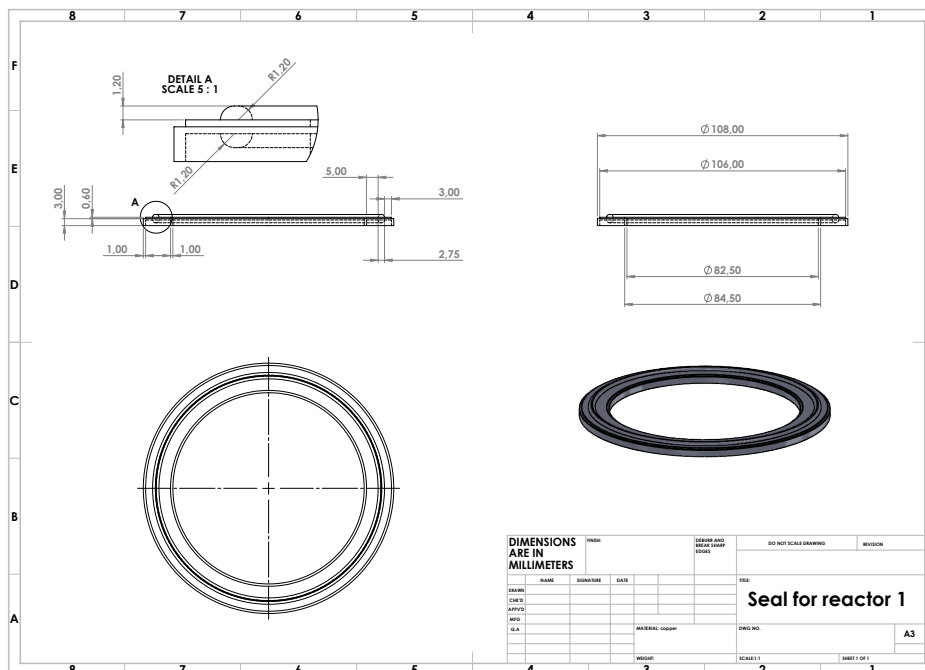


Figure 30. Drawing of a new seal (2020).



*Figure 31. Manufactured seal (2020).*

Once the new copper seal had arrived, it was assembled with the reactor and tested using a pressure gauge. It appeared, that the seal alone was not able to keep the pressured air inside the reactor, easily leaking all of it. Therefore, two rings were cut out of the aluminium foil and placed on the top and on the bottom of the seal. This time, pressured air at about 5 to 7 bars stayed inside the reactor much longer. It was assumed that under the high temperature, aluminium foil will expand, blocking most of the gaps and preventing major leakages. To prove the following assumption, calculations based on the thermal expansion of the solid materials were made.

The volumes of the steel reactor, copper seal and aluminium seal were calculated roughly as 114472mm<sup>3</sup>, 6000mm<sup>3</sup> and 111,9mm<sup>3</sup> respectively by using the formula for calculating the volume of the hollow cylinder, which is  $V = \pi \times h \times (R^2 - r^2)$ , where  $\pi$  is equal to 3.14,  $h$  is a height,  $R$  is an external radius and  $r$  is an internal radius (Engineers Edge, 2020).

Coefficient of volume expansion of steel, copper and aluminium were found to be  $35 \times 10^{-6}$ ,  $51 \times 10^{-6}$  and  $75 \times 10^{-6}$  respectively. The formula for the volume expansion is  $\Delta V = \beta \times V \times \Delta T$ , where  $\beta$  is a coefficient of volume expansion,  $V$  is a volume and  $\Delta T$  is a temperature difference. (Lumen Learning, 2020). Therefore, volume expansions of the steel reactor, copper seal and aluminium seal at the temperature of 500°C are 2376mm<sup>3</sup>, 143mm<sup>3</sup> and 3.9mm<sup>3</sup> or 2%, 2.3% and 3.4% of their initial volume respectively. As it follows from the calculations, two aluminium seals are supposed to expand the most, improving reactor's hermetic properties.

However, a new reactor was bigger than the one used during previous experiments and would not fit in the original, now repaired, furnace. Therefore, the heating procedure had to be changed. This time, instead of placing the reactor into a furnace, a special heating element was modelled

according to the new reactor’s dimensions and ordered to be manufactured from Henan Synthe Corporation.

The idea of the heating element usage was also better for the safety reasons – being not surrounded by the hot air, unexpected ethylene leakages would less likely cause ethylene autoignition, unlike when the reactor was inside the furnace.

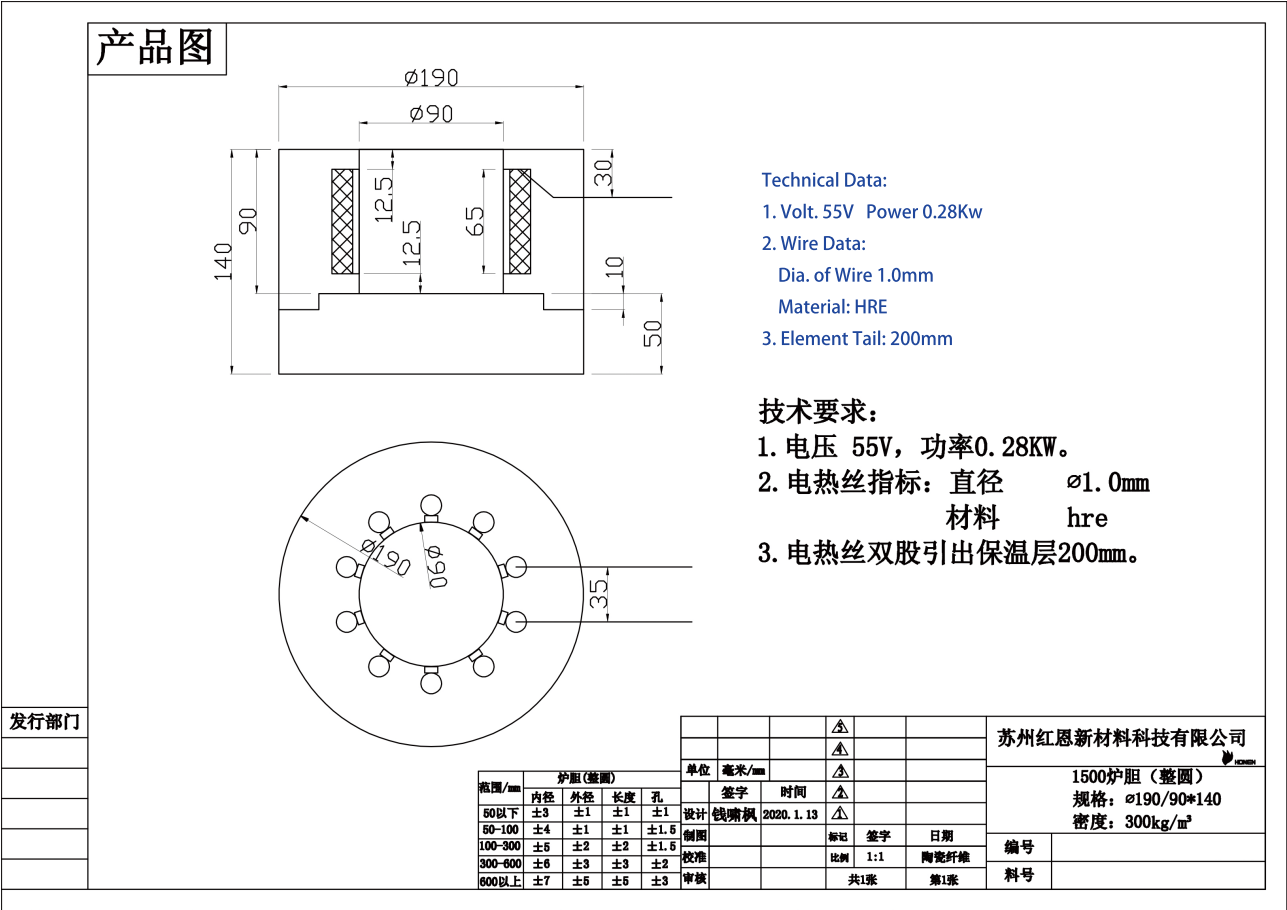


Figure 32. Drawing of the ordered heating element (2020).

Unfortunately, due to the COVID-19 coronavirus disease started at the beginning of 2020 in China, most of the Chinese manufacturers were forced to stop or slow down their production (Bradsher, 2020). Therefore, the arrival of the new heating element was postponed for two months. Due to the lack of time and inability to wait for the delivery, another heating element was found in Arcada’s laboratory, which had almost the same dimensions as the new reactor. The new heating element was checked carefully. It appeared it was working fine, however, no temperature control option was available. The maximum temperature of the heating element was stated to be 1000°C, which was twice as much as the experiment needed. It was not possible to use it without adjusting

the temperature. To do so, it was decided to use one of external temperature controllers plenty of which happened to be in Arcada's laboratory. Also, a high-temperature thermocouple was ordered.

Once the controller and thermocouple were ready to be used, a performance of the heating element and controller itself was checked. For that, two thermometers were inserted into the heating element in addition to the controller's thermocouple. Heating element's temperature limit was set up to 200°C. Once the heating process started, all data from two thermometers and controller were recorded carefully every minute. Later, the controller's temperature values were subtracted from the average temperature of the thermometers at every point of time and a graph was plotted. It appeared to be that, on average, the actual heating element's temperature was 63.95°C higher than the controller was showing. Therefore, during the future experiments, temperature limit on the temperature controller was needed to be set up according to the formula: *desired temperature* – 63.95°C.

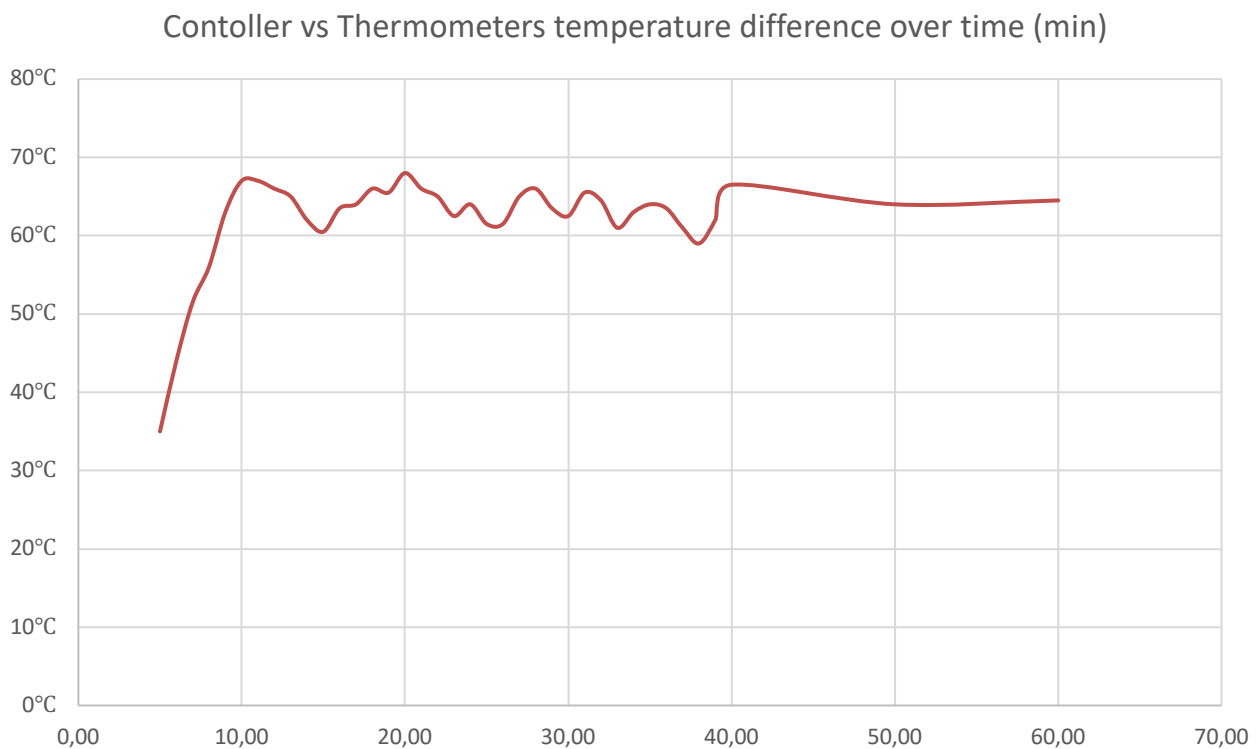


Figure 33. Temperature difference (2020).

At the same time, improvements to the new reactor continued. A Swagelok valve on the lid of the reactor was changed to a newer one. Also, another special Swagelok pipe connector between the reactor and the pipe, leading to the water column, was ordered from Swagelok.

## 4.1. List of the new equipment

Eventually, to perform new experiments, the following equipment was chosen: one heating element, one temperature controller for the heating element, an additional thermocouple, one reactor with one copper and two aluminium seals, two water columns, a nitrogen gas bottle and a few Swagelok pipes, connectors and valves.



*Figure 34. Arcada's heating element (2020).*



*Figure 35. Heating element with reactor (2020).*



*Figure 36. Temperature controller (2020).*

The overall setup was quite similar to the one used during the first three experiments. Following the nitrogen flow, ethylene formed in the reactor was supposed to go to the water columns via steel pipes. The final pipe of the system was inserted into the water tank to monitor the stability of the gas flow. A thin gap between the reactor and the heating element's inner walls was filled with sand, borrowed from the nearest kindergarten's sandbox.

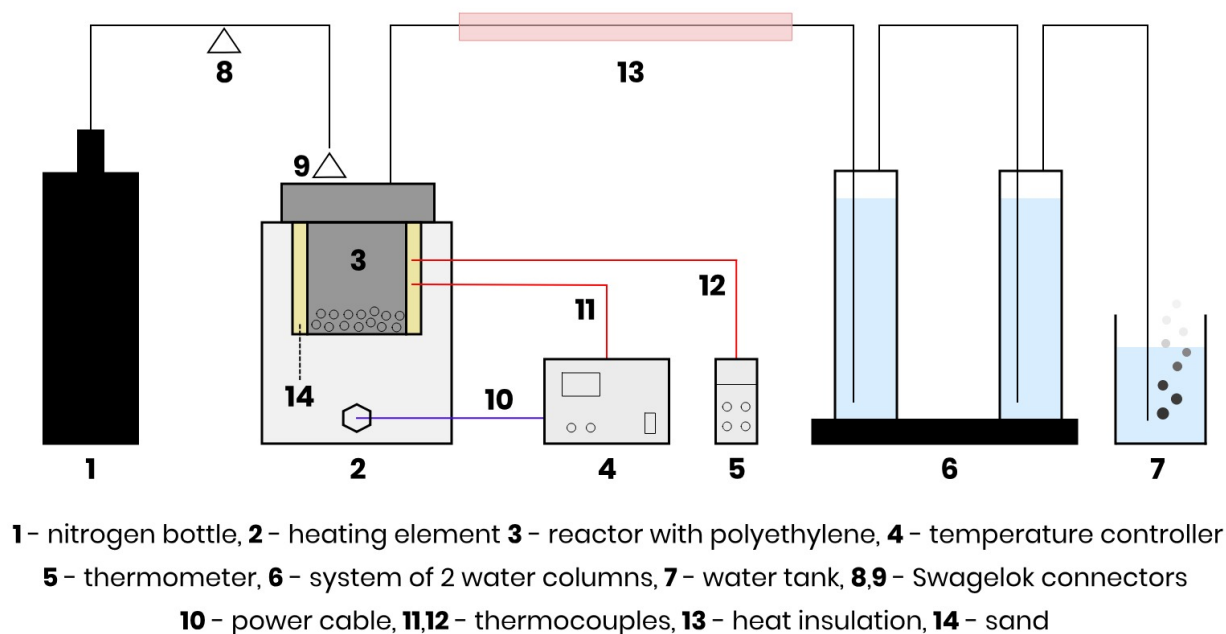


Figure 37. Schematic drawing of the setup for the 4<sup>th</sup> experiment (2020).

## 4.2. New experiments

- **Experiment #4 (i.e. LDPE 3.0)**

The fourth experiment was held on March 16<sup>th</sup>, 2020 at 13.20. The setup was put inside the fume cupboard and assembled. Both water columns were filled with 600 mL of deionised water. 50 g of LDPE was put into the reactor. The temperature limit on the controller was set to 436°C. After 6 minutes of the constant nitrogen flow, heating was turned on. At 13.51, when both the temperature controller and the thermometer showed 460°C, white smoke was noticed at the last output of the system indicating the beginning of reaction inside the reactor. At 13.58 thermometer showed 517°C; white smoke continued coming from the last pipe; connectors between the reactor and the water column's pipe started to leak unknown transparent liquid and white steam. At 14.00 nitrogen flow

became unstable, the thermometer showed 534°C. It was decided to unplug the heating element to prevent overheating and possible ignition. At 14.15 the leakage between the reactor and the pipe stopped, nitrogen flow became stable again. At 14.30 the temperature controller, thermometer and nitrogen bottle were unplugged. The unknown liquid was collected from the lid of the reactor. After disassembling the system, liquids from both water columns were observed to have a strong petrol oil smell. The first water column had a lot of white waxy substance inside. The second one had almost none, although water there became very cloudy. Inside the reactor 12 g of molten LDPE was found. The liquid collected from the lid of the reactor into the plastic jar solidified immediately.



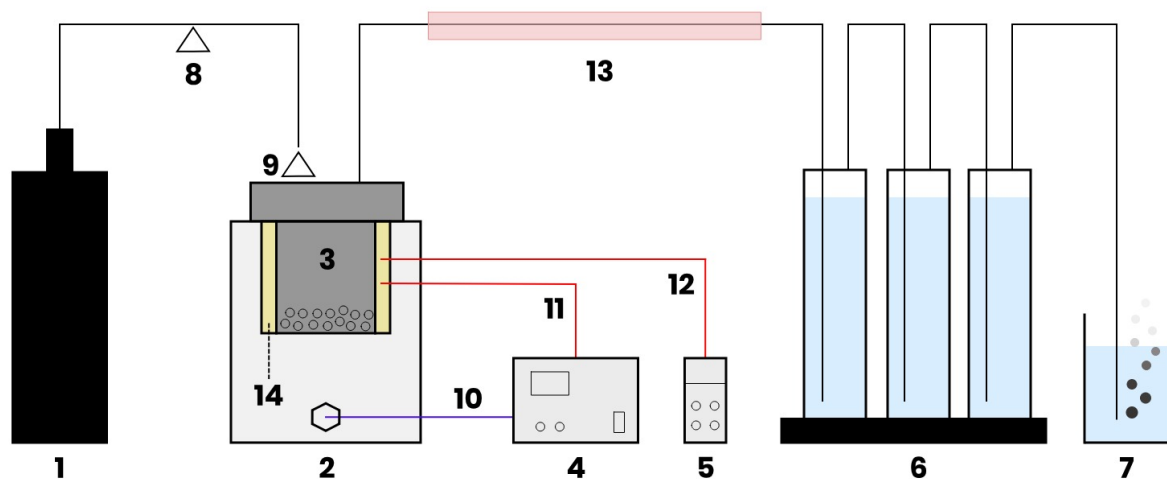
*Figure 38. Unknown liquid leaking to the lid of the reactor (2020).*

- **Experiment #5 (i.e. LDPE 4.0)**

The fifth experiment was made on the next day after the fourth one. This time three water columns instead of two were used to increase time and possibility of ethylene and water reaction. What is more, Teflon tape was applied to the connectors between the reactor and the water column's pipe (at the connection which was leaking during the previous experiment). Each column was filled

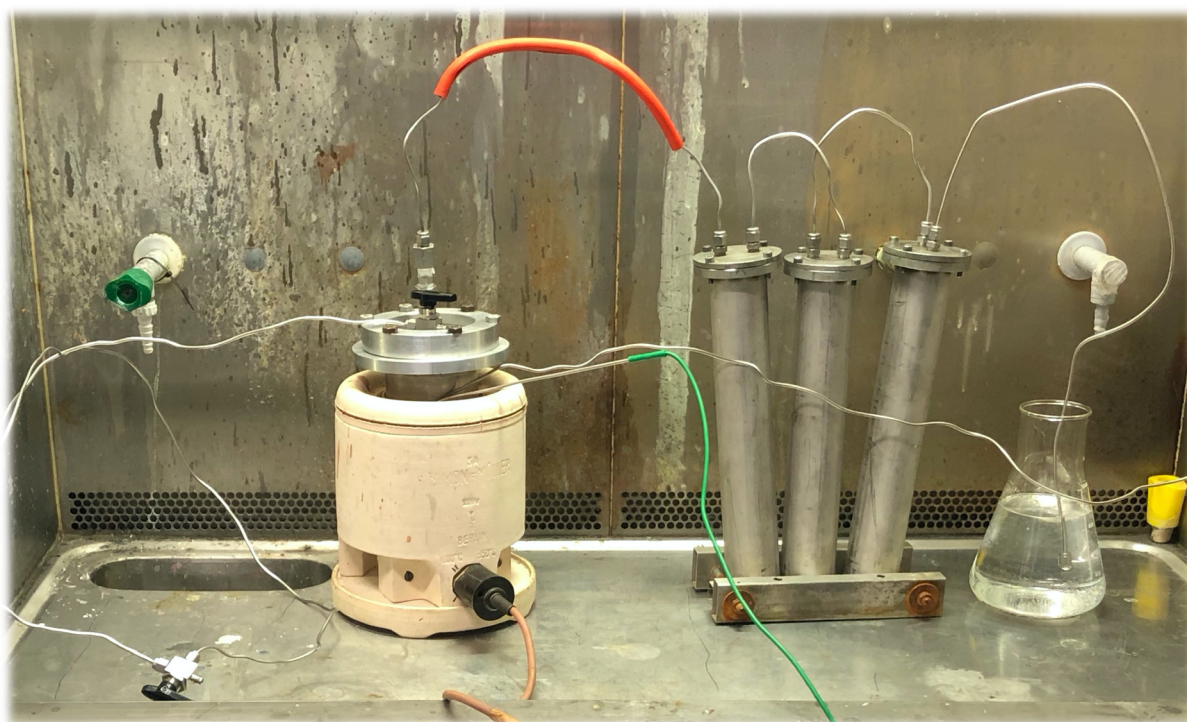
with 600mL of deionised water. 50g of LDPE was put into the reactor. This time, the temperature limit at the temperature controller was gradually increased during the heating to avoid unexpected overheating acquired during the previous experiment. At 9.56 am nitrogen bottle was opened and at 10.00 heating started. At 10.15, when the thermometer showed 319°C (or 299°C according to the controller), nitrogen flow became unstable. Instability and gaps in the gas flow kept happening until 10.26 (455°C according to the thermometer), when the nitrogen pressure was increased, and white smoke started to come from the system's last pipe. At 10.33 (509°C according to the thermometer) gas flow became stable again and nitrogen pressure was decreased; white steam started to come from the connector with the Teflon tape, however, this time no liquid was noticed. Between 10.35 and 10.53 gas flow was changing from stable to unstable and back, the temperature has fluctuated between 488°C and 512°C. Nitrogen pressure was regulated according to the system's behaviour. White steam kept leaking from the same connectors in a tolerable amount.

At 10.54 a lot of smoke started to come from the area of the heating element and the gas flow stopped completely. It was impossible to understand whether leakage from the reactor increased or something started to overheat inside the heating element. Considering the experiment was already longer than the previous one (with the same amount of LDPE) and to prevent possible ignition, the heating element and controller were unplugged. Swagelok #8 (Figure 39) was switched to an opened gate and the nitrogen bottle was then shut. Swagelok #9 (Figure 39) was also switched to an opened gate to release pressure from the reactor. A lot of white steam came out. Liquids from all three water columns were collected. All of them had the same oil smell. The first column was filled with the same waxy substance. The second one had about twice less of it. The third one had almost none.



1 - nitrogen bottle, 2 - heating element 3 - reactor with polyethylene, 4 - temperature controller  
5 - thermometer, 6 - system of 3 water columns, 7 - water tank, 8,9 - Swagelok connectors  
10 - power cable, 11,12 - thermocouples, 13 - heat insulation, 14 - sand

*Figure 39. Schematic drawing of the setup for the 5<sup>th</sup> experiment (2020).*



*Figure 40. 5<sup>th</sup> experiment setup (without nitrogen bottle, thermometer and controller) (2020).*

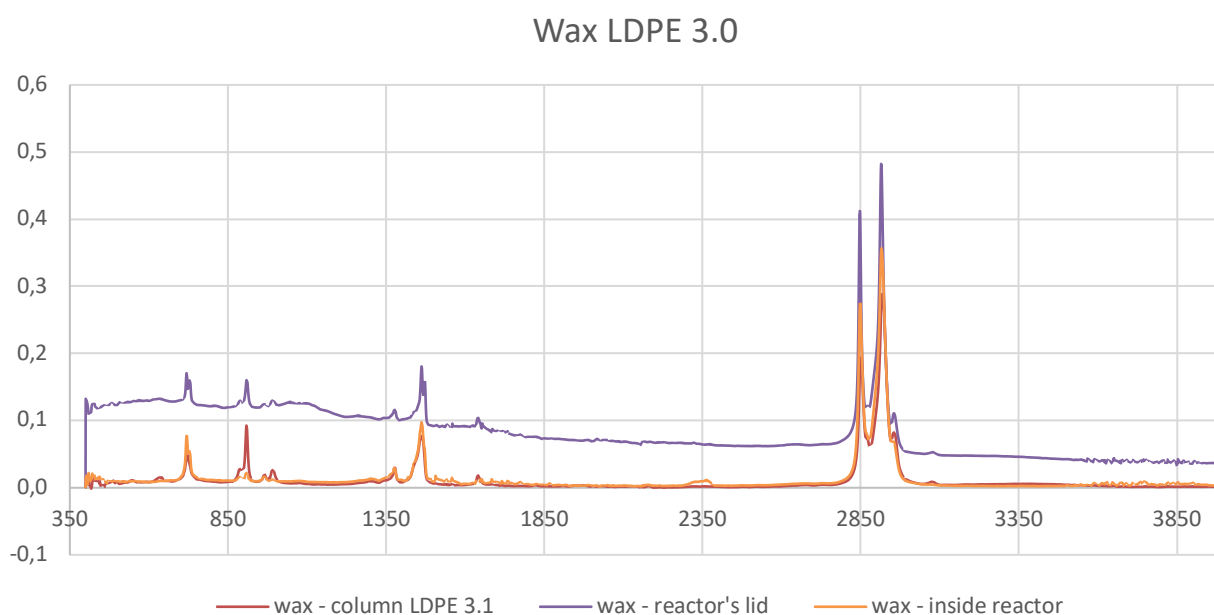
### 4.3. New analyses

Due to the COVID-19 pandemic, from 18.03.2020 Finland closed all the schools and universities. That meant, no time for the further experiments was left. Every water solutions and waxy substances from the fourth and fifth experiments had to be tested as soon as possible, while Arcada's laboratory was still accessible, to be able to analyse received data. The fastest and the easiest way to perform analyses was once again FTIR spectrometry.

All tests were divided into two groups – analyses of waxy substances and analyses of the liquid solutions from every water column.

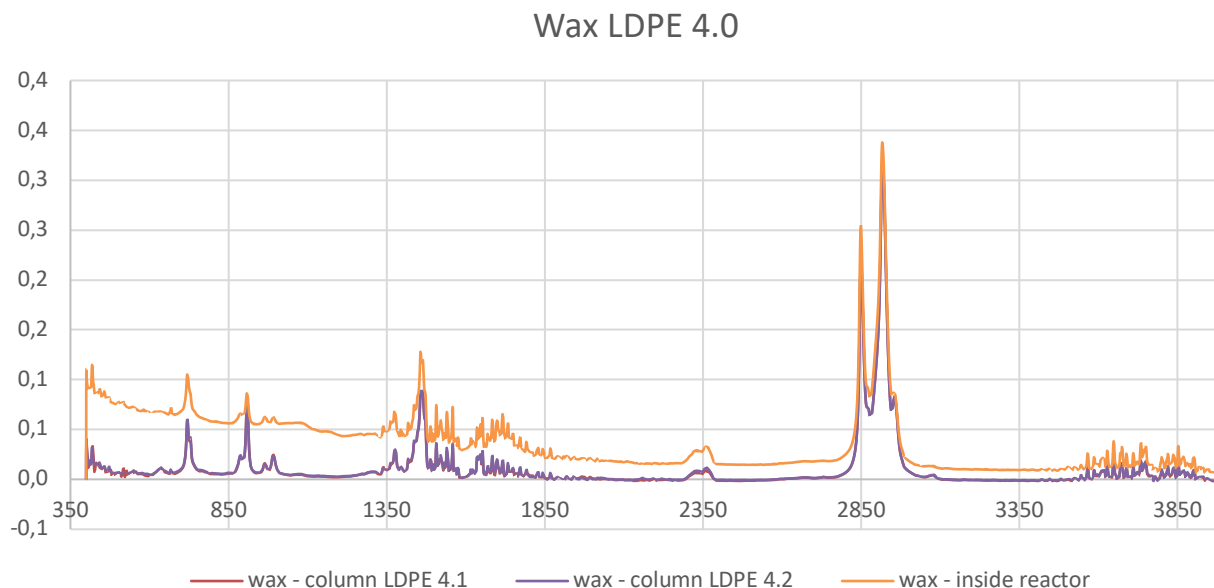
- **Wax analyses**

From the fourth experiment three waxy substances were available – leftovers of the LDPE in the reactor, solidified liquid leaked to the lid of the reactor and what was found in the first water column (i.e. LDPE 3.1). Every FTIR spectrum was measured over the region from  $400\text{cm}^{-1}$  to  $4000\text{cm}^{-1}$  and absorbance was recorded. Received data was collected, transferred into an Excel software and three graphs combined in one were plotted. It appeared, that the all the substances had similar peaks – at  $\sim 2916\text{cm}^{-1}$ ,  $\sim 2848\text{cm}^{-1}$ ,  $\sim 1463\text{cm}^{-1}$ ,  $\sim 912\text{cm}^{-1}$  and  $\sim 730\text{cm}^{-1}$ , which corresponded to various C-H bonds and identified FTIR spectra of low-density polyethylene (Doğan & Kayacan, 2008, p. 396).



*Figure 41. FTIR graph of wax substances from LDPE 3.0 experiment (2020).*

The same analyses have been made with the wax from the last experiment. This time, substances found in the reactor, first water column (LDPE 4.1) and second water column (LDPE 4.2) were tested.



*Figure 42. FTIR graph of wax substances from LDPE 4.0 experiment (2020).*

The results appeared to be almost identical with the previous ones, except clearer peaks at  $\sim 2350\text{cm}^{-1}$ , indicating the presence of  $\text{O}=\text{C}=\text{O}$  bonds in the compound (Libretexts, 2020). That meant low-density polyethylene underwent oxidation process during the experiment. As oxidation, obviously, requires oxygen, the question was where the oxygen came from. Three main suggestions were made – an impurity of  $\text{N}_2$  gas, an impurity of polyethylene and oxygen leaking into the reactor. However, during the first three experiments, the same polyethylene and  $\text{N}_2$  gas were used (although, this time the amount of LDPE was almost ten times higher) and no  $\text{O}=\text{C}=\text{O}$  peaks were noticed. Unfortunately, it was impossible to perform analysis of the solid LDPE granules used for the experiment, as Arcada was shut down due to COVID-19. The logical option left is the leakage of oxygen into the reactor. A lot of white smoke appeared during the fifth experiment might be explained by the presence of oxygen inside the reactor, causing not only smoke but oxidation as well. Indeed, the leftovers of LDPE inside the reactor was found to be dark, “burned” colour, proving earlier suggestion.

Oxidised ethylene (or oxidised polyethylene wax) is used widely, for example, as a slip agent. Also, it is an authorised food additive E914. It is used for the surface treatment of most citrus fruits, where the peel is usually not eatable. (Oskarsson, 2015 p. 2). Comparing properties of oxidised ethylene and waxy substance received during the experiments many similarities were found.

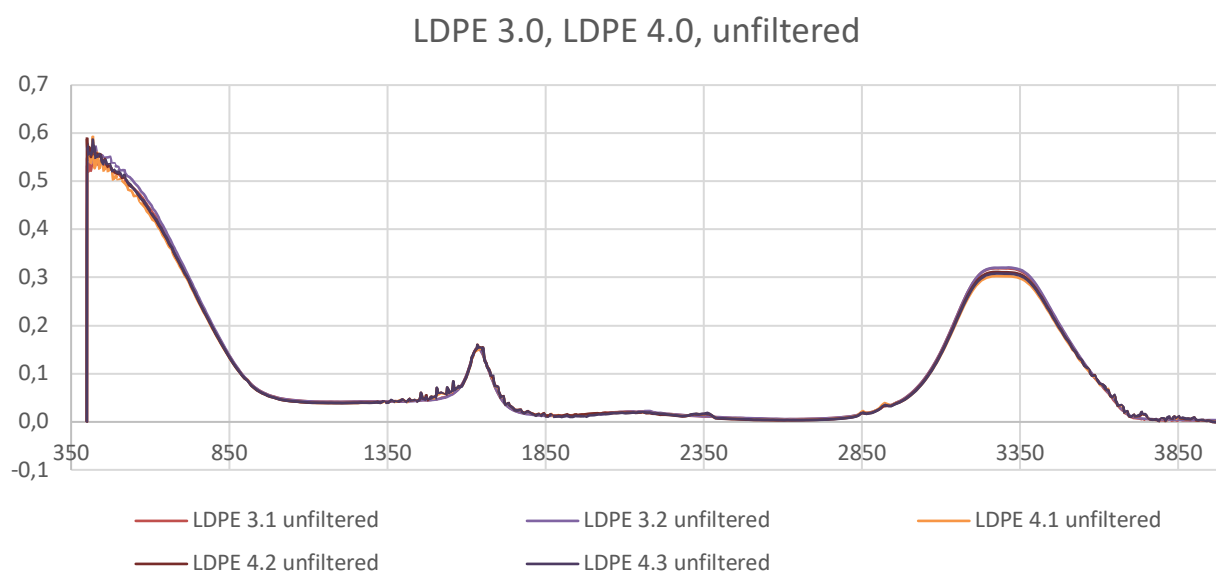
- **Liquids analyses**

Liquids from every water column were collected and named according to the experiment's number and column's number. For example, LDPE 3.2 refers to the second water column of LDPE 3.0 experiment.

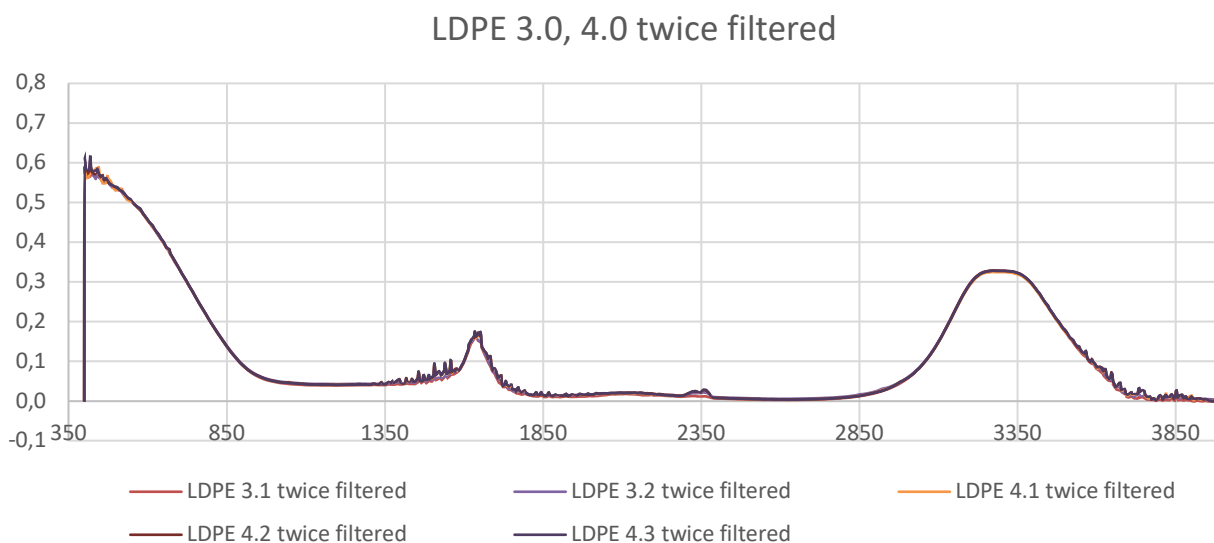
FTIR spectrums of every liquid were plotted on the same graph. All the curves were almost identical, following the same path. Similar to all the previous analyses, two big peaks at  $\sim 3300\text{cm}^{-1}$  and  $\sim 1650\text{cm}^{-1}$  clearly indicated water.

In addition to the standard “water peaks” and identified earlier  $\text{O}=\text{C}=\text{O}$  peaks ( $\sim 2350\text{cm}^{-1}$ ), smaller peaks at the region between  $\sim 2850\text{cm}^{-1}$  and  $\sim 2960\text{cm}^{-1}$  were noticed. Same peaks might be observed on the spectra of LDPE 3.0 and LDPE 4.0 wax analyses – they indicate C-H bonds. However, it was impossible to say for sure whether those C-H bonds corresponded to the presence of ethanol inside the water solution or to the leftovers of polyethylene. Therefore, all liquids were carefully filtered twice through the paper filters until they became completely transparent. Then, new FTIR analyses were performed.

After filtration C-H peaks disappeared, proving suggestion about their polyethylene origin. Ethanol was not presented in the final solutions.  $\text{O}=\text{C}=\text{O}$  peaks, on the contrary, were noticed again.



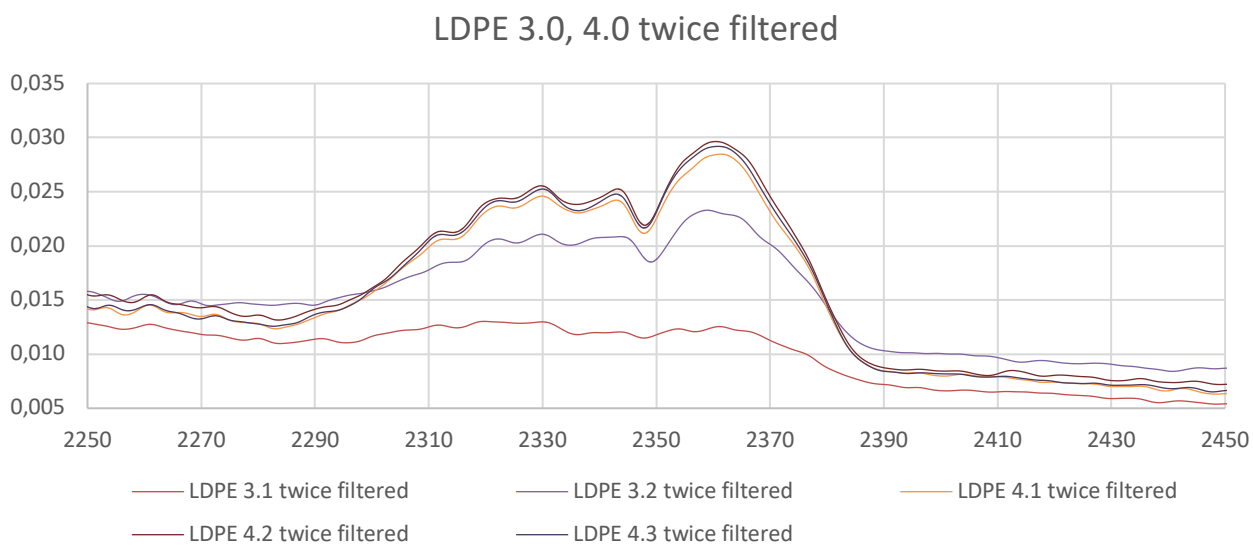
*Figure 43. FTIR graph of unfiltered liquids from LDPE 3.0, LDPE 4.0 experiment (2020).*



*Figure 44. FTIR graph of filtered liquids from LDPE 3.0, LDPE 4.0 experiment (2020).*

O=C=O peaks in water indicated higher than normal concentration of CO<sub>2</sub> in water. Usually, CO<sub>2</sub> peaks at FTIR spectra appears because of the instrumental atmospheric conditions, however, during the analyses, all liquids were placed directly onto the ATR crystal. Therefore, this theory of peaks origin was untenable. The probable explanation was that oxidized polyethylene dissolved in water and went through the filtration of the solutions successfully. As proof of this theory, a closer view of the FTIR graph of all filtered liquids in the region between 2250cm<sup>-1</sup> and 2450cm<sup>-1</sup> was used.

It appeared, that the longer ethylene from the reactor reacted with water the higher peaks were. For instance, almost no data was recorded for the LDPE 3.1, while LDPE 3.2 had a clearer peak. The clearest peaks could be observed during the last analyses of LDPE 4.1, 4.2 and 4.3. Presumably, due to the longer time of the experiment and a bigger amount of oxygen reacted (which is following from the comparison of wax from LDPE 3.0 and wax from LDPE 4.0 analyses).



*Figure 45. FTIR graph of filtered liquids between 2250cm<sup>-1</sup> and 2450cm<sup>-1</sup> (2020).*

## 5. RESULTS OF THE EXPERIMENTS

As the results of the experiments, oxidized polyethylene wax and water with dissolved polyethylene wax were received. Probably, that meant that the processes of pyrolysis and following depolymerisation of polyethylene were done successfully. However, instead of projected hydration of ethylene in contact with water and future obtaining of ethanol solution, presumably, due to unwanted presence of oxygen, ethylene oxidised and formed polyethylene wax.

Alternatively, polyethylene pyrolysed partially to a lower molar mass polymer that was either a gas or liquid at 500°C, but waxy at room temperature and reacted with presented in the system oxygen, forming oxidation products as well.

The results of the experiments correlate with some of the previously researched publications but contradict the others. For example, a strong petrol-like smell and the waxy substances received after every experiment indicate the presence of the fuel-like products. However, the ethylene itself was not among the received substances (or at least it was not found), as it was shown in some of the publications. Presumably, that happened due to the one-step pyrolysis process instead of the two-steps process, described in the publications. Therefore, polyethylene pyrolysis was not completed entirely – although the polyethylene's molar mass was decreased significantly, the cracking process of polyethylene down to the singular ethylene molecules did not happen to any measurable degree.

## 6. DISCUSSION AND CONCLUSION

Results of the theoretical part of the thesis were literature research performed in order to understand how different countries and regions in the world completing waste management and what ways of waste treatment are implemented. A general overview was trying to be delivered, including possible future tendencies. Also, particular waste management methods were described.

Results of the practical part of the thesis could be divided into three parts, corresponding to the goals of the practical part of the thesis, mentioned in the Objectives. For the first and second steps of the practical work – polyethylene pyrolysis and ethylene hydration – two different systems were built. Both systems could perform pyrolysis and hydration at the same time, however, due to accident with the first system, another way of reactor's heating had to be found. Eventually, the first step – pyrolysis of polyethylene – was performed successfully and polyethylene underwent the depolymerisation process, at least to the extent that the pyrolysis product has a sufficiently low molar mass that it was transported as a gas or aerosol at the reactor temperature. The results of the second step, however, was not achieved. Any ethylene generated did not hydrate in water to form ethanol.

Instead, it reacted with oxygen, forming polyethylene wax. That happened due to the technical issues of the used equipment. For the purity of the experiment, it was necessary to assemble the system with no presence of oxygen inside. However, creating a gas-tight system – unlike, for example, liquids – is more challenging, especially when using and modifying equipment which is not supposed to be used for such purposes. Therefore, the first attempts led to the ignition of the system and significantly slowed down future work. What is more, it is believed, that the amount of polyethylene used for pyrolysis was too little to create enough ethylene to react with water to yield measurable quantities of ethanol. The third step – analyses – were performed as planned. All products received during the experiment were examined using UV spectroscopy or/and FTIR spectroscopy. The data collected made it possible to make suggestions of how the process went, helped to make changes in the experimental setup and gave eventual results of the experiments. Here, however, should be added, that it was impossible to collect and analyse the nitrogen gas going through the system in case it would have contained something else than just N<sub>2</sub>. Perhaps, if a gas chromatography would be used as a part of the analyses, more theories of why ethylene did not react with the water (and was it presented in the system at all) could have been made. Unfortunately, due to the lack of the access to the gas chromatograph, following analyses could not be done.

As for recommendations for future similar experiments, it should be suggested to try to implement two-steps pyrolysis process to divide heating rates and temperatures according to the publications mentioned in the section 2.3. Another strong recommendation is to collect any gases coming out of the system for the better understanding of the ongoing process inside the system during the pyrolysis. Here, for example, gas chromatography could be implemented to analyse gaseous products of the pyrolysis.

The general conclusion of the thesis is that plastic waste and polyethylene, in particular, must be treated as a valuable source of basically free material (or energy) for many purposes. Although, it was not possible to convert polyethylene into ethanol during this work, even unwanted material – polyethylene wax – could be used for various purposes, such as a slip agent, mould release agent or even food additive.

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