



Universität für Bodenkultur Wien

Rating of fuels produced by pyrolysis of decentralized plastic waste

Master thesis

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Abstract

Increasing production of plastic products causes many problems like accumulation of plastic in landfills and environmental problems. High workload of plastic recycling make plastic recycling less sustainable. (ANUAR et al., 2016)

An alternative to recycling and burning of plastic is pyrolysis of plastic. At this process the waste plastic is heated to several hundred degrees Celsius at anaerobic conditions, which leads to a degradation and depolymerization of plastics (MARTENS, 2011).

In this master thesis, the pyrolysis products of plastic mixtures (PP, LD-PE, HD-PE, PVC, PUR, PET and PS) and of sea plastic are evaluated. The plastic samples are pyrolyzed at different pyrolysis temperatures between 344 °C and 615 °C in a batch reactor. The aim is to optimize the production of fuel-like products.

Pyrolysis temperatures under 400 °C do not lead to a satisfying yield and the product itself is not fuel-like. At a pyrolysis temperature of about 400 °C and upwards a solid and high boiling product fraction is produced, which can block pipes and vessels. With increasing pyrolysis temperature this product fraction is more and more degraded. The analysis of density, pour point, flash point and distillation characteristics show that the characteristics of the pyrolyzed plastic mixture become more similar to the characteristics of petrol and diesel the higher the pyrolysis temperature is. The products of the pyrolysis experiments are waxy and pasty and need to be distilled to get a fuel-like product. The distillation characteristics show that after pyrolysis of the plastic mixture at 615 °C and distillation at 250 °C a total product yield of 41.6 % (w/w) purified oil can be expected in a batch system. The actual pyrolysis product after distillation is fuel-like, transparent and clear and does not contain visible impurities.

Kurzzusammenfassung

Die steigende Produktion von Kunststoffen verursacht viele Probleme wie die Ansammlung von Kunststoffen in Mülldeponien und Plastikmüll in der Umwelt und den Weltmeeren. Der hohe Arbeitsaufwand beim Kunststoffrecycling senkt die Nachhaltigkeit des Recyclings von Kunststoffen. (ANUAR et al., 2016)

Eine Alternative zum Recycling und zum Verbrennen von Kunststoffen ist die Pyrolyse von Kunststoffen. Bei diesem Prozess wird der Altkunststoff auf mehrere hundert Grad Celsius unter Ausschluss von Sauerstoff erhitzt, wobei es zu einem Abbau und einer Depolymerisation kommt (MARTENS, 2011).

Bei dieser Masterarbeit werden die Pyrolyseprodukte von Kunststoffgemischen (PP, LD-PE, HD-PE, PVC, PUR, PET und PS) und von Meeresplastik bewertet. Die Kunststoffproben werden bei verschiedenen Temperaturen zwischen 344 °C und 615 °C in einem Batch-Reaktor pyrolysiert. Das Ziel der Masterarbeit ist es, die Produktion von treibstoffähnlichen Produkten zu optimieren.

Pyrolysetemperaturen unter 400 °C führen zu keiner zufriedenstellenden Ausbeute und das Produkt ist als Treibstoff ungeeignet. Bei einer Pyrolysetemperatur von 400 °C und höher entsteht eine feste und hochsiedende Produktfraktion, welche zu Verstopfungen in den Rohren und Ventilen führen kann. Mit steigender Temperatur wird diese Fraktion jedoch zersetzt. Die Analyse von Dichte, Erstarrungspunkt, Flammpunkt und Destillationsverlauf zeigen, dass sich die Eigenschaften des pyrolysierten Plastikgemisches bei steigender Pyrolysetemperatur den Eigenschaften von Benzin und Diesel annähern. Da die Pyrolyseprodukte wachsartig und pastös sind, müssen sie destilliert werden um treibstoffähnliche Produkte zu erhalten. Laut dem Destillationsverlauf kann man bei einem Batchsystem nach einer Pyrolyse bei 615 °C und einer anschließenden Destillation bei 250 °C mit einer absoluten Produktausbeute von 41,6 % (m/m) reinem Öl rechnen. Das Pyrolyseprodukt ist nach der Destillation treibstoffähnlich, transparent, klar und enthält keine sichtbaren Verunreinigungen.

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1 Introduction

Worldwide 72 % of plastic packages are not reused, 40 % are deposited in landfills and 32 % are released uncontrolled into the environment and the sea. Estimates range from 4.8 to 12.7 million tonnes plastic that land in the sea. There it causes great damages on the environment and the marine fauna. (WWF DEUTSCHLAND, 2017)

Plastic has many advantageous properties that make it indispensable for our society and a complete reduction of the production of plastic is not possible. Due to oxidation and degradation plastic can not be recycled infinitely (Martens, 2011). This makes waste plastic an infinitely available source of raw materials and energy. Therefore sustainable solutions for the handling of waste must be found. Austria already reuses 100 % of the collected plastics as source of raw material or energy and an average of 30 % of PET bottles are produced from recycling material (ALTSTOFF RECYCLING AUSTRIA, 2017).

The pyrolysis of waste plastic is an innovative way to convert waste plastic into a storable, space saving and convenient useable fuel and to increase the value of waste plastic. Further it is a possibility to get decentralized plastic waste like sea plastic back into the raw material cycle.

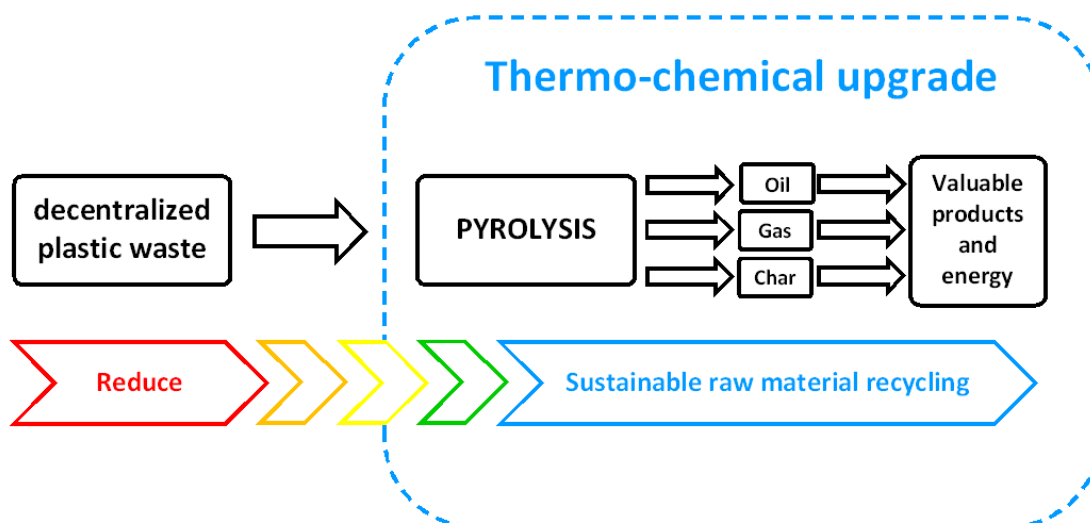


Figure 1 - Integration of pyrolysis of waste plastic in the raw material recycling

1.1 Aim and scope

The aim of this master thesis is the optimization of the process of the pyrolysis of waste plastic to generate high grade fuels.

Therefore different characteristics of fuels are selected and compared with the characteristics of the pyrolysis products of plastic mixtures (PP, LD-PE, HD-PE, PVC, PUR, PET and PS) and of sea plastic, which were produced in the previous master thesis "Pyrolyse von Kunststoffabfällen – Vergleich der Massenbilanz von verschiedener Einsatzstoffe" by Angelika Pausweg (PAUSWEG, 2017). A concept for the determination of these characteristics is made and the characteristics of the pyrolysis products are determined. The pyrolysis products are evaluated and the parameters of the most promising products are determined to improve the process. Additionally a concept and process parameters for a continuous pyrolysis plant is suggested.

2 Fundamentals and related work

2.1 Plastics

Plastic is widely used group of materials. Main applications of plastics are packaging, building and construction, transportation, electrical and electronic, household goods, agriculture and medical and health. The main advantages of plastics are low density, good thermal and electrical insulating properties and good chemical resistance. Further it is possible to form complex shapes and forms. Some plastics are transparent which makes the production of optical devices possible. The properties of plastics can be modified by adding additives. (PLASTICSEUROPE, 2017) (ELSNER et al., 2012)

The most common plastics used are high-density polyethylene (PE-HD), low-density polyethylene and linear low-density polyethylene (PE-LD), polypropylene (PP), polystyrene (PS), polyvinylchloride (PVC), polyethylene terephthalate (PET) and polyurethanes (PUR). (GEYER et al., 2017)

The worldwide plastics production in 2015 was 322 million metric tons. In 2015 the European plastics demand was 49 million metric tons whereby the mayor part of the used plastics was polypropylene (PP) with 19.1 %, followed by low-density polyethylene (PE-LD) with 17.3 % and high-density polyethylene (PE-HD) with 12.1 %. The rest was polyvinylchloride (PVC) with 10.1 %, polyurethane (PUR) with 7.5 %, polyethylene terephthalate (PET) with 7.1 %, polystyrene (PS) with 6.9 % and others. (PLASTICSEUROPE DEUTSCHLAND e.V., 2016)

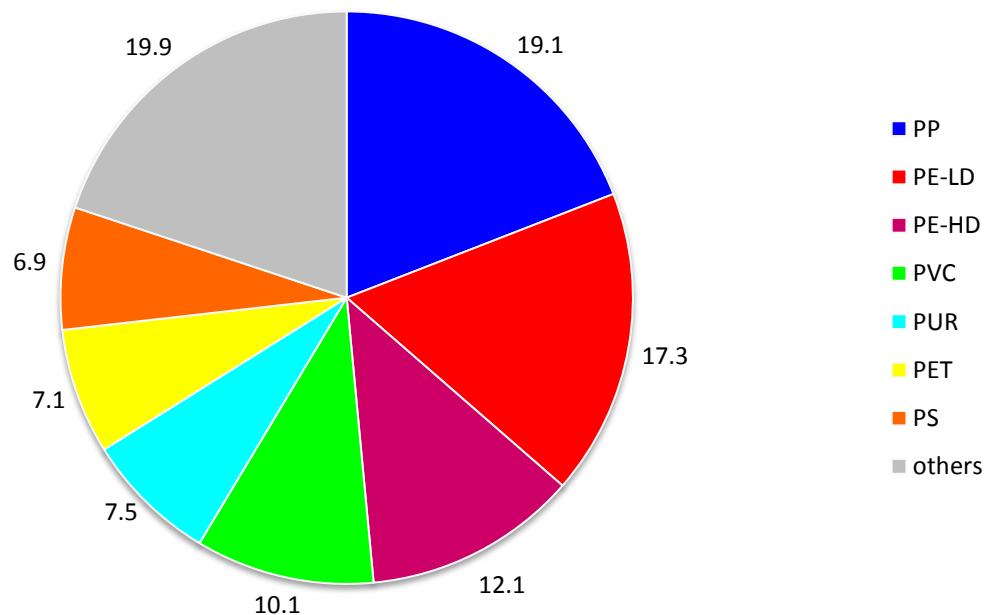


Figure 2 - European plastic demand by polymere type (2015) (PLASTICSEUROPE DEUTSCHLAND e.V., 2016)

2.2 Classification of plastics

Plastics can be divided into **thermoplastics**, **thermosets** and **elastomers**.

Thermoplastics are non-cross linked plastics. Above the melting point thermoplastics become liquid and can be shaped by e.g. injection molding, extrusion or injection blow molding. Examples for thermoplastics are polyolefins like polyethylene and polypropylene.

Thermosets are plastics with an irreversible chemical bond of the prepolymers and a usually high crosslinking density. This leads to a high dimensional stability at high temperatures. Examples for thermosets are technical resins like epoxy resin.

Elastomers are widely chemical cross linked plastics. They are elastic. An example is rubber, which is used in car tires. (ELSNER et al., 2012)

2.3 Properties of the mainly used plastics

2.3.1 Polypropylene (PP)

The global demand for polypropylene was 56.4 million metric tons in 2016 (RESEARCH AND MARKETS, 2017). Polypropylene has a lot of beneficial characteristics. The most important are low density, high melting point, low stress cracking sensitivity, easy to process, food grade and sterilizability. Therefore it is often used as packaging material especially for foods, as sweet and snack wrappers and as microwave-proof containers. Further it is used in automotive parts, pipes and other consumer sector. (ELSNER et al., 2012) (PLASTICSEUROPE DEUTSCHLAND e.V., 2016)

The molecular structure has a great influence on the characteristics of polypropylene. The molecular structure depends on the used catalysts, polymerisation and compounding. The crystallizability of polypropylene is mainly influenced by different arrangements of the methyl-groups. (ELSNER et al., 2012)

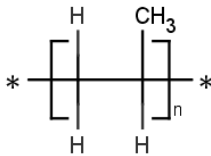


Figure 3 - Structural formula of PP (ELSNER et al., 2012)

Depending on the arrangement of the methyl-groups the polymer is called isotactic polypropylene (iPP), syntactic polypropylene (sPP) or atactic propylene (aPP). Technically most important is isotactic polypropylene. Melting point and density also depend on the crystal modification. The melting temperature of the α -modification is between 185 °C and 220 °C and the density is between 0.850 g/cm³ and 0.936 g/cm³ – 0.946 g/cm³. The melting temperature of the β -modification is between 170 °C and 200 °C. (ELSNER et al., 2012) Polypropylene has a wide melting range, which is caused by the varying chain length of the polymer.

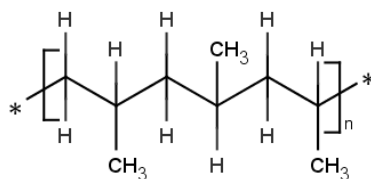


Figure 4 - Structural formula of isotactic PP (iPP) (ELSNER et al., 2012)

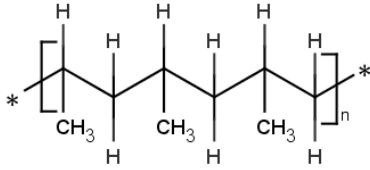


Figure 5 - Structural formula of syndiotactic PP (sPP) (ELSNER et al., 2012)

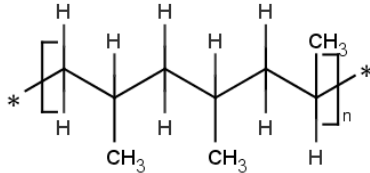


Figure 6 - Structural formula of atactic PP (aPP) (ELSNER et al., 2012)

2.3.2 Polyethylene (PE)

Depending on the production method of polyethylene and thereby the number and length of the side chain branching the density and crystallinity can vary. The characteristics of standard polyethylene are low density, high toughness, tear resistance, low water uptake, low water vapour permeability, good chemical resistance and good electrical properties. (ELSNER et al., 2012)

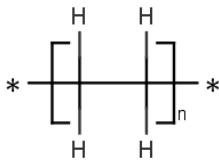


Figure 7 - Structural formula of PE (ELSNER et al., 2012)

2.3.2.1 Low-density polyethylene (PE-LD)

Low-density polyethylene (PE-LD) has a density between 0.915 g/cm³ and 0.935 g/cm³ and a melting temperature between 105 °C and 115 °C. PE-LD is mainly used for the production of films like carrier bags, shrink films, agricultural films and laminating and coextrusion films in multilayer films. Further it is used for food packaging, as containers, trays and coating material for wires and pipes. (ELSNER et al., 2012) (PLASTICSEUROPE DEUTSCHLAND e.V. 2016)

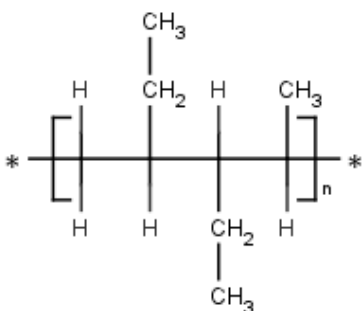


Figure 8 - Structural formula of branched PE (PE-LD) (ELSNER et al., 2012)

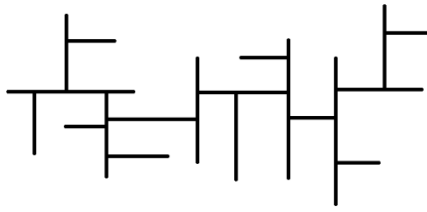


Figure 9 - Schematic representation of PE-LD (ELSNER et al., 2012)

2.3.2.2 High-density polyethylene (PE-HD)

High-density polyethylene has a density between 0.94 g/cm³ and 0.97 g/cm³ and a melting temperature between 128 °C and 136 °C. PE-HD is preferable used for the production of injection molded articles like toys and household articles. Further milk and shampoo bottles, plastic barrels, garbage bins and pipes. (ELSNER et al., 2012) (PLASTICSEUROPE DEUTSCHLAND e.V., 2016)

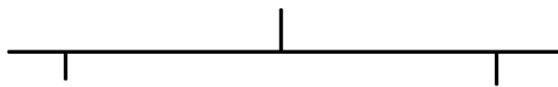


Figure 10 - Schematic representation of PE-HD (ELSNER et al., 2012)

2.3.3 Polyvinylchloride (PVC)

Polyvinylchloride is the third most common plastic after PE and PP with a global production of 32 million metric tons per year. The properties of PVC are high mechanical stability, strength and hardness, transparency, good electrical properties and chemical resistance. It is often used in the building and construction sector for e.g. the production of pipes, window frames, floor coverings and insulations of cables and wires. (ELSNER et al., 2012) (PLASTICSEUROPE DEUTSCHLAND e.V., 2016)

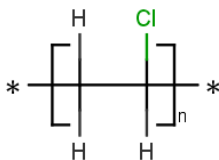


Figure 11 - Structural formula of PVC (ELSNER et al., 2012)

2.3.4 Polyurethane (PUR)

There is a great diversity of polyurethanes and therefore there are also many application possibilities. Most common are elastomers, flexible foams and rigid foams, casting resins, varnishes and adhesives. (ELSNER et al., 2012)

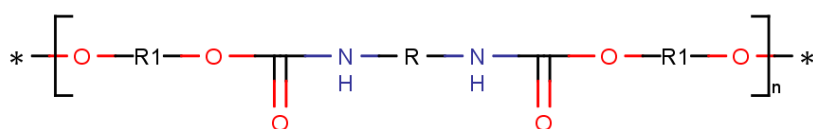


Figure 12 - Structural formula of PUR (ELSNER et al., 2012)

2.3.5 Polyethylene terephthalate (PET)

The world production of polyethylene terephthalate and polyester polymers was about 40 million metric tons in 2010. The density of PET is 1.38 g/cm^3 and the melting temperature is about $255 \text{ }^\circ\text{C}$. The Properties of PET are high transparency, toughness, low water uptake, a hard surface, resistance against stress cracking and good chemical resistance. PET is resistant against weak acids and bases, oils and fats, hydrocarbons, neutral and sour salts, alcohols, ethers and water at room temperature. It is not resistant against strong acids and bases, phenols, hot water and hot steam (hydrolysis). Main applications of PET are fibres and packaging materials like bottles for water, soft drinks and juices. Further it is used for the production of injection molded parts and films. (ELSNER et al., 2012) (PLASTICSEUROPE DEUTSCHLAND e.V., 2016)

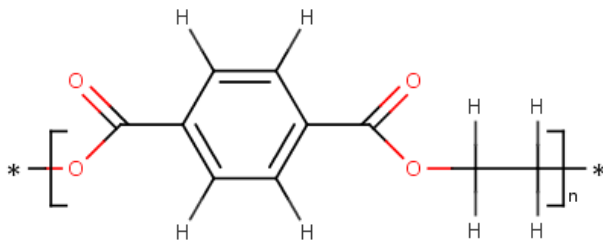


Figure 13 - Structural formula of PET (ELSNER et al., 2012)

2.3.6 Polystyrene (PS)

Polystyrene has a density of 1.05 g/cm^3 and a melting temperature of $270 \text{ }^\circ\text{C}$ (syntactic polystyrene). The properties of PS are rigidity and hardness, transparent and brilliant surface, good electrical and dielectric properties and it is easy to process. The disadvantages of PS are low chemical resistance and stress cracking. It is used as packaging material for foodstuffs like dairy products, beverages, meat, desserts but also for commodities like clothespins, different containers, toys and electrical applications. Foamed polystyrene is for example used as packaging material and insulation material. (ELSNER et al., 2012)

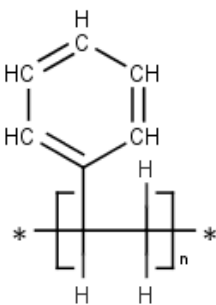


Figure 14 - Structural formula of PS (ELSNER et al., 2012)

2.4 Plastic recycling

Sooner or later, the plastic products will exceed their lifespan and be disposed. There are several ways to use plastic waste as a secondary raw material. In this graphic the different processes of plastic recycling are summarized. (MARTENS, 2011)

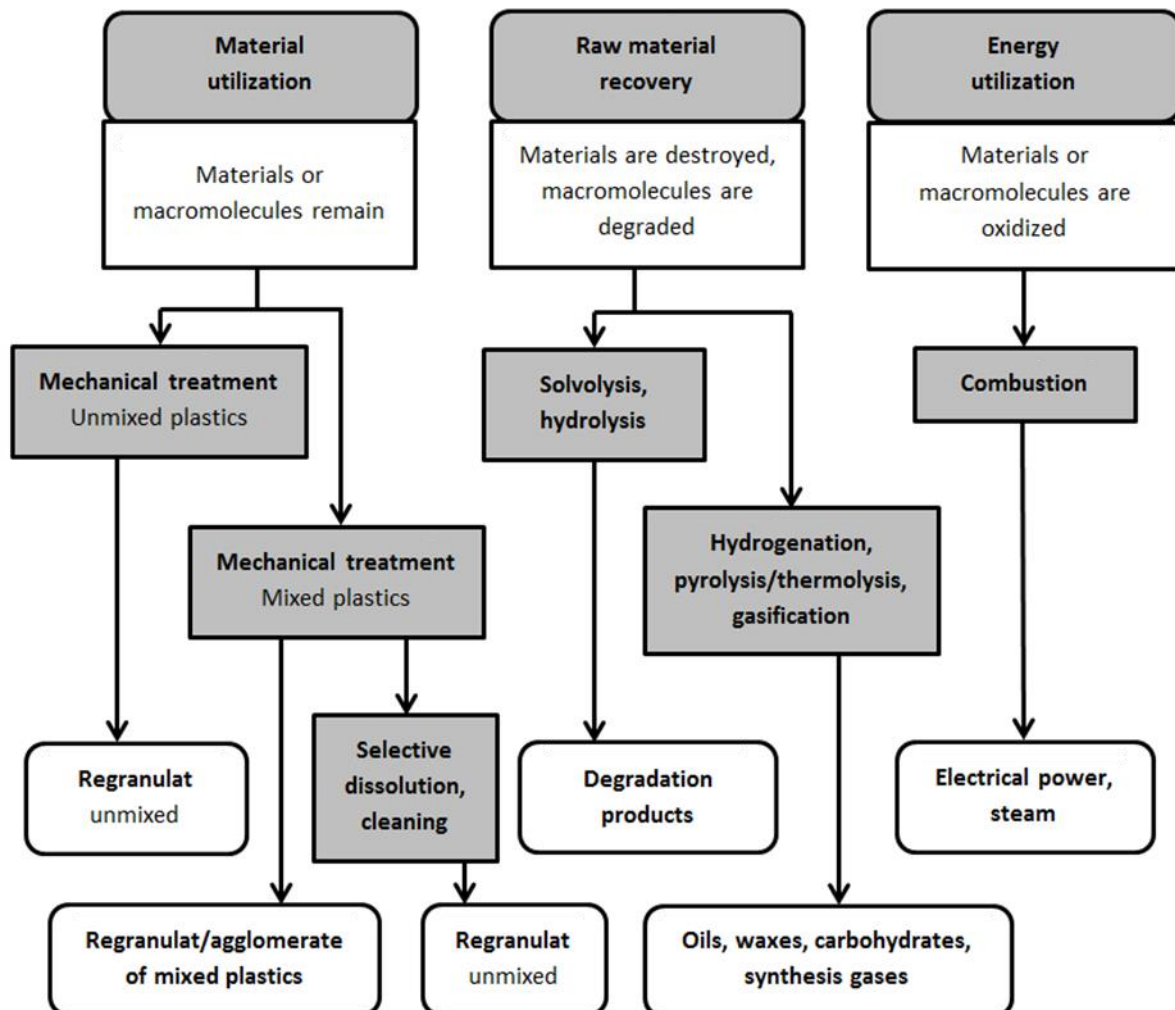


Figure 15 - Processes of plastic recycling (MARTENS, 2011)

2.4.1 Material recycling

At the material recycling macromolecules remain whole. Unmixed plastics only need to be cleaned. Mixed plastics should also be separated. Especially thermoplastics could be simply melted down and poured into shape but there are effects that hinder this form of recycling like oxidative degradation, low miscibility with other types of plastic and impurities which reduce material properties. (MARTENS, 2011)

2.4.2 Raw material recycling

At the raw material recycling the macromolecules are broken down and other forms of raw materials remain, e.g. oils, waxes and synthesis gases. Pyrolysis belongs to this form of recycling. (MARTENS, 2011)

2.4.3 Energy recovery

At the energy recovery the plastic is burned to produce heat and electrical energy (MARTENS, 2011).

2.5 Pyrolysis

In this master thesis pyrolysis was chosen as recycling method. Pyrolysis has several advantages over other processes like material recycling or other raw material recycling methods. Apart from the feedstock, catalysts for accelerating the reaction rate and thermal energy, no raw materials are needed. Because the plastic is evaporated and transformed into other substances, impurities and oxidative degradation of the plastic are less problematic. In contrast to energy recovery, raw materials are formed, which can be used for the synthesis of other substances.

Pyrolysis is a process in which organic substances are decomposed by the use of high temperatures and under anaerobic conditions. The high temperatures lead to depolymerization, to the breaking of chemical bonds and to cracking. Usual pyrolysis temperatures are between 450 °C and 550 °C. Most metals and nonorganic substances remain solid and can be separated from coke easily. (MARTENS, 2011)

Pyrolysis is divided into slow carbonization, slow pyrolysis, fast pyrolysis and flash pyrolysis. Slow carbonization has very low heating rates and residence times of days at pyrolysis temperatures of 450 °C to 600 °C. Slow pyrolysis has heating rates of 10 – 100 K/min and residence times of 10 – 60 minutes at 450 °C to 600 °C. Fast pyrolysis has heating rates up to 1000 K/s and residence times of 0.5 – 5 seconds at 550 °C to 650 °C. Flash pyrolysis has heating rates up to 10 000 K/s and residence times < 1 second at a pyrolysis temperature of 450 °C – 900 °C. (SCHEIRS & KAMINSKY, 2006)

2.5.1 Pyrolysis of plastic

Pyrolysis of plastics is achieved at higher temperatures between 600 and 800 °C. The pyrolysis products are pyrolysis gases, pyrolysis oils and coke. The pyrolysis of plastics at high temperatures lead to a complete decomposition of the plastics and the formation of volatile gases, oils rich in hydrogen and residues poor in hydrogen. The ration of the product fractions depends strongly on the type of plastic. The formation of big amounts of gas and oil is characteristic for the pyrolysis of plastic. These oils can be used for the production of chemical products. (MARTENS, 2011)

2.5.1.1 Pyrolysis of polypropylene (PP)

At 450 °C the highest condensable product yield is observed with a yield of 92.3 % (w/w) and a minimal non-condensable product yield of 4.1 % (w/w). An increasing temperature leads to a decreasing condensable product yield and to the production of low molecular weight products and an increasing gaseous product yield. The coke yield increases with increasing temperature. At 510 °C the condensable product yield is 76.1 % (w/w), the non-condensable product yield is 17.1 % (w/w) and the coke yield is 6.8 % (w/w). (ABBAS-ABADI et al., 2014)

2.5.1.2 Pyrolysis of polyethylene (PE)

At a temperature of 250 °C no cracking of high density polyethylene is observed. At 350 °C the conversion rate is 98.12 % (w/w). At this temperature 80.88 % (w/w) liquid, 17.24 % (w/w) gas and 1.88 % (w/w) residue are observed. At 400 °C the gas yield increases up to 45.29 % (w/w) which leads to a decrease in the oil yield. (AHMAD et al., 2014)

Lower temperatures result into higher char yields. Higher temperatures also decrease oil yields. Most common temperatures for the pyrolysis of PE-HD are between 350 °C and 550 °C. (CZAJCZYNSKA et al., 2017)

The maximal decomposition rate of high density polyethylene is observed at 475 °C (SCHEIRS & KAMINSKY, 2006).

At 350 °C low density polyethylene only melts with a little percentage gas formation of 0.7 % (w/w). At 400 °C a waxy material is formed. The conversion to oil starts at 410 °C with an oily

wax. At 425 °C 89.5 % (w/w) liquid oil is formed and 10.0 % (w/w) gas. Higher temperatures lead to an increased gas yield and decreased oil yield. (ONWUDILI et al., 2009)

2.5.1.3 Pyrolysis of polyvinylchloride (PVC)

At about 200 °C the pyrolysis of PVC starts. The oil yield is with about 5 % (w/w) very low. (MA et al., 2002)

Due to the formation of HCl and harmful chlorinated components such as chlorobenzene and a low oil yield pyrolysis is not suitable for PVC. (CZAJCZYNSKA et al., 2017)

A suitable temperature for dechlorination of PVC is 300 °C. After it is melting 99.5 % (w/w) of Cl in PVC can be removed in form of HCl within a minute. In this experimental setup a gas-liquid fluidized bed reactor was used with hot nitrogen as fluidizing gas. The emitted HCl is carried away immediately by the nitrogen flow. (YUAN et al., 2014)

The maximal decomposition rate of polyvinylchloride is observed at 425 °C (SCHEIRS & KAMINSKY, 2006).

2.5.1.4 Pyrolysis of polyethylene terephthalate (PET)

At 500 °C the solid residue of PET is below 10 % (w/w). The liquid product yield is up to 39 % (w/w) depending on the heating rate and the gaseous product yield is up to 65.12 % (w/w). (CZAJCZYNSKY et al., 2017)

The maximal decomposition rate of polyethylene terephthalate is observed at 400 °C (SCHEIRS & KAMINSKY, 2006).

PET can cause difficulties in the pyrolysis reaction because it can turn the plastic waste into a sludge-like substance due to oxidation reactions (RICARDO-AEA Ltd, 2013).

2.5.1.5 Pyrolysis of polystyrene (PS)

At 300 °C no reaction of polystyrene is observed but at 350 °C the whole polystyrene is converted into highly viscous oil and about 1 % (w/w) char. An increasing temperature leads to an increasing gas and char formation and to a decrease of viscosity of the oil. (ONWUDILI et al., 2009)

The maximal decomposition rate of polystyrene is observed at 355 °C (SCHEIRS & KAMINSKY, 2006).

2.6 Quality criteria of fuels

In Austria diesel fuels and petrol are regulated in the “ordinance of the federal minister of agriculture, forestry, environment and water management on the quality of fuels and the sustainable use of biofuels” (fuel regulation 2012). This regulation regulates quality criteria. To determine the quality parameters the regulation refers to the norm ÖNORM EN 228 “Automotive fuels – Unleaded petrol – Requirements and test methods” and the norm ÖNORM EN 590 “Automotive fuels – Diesel – Requirements and test methods”. (Verordnung des Bundesministers für Land- und Forstwirtschaft, Umwelt und Wasserwirtschaft über die Qualität von Kraftstoffen und die nachhaltige Verwendung von Biokraftstoffen (Kraftstoffverordnung 2012). In: BGBl. II Nr. 398/2012, 2012)

Table 1 - Requirements and test methods for unleaded petrol (ÖNORM EM 228:2017-07, Automotive fuels – Unleaded petrol – Requirements and test methods, 2017) (Verordnung des Bundesministers für Land- und Forstwirtschaft, Umwelt und Wasserwirtschaft über die Qualität von Kraftstoffen und die nachhaltige Verwendung von Biokraftstoffen (Kraftstoffverordnung 2012). In: BGBl. II Nr. 398/2012, 2012)

Property	Limits		Test Method
	Min	Max	
Appearance	Clear and bright		Visual inspection
Research octane number, RON	95.0		EN ISO 5164
Motor octane number, MON	85.0		EN ISO 5163
Density (at 15 °C)	720 kg/m ³	775 kg/m ³	EN ISO 3675 EN ISO 12185
Lead content		5.0 mg/L	EN 237
Sulfur content		10.0 mg/kg	EN ISO 13032 EN ISO 20846 EN ISO 20884
Oxidation stability	360 minutes		EN ISO 7536
Copper strip corrosion (3h at 50°C)	Class 1		EN ISO 2160
Hydrocarbon type content - olefines - aromatics - benzole		18.0 % (v/v) 35.0 % (v/v) 1.0 % (v/v)	EN 15553 EN ISO 22854 EN 238 EN 12177
Oxygen content		2.7 % (w/w)	EN 1601 EN 13132 EN ISO 22854
Oxygenates content - methanol - ethanol - isopropylalcohole - tert. butylalcohole - isobutylalcohole - ether - others		3.0 % (v/v) 5.0 % (v/v) 10.0 % (v/v) 7.0 % (v/v) 10 % (v/v) 15.0 % (v/v) 10.0 % (v/v)	EN 1601 EN 13132 EN ISO 22854
Vapour pressure		60.0 kPa	
% evaporated at 70 °C, E70	22.0 % (v/v)	50.0 % (v/v)	EN ISO 3405
% evaporated at 100 °C, E100	46.0 % (v/v)	72.0 % (v/v)	EN ISO 3405
% evaporated at 150 °C, E150	75.0 % (v/v)		EN ISO 3405

Table 2 - Requirements and test methods for diesel and diesel-like fuels (ÖNORM EN 590:2017-11, Automotive fuels – Diesel – Requirements and test methods, 2017) (Verordnung des Bundesministers für Land- und Forstwirtschaft, Umwelt und Wasserwirtschaft über die Qualität von Kraftstoffen und die nachhaltige Verwendung von Biokraftstoffen (Kraftstoffverordnung 2012). In: BGBl. II Nr. 398/2012, 2012)

Property	Limits		Test Method
	Min	Max	
Cetane number	51.0		EN ISO 5165 EN 15195 EN 16144 EN 16715
Cetane index	46.0		EN ISO 4264
Density at 15 °C	820.0 kg/m ³	845.0 kg/m ³	EN ISO 3675 EN ISO 12185
Polycyclic aromatic hydrocarbons		8.0 % (w/w)	EN 12916
Sulfur content		10.0 mg/kg	EN ISO 20846 EN ISO 20884 EN ISO 13032
Flash point	> 55 °C		EN ISO 2719
Carbon residue (on 10 % distillation residue)		0.30 % (w/w)	EN ISO 10370
Ash content		0.010 % (w/w)	EN ISO 6245
Water content		0.020 % (w/w)	EN ISO 12637
Total contamination		24 mg/kg	EN 12662
Copper strip corrosion (3h at 50°C)	Class 1		EN ISO 2160
Fatty acid methyl ester (FAME) content		7.0 % (v/v)	EN 14078
Lubricity at 60 °C		460 µm	EN ISO 12156-1
Viscosity at 40 °C	2.000 mm ² /s	4.500 mm ² /s	EN ISO 3104
Distillation % (v/v) recovered at 250 °C % (v/v) recovered at 350 °C 95 % (v/v) recovered at	85 % (v/v)	< 65 % (v/v) 360 °C	EN ISO 3405 EN ISO 3924
Cloud point		-10 to -34 °C	EN 23015
Acid number (FAME)		0.5 mg KOH/kg	ÖNORM 14104
Neutralization number (pure plant oil)		2.0 mg KOH/kg	ÖNORM 14104
Heating value (pure plant oil)	35000 kJ/kg		DIN 51900-3

2.6.1 Density

Definition

Density is mass per volume at 15 °C and 101.325 kPa in kg per m³ or g per mL. (EN ISO 3675:1998, Crude petroleum and liquid petroleum products – Laboratory determination of density – Hydrometer method (ISO 3675:1998), 1998)

Method

The temperature of the sample is set to 15 °C and the sample is put into a hydrometer cylinder. A tempered hydrometer is put into the liquid sample and after a short temperature equalizing the value of the hydrometer scale is read and noted.

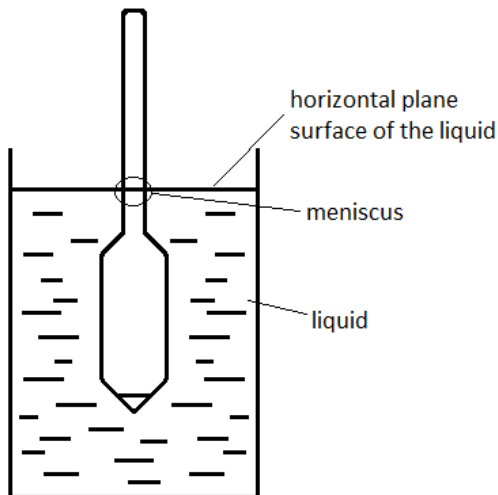


Figure 16 - Experimental setup for the determination of the density of petroleum oils

(EN ISO 3675:1998, Crude petroleum and liquid petroleum products – Laboratory determination of density – Hydrometer method (ISO 3675:1998), 1998)

An alternative to this method is the determination of density with the oscillation U-tube method. (EN ISO 12185:1996, Crude petroleum and petroleum products – Determination of density – Oscillation U-tube method, 1996)

At the oscillating U-tube method a U-tube is oscillated and the natural frequency of the U-tube is determined. The natural frequency depends on the mass of the U-tube. Because the U-tube has a defined volume, the frequency depends on the density of the sample in the U-tube. The density can be calculated from the duration of the oscillation with a calibration function. The references for this calibration function are mostly air and water. (Hradetzky & Sommer, 2002)

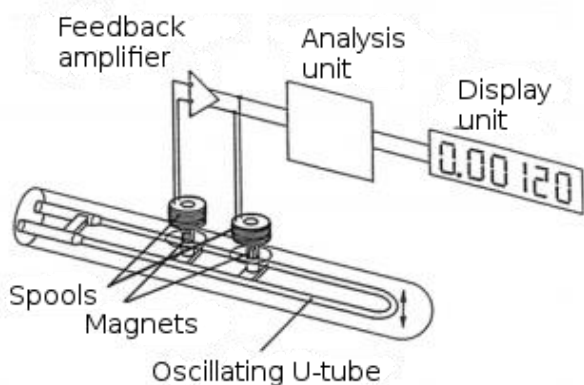


Figure 17 - Oscillating U-tube (Hradetzky & Sommer, 2002)

2.6.2 Cloud point

Definition

The cloud point is the temperature at which a cloud of paraffin crystals (cloudiness) first occurs in a liquid if it is cooled at determined testing conditions. (ISO 23015:1994-05, Petroleum oils; determination of cloud point (ÖNORM ISO 3015:1992), 1994)

Equipment

- Cooling bath
- Sample container incl. cork
- Jacket vessel incl. spacer and insulating
- Thermometer

Method

The sample is heated up to a temperature 14 °C above the expected cloud point but to a maximal temperature of 49 °C. To avoid impurities and water in the sample it can be filtered. The sample is put into a sample container and it is closed with a cork and a thermometer. The sample container is put into a jacket vessel which is cooled in a cooling bath. The cooling bath is gradually cooled and the sample is tested in periodic temperature intervals by pulling it out of the jacket vessel and checking for cloudiness. The sample should be replaced within three seconds. The temperature at which the first clouds occur at the bottom of the sample container is called cloud point.

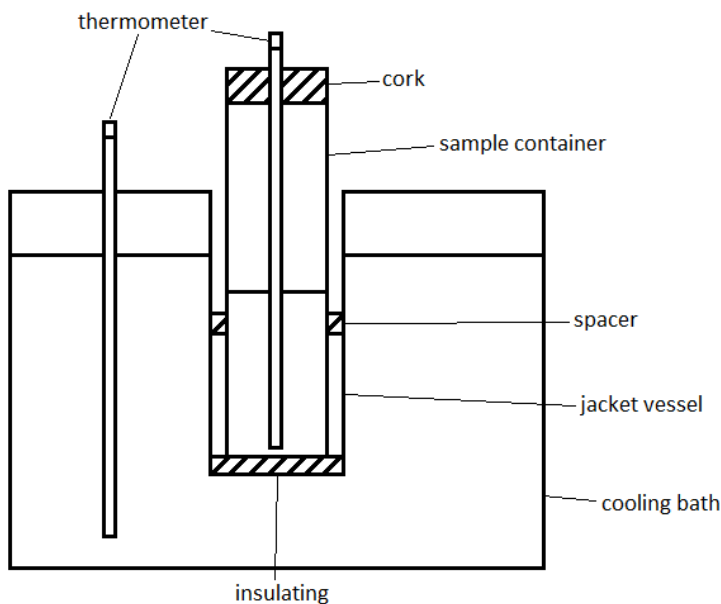


Figure 18 - Experimental setup for the determination of the cloud point of petroleum oils

(ISO 23015:1994-05, Petroleum oils; determination of cloud point (ÖNORM ISO 3015:1992), 1994)

2.6.3 Flash point

Definition

The flash point is the lowest temperature of a sample, corrected to a standard air pressure of 101.3 kPa, under specified test conditions, at which the fumes of a sample are ignited by the use of an ignition source and the flame spreads over the surface of the liquid. (EN ISO 2719:2016, Determination of flash point - Pensky-Martens closed cup method (ISO 2719:2016), 2016)

Equipment

- Flame point test device
- Thermometer
- Barometer
- Heating bath or heat chamber

Method

The sample is put into a flame point test device and the temperature is increased constantly while stirring. The sample is ignited with an ignition source in constant temperature intervals while stirring is stopped. The lowest temperature at which the fumes are ignited and the flame spread over the surface of the liquid is called flash point. It is corrected to a standard pressure of 101.3 kPa.

Calculation

$$T_c = T_d + 0.25 * (101.3 - p)$$

T_c...corrected flash point [°C]

T_d...determined flash point [°C]

p...absolute air pressure [kPa]

0.25...constant [°C/kPa]

101.3...standard air pressure [kPa]

(EN ISO 2719:2016, Determination of flash point - Pensky-Martens closed cup method (ISO 2719:2016), 2016)

2.6.4 Distillation characteristics

Distillation characteristics are used to distinguish between low boiling fractions and middle distillates. Low boiling fractions are substances like fuels, fuels with ethanol content up to 10 % (v/v) and aircraft petrol. Middle distillates are aviation turbine fuels, kerosene, diesel with a fatty acid methyl ester (FAME) content up to 20 % (v/v), fuels and marine fuels.

Equipment

- Distillation flask (125 mL)
- Cooling tube and cooling bath
- Heating source (electric heating, gas heating)
- Holder
- Collecting container (measuring cylinder)
- Thermometer
- Barometer

Method

100 mL of the sample are distilled at specific conditions according to the expected distillation characteristics. Distillation temperature and volume are noted systematically and distillation residue and loss are noted. The values are air pressure corrected and the characteristic values are calculated.

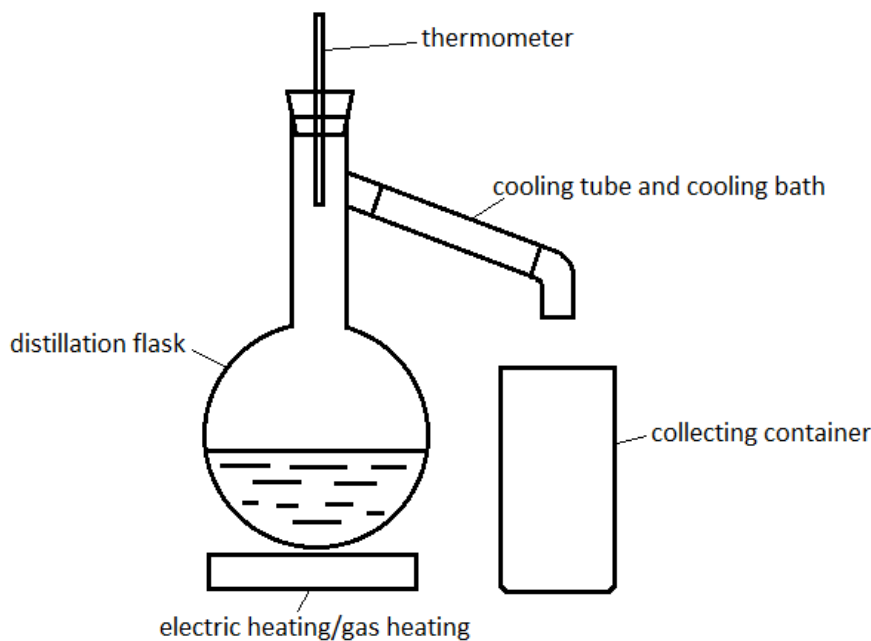


Figure 19 - Experimental setup for the determination of distillation characteristics of petroleum oils

(DIN EN ISO 3405:2011-04, Petroleum products - Determination of distillation characteristics at atmospheric pressure (ISO 3405:2011), 2011)

2.6.5 Acid number, neutralization number

Definition

The acid number is the amount of potassium hydroxide (in mg) that is necessary to neutralize the free fatty acids in 1 g FAME. (ÖNORM EN 14104:2003-10, Fat and oil derivatives - Fatty Acid Methyl Esters (FAME) - Determination of acid value, 2003)

The neutralization number is the amount of alkali expressed in potassium hydroxide (KOH) that is necessary to neutralize the acidic ingredients in 1 g of a sample. (DIN 51558-2:2017-07, Testing of mineral oils – Determination of neutralization number – Part 2: Color-indicator titration, insulating oils, 2017)

Equipment

- Alcoholic potassium standard solution: $c(\text{KOH}) = 0.1 \text{ mol/L}$
- Solvent:
 - Diethyl ether (50 % v/v) + 95 % ethanol (50 % v/v) or
 - Toluene (50 % v/v) + 95 % ethanol (50 % v/v) or
 - Toluene (50 % v/v) + 99 % propan-2-ol (50 % v/v) or
 - 99 % propan-2-ol
- Indicator: phenolphthalein, 10 g/L solved in ethanol
- Burette, titration flask

Method

Immediately before each use of the solvent solution, the mixture has to be neutralized with alcoholic potassium solution in the presence of 0.3 mL indicator solution per 100 mL solvent. About 20 g of the sample is weighed in a titration flask and it is dissolved in 100 mL neutralized solvent solution. The sample is permanently mixed while it is titrated with the potassium solution until the colour changes.

Calculation

$$\text{acid number: } \frac{56.1 * V * c}{m}$$

V...volume KOH-solution [mL]

c...concentration KOH-solution [mol/L]

m...mass of the sample [g]

56.1...molar mass of KOH [g/mol]

The unit of the result is mg KOH per g sample.

(ÖNORM EN 14104:2003-10, Fat and oil derivatives - Fatty Acid Methyl Esters (FAME) - Determination of acid value, 2003)

(DIN 51558-2:2017-07, Testing of mineral oils – Determination of neutralization number – Part 2: Color-indicator titration, insulating oils, 2017)

2.6.6 Viscosity

The lubricity of many liquid mineral oil products and other substances which are used as lubricants and the right storage temperature and operating temperature depends on the right viscosity of the liquid.

Definition

Kinematic viscosity (ν): flow resistance of a liquid under the influence of gravity

Density (ρ): the mass of a substance divided by its volume at a certain temperature

Dynamic viscosity (η): the relation between the applied shear stress and shear rate of a liquid – the dynamic viscosity is a measure for the flow resistance or the deformability of a liquid

(DIN EN ISO 3104:1999-12, Petroleum products - Transparent and opaque liquids - Determination of kinematic viscosity and calculation of dynamic viscosity (ISO 3104:1994 + Cor. 1:1997), 1999)

Method

A defined volume of a sample is put into a viscometer at a specified temperature and under the influence of gravity. The flow time of the sample through the capillary is measured and the kinematic viscosity is calculated by the flow time and the calibration constant of the viscometer. The calibration constant has to be determined by a certified reference material.

Calculation

$$\nu = C * t$$

ν ...kinematic viscosity [mm^2/s]

C ...calibration constant [mm^2/s^2]

t ...mean flow time [s]

$$\eta = \nu * \rho * 10^{-3}$$

η ...dynamic viscosity [mPa/s]

ρ ...density [kg/m^3] (at the same temperature)

ν ...kinematic viscosity [mm^2/s]

(DIN EN ISO 3104:1999-12, Petroleum products - Transparent and opaque liquids - Determination of kinematic viscosity and calculation of dynamic viscosity (ISO 3104:1994 + Cor. 1:1997), 1999)

3 Methods

3.1 Samples

3.1.1 Samples of the preliminary experiments

First preliminary experiments are carried out to get a general overview of the pyrolysis behaviour of a plastic mixture depending on different pyrolysis temperatures. The experimental setup is designed by Angelika Pausweg. (PAUSWEG, 2017)

As feedstock a mixture of different plastics and a sample of sea plastic are used. The plastic mixture refers to the worldwide plastic production and is a mixture of polypropylene (27 % (w/w)), low density polyethylene (20 % (w/w)), polyvinylchloride (19 % (w/w)), high density polyethylene (18 % (w/w)), polystyrene (8 % (w/w)) and polyethylene terephthalate (8 % (w/w)). Plastics with a minor proportion are not considered. The sea plastic sample was collected on a Mediterranean island. Each sample is pyrolyzed at 400°C, 500°C, 600°C and 700°C muffle furnace temperature and a reaction time of 60 minutes. (PAUSWEG, 2017)

The plastic mixture used by Angelika Pausweg is called “plastic mixture (A)” and the sea plastic sample is called “sea plastic”.




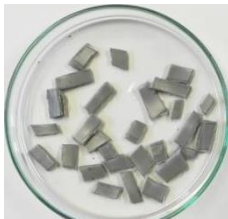



3.1.2 Samples of the complementary experiments

Based on the results of Angelika Pausweg further experiments are carried out. As feedstock also a mixture of different plastics is used. The mixture is based on the European plastic demand of 2015 (PLASTICSEUROPE DEUTSCHLAND e.V., 2016). It consists of polypropylene (23.8 % (w/w)), low density polyethylene (21.6 % (w/w)), high density polyethylene (15.1 % (w/w)), polyvinylchloride (12.6 % (w/w)), polyurethane (9.4 % (w/w)), polyethylene terephthalate (8.9 % (w/w)) and polystyrene (8.6 % (w/w)). The mixture is similar to the mixture that was used by Angelika Pausweg but it contains additionally polyurethane. This plastic mixture is called “plastic mixture (B)” in this master thesis.



Figure 20 - Plastic mixture (B)

Table 3 - Individual plastic fractions of the plastic mixture (B)

Picture	Name	Proportion of the plastic mixture (B)
	Polypropylene (PP)	23.8 % (w/w)
	Low density polyethylene (PE-LD)	21.6 % (w/w)
	High density polyethylene (PE-HD)	15.1 % (w/w)
	Polyvinylchloride (PVC)	12.6 % (w/w)
	Polyurethane (PUR)	9.4 % (w/w)
	Polyethylene terephthalate (PET)	8.9 % (w/w)
	Polystyrene (PS)	8.6 % (w/w)

3.2 Experimental setup – pyrolysis

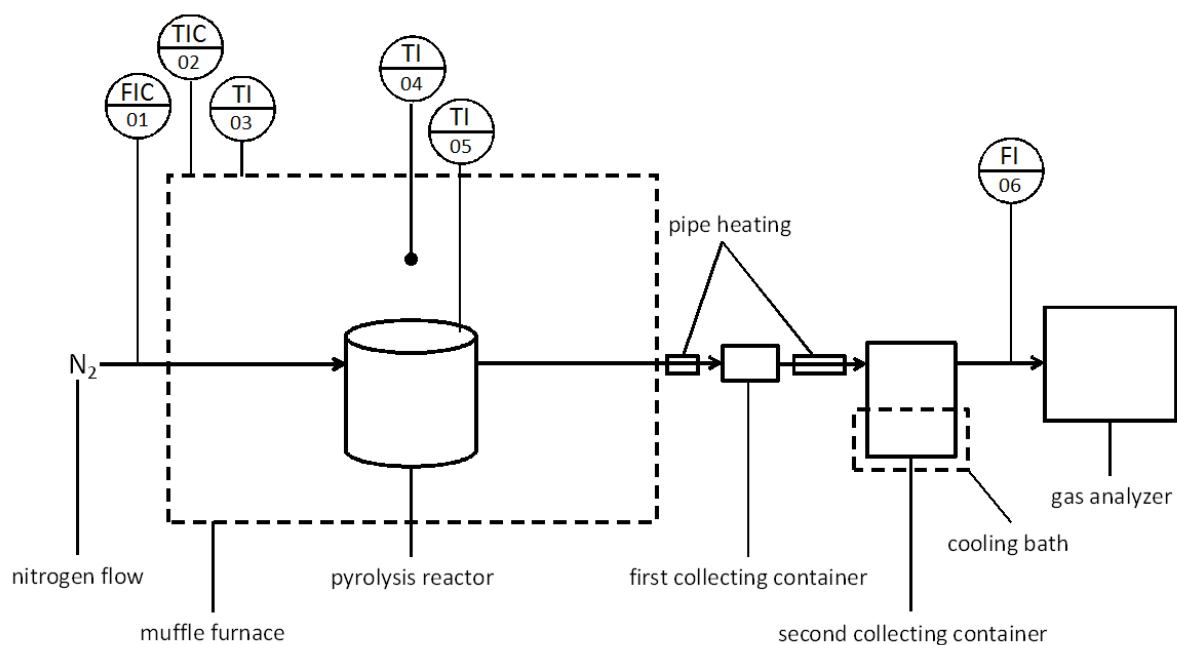


Figure 21 - process flow diagram



Figure 22 - Muffle furnace and pyrolysis reactor



Figure 23 - First collecting container



Figure 24 - Second collecting container

The pyrolysis reactor itself consists of a metal cylinder with an outer diameter of 11 cm and an inner diameter of 5 cm. The reactor is heated within a muffle furnace (Nabertherm). The gaseous pyrolysis product passes through metal pipes into the two collecting containers. While pyrolysis nitrogen gas flow is used as propellant to avoid oxygen in the reactor and blockages in the pipes. The first collecting container is used to collect high boiling product fractions, which would cause blockages. The second collecting container is cooled in an ice water bath. In the second collecting container the rest of the non-volatile product is collected. The gaseous product and the nitrogen gas flow continue into a gas analyzer.

The temperature is recorded at four places, namely at the muffle furnace, the heating coil, in the muffle furnace and in the reactor.

3.2.1 Temperature correction

At the preliminary experiments only the temperature of the muffle furnace was recorded. For the reaction the temperatures in the reactor are important. Because it is possible that the oven is interfering with a digital thermometer, the calibration line is created with a mechanical thermometer. The temperature is corrected with a simple calibration line.

The used thermometer is a capillary tube thermometer. The principle of a capillary tube thermometer is that there is a vessel which is filled with a liquid. Due to a temperature change the pressure in the vessel changes too. The vessel is connected with a manometer which indicated the temperature.

The used thermometer is an “Arthermo Italy” with a temperature range from 50 °C to 600 °C. It measures the temperature inside the reactor (see figure 27).



Figure 25 - Capillary tube thermometer “Arthermo Italy”

The temperature of the muffle furnace is increased in 100 °C steps and it is hold until the temperature does not change anymore. The temperature of the muffle furnace and the capillary tube thermometer is recorded in five minutes steps.

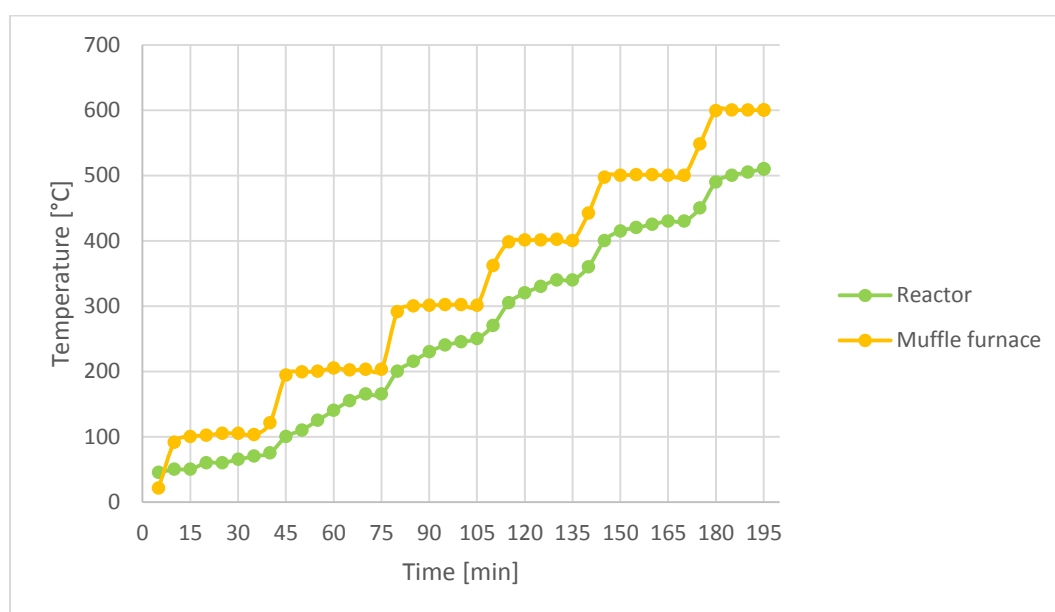


Figure 26 - Temperature curve muffle furnace and reactor

The curve shows that the temperatures of the muffle furnace and inside the furnace differ enormously. It is also visible, that the heating rate of the furnace and the reactor differ. With the data of the temperature curve a calibration line is made. The equilibrium temperatures are used. Because over 500 °C the capillary tube thermometer is not linear anymore, the 600 °C value is eliminated.

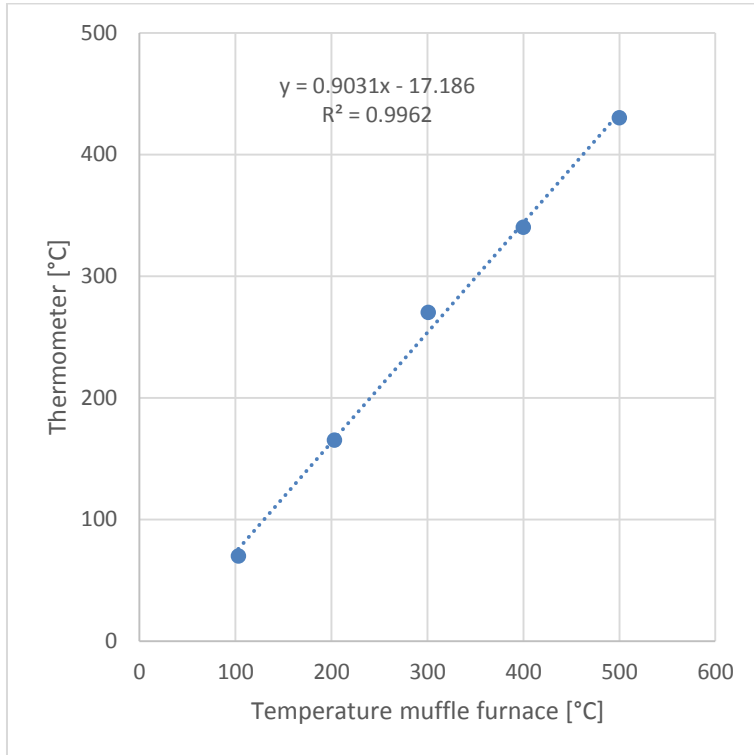


Figure 27 - Temperature calibration line muffle furnace and capillary tube thermometer

The temperature of the muffle furnace and the capillary tube thermometer show a linear relationship. The temperature values of the furnace can be corrected with the following equation:

$$y=0.9031x-17.186$$

Whereby y is the temperature of the capillary tube thermometer respectively the reactor and x is the temperature of the muffle furnace.

In the case of the used temperatures of the muffle furnace the following temperatures result in the reactor:

- A displayed temperature of 400°C on the muffle furnace corresponds to 344°C reactor temperature.
- A displayed temperature of 500°C on the muffle furnace corresponds to 434°C reactor temperature.
- A displayed temperature of 600°C on the muffle furnace corresponds to 525°C reactor temperature.
- A displayed temperature of 700°C on the muffle furnace corresponds to 615°C reactor temperature.

3.2.2 Temperature curves of the complementary experiments

At the complementary experiments the temperature is recorded with a PLC control device. The temperature is measured at the heating coil, inside the muffle furnace and inside the reactor.

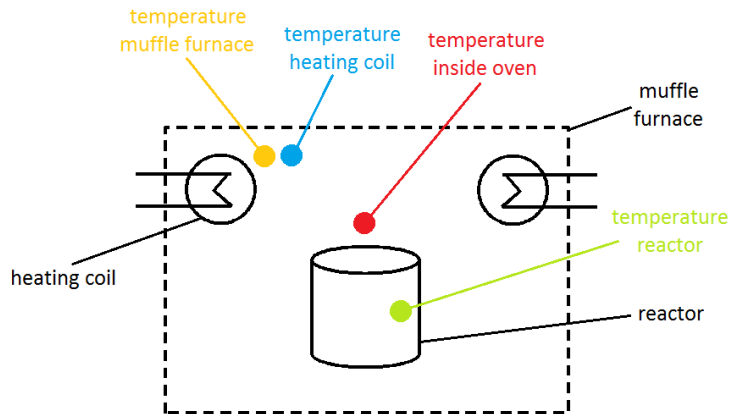


Figure 28 - Temperature measuring points

3.2.2.1 Pyrolysis at 344 °C – 180 minutes

The temperature curves of the displayed temperature of the muffle furnace and inside the reactor show that the temperatures and the heating rates differ. At the preliminary experiments of Angelika Pausweg the reaction time was oriented on the displayed temperature of the muffle furnace (PAUSWEG. 2017). It is assumed, that the temperature of the reactor did not reach the end-temperature at this time. Therefore the experiment is carried out at the same temperature but the reaction time is increased to 180 minutes.

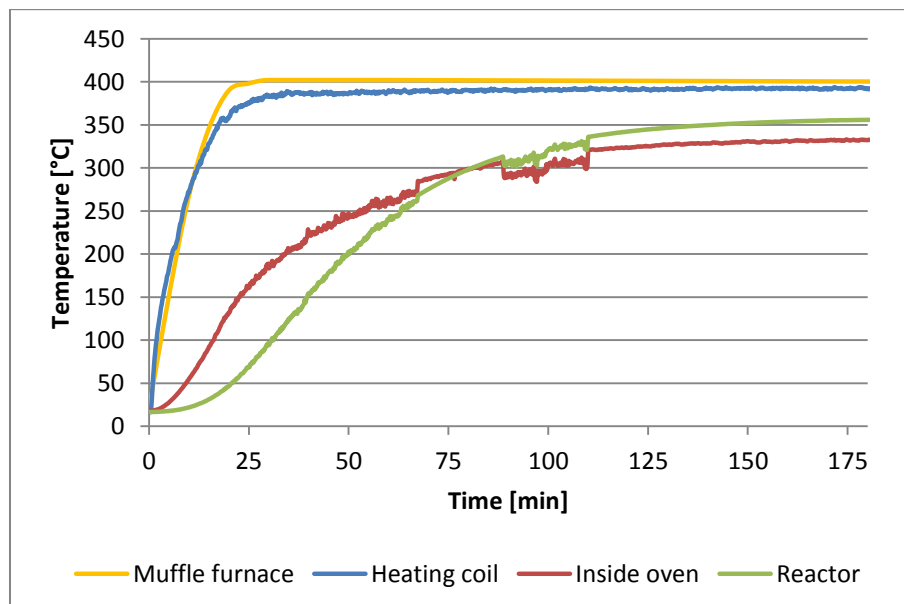


Figure 29 - Temperature curve - pyrolysis at 344 °C

In this experiment the end-temperature of the reactor is slightly over 344 °C according to the digital temperature measurement. Some measurement disturbances are visible at the curve. These are probably caused by the muffle furnace or any other influences. Moreover the temperature of the reactor gets higher than the temperature inside the oven which indicates

an error in the measurement. Maybe there is a problem with the sensor or the muffle furnace disturbs the measuring device.

This temperature curve shows how difficult it is to specify a reaction temperature. One problem are influences of the muffle furnace like induction currents while heating which can disturb the measurement and another problem is the low heat transfer of the pyrolysis reactor. Therefore the temperature is calculated with the previously determined calibration line.

3.2.2.2 Pyrolysis at 400 °C – 200 minutes

Because the turnover rate at a pyrolysis temperature of 344 °C in the reactor and 180 minutes reaction time is very low, an experiment is carried out at 400 °C. Again the reaction time is extended compared to the experiments of Angelika Pausweg (PAUSWEG, 2017). The muffle furnace is heated for 120 minutes and then muffle furnace is turned off. The temperature is further recorded up to a total reaction time of 200 minutes.

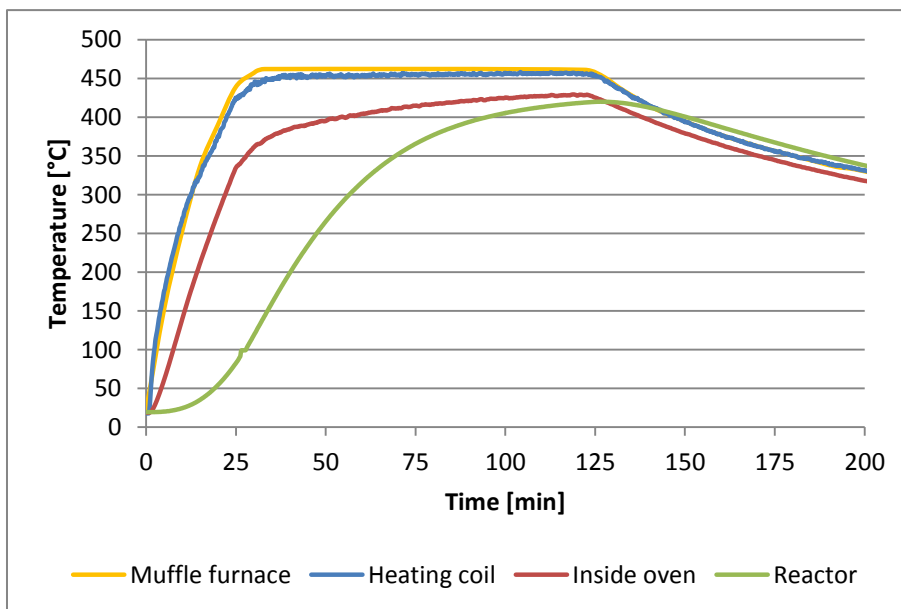


Figure 30 - Temperature curve - pyrolysis at 400 °C

At this experiment the end-temperature is slightly higher than the calculated temperature but only after a total reaction time of more than 90 minutes. Again the big difference between the muffle furnace temperature and the reactor is visible. After about 120 minutes the temperatures of the muffle furnace, the heating coil and inside the oven go down because the muffle furnace is turned off. The temperature of the reactor goes down time-delayed.

3.2.2.3 Pyrolysis at 615 °C

This experiment is carried out at 615 °C to compare the difference between the two plastic mixtures (A) and (B) and to record the temperature inside the reactor at this temperature. The reaction time is comparable to the reaction time of the preliminary experiments of Angelika Pausweg, which was 60 minutes after the muffle furnace reached the target temperature (PAUSWEG, 2017).

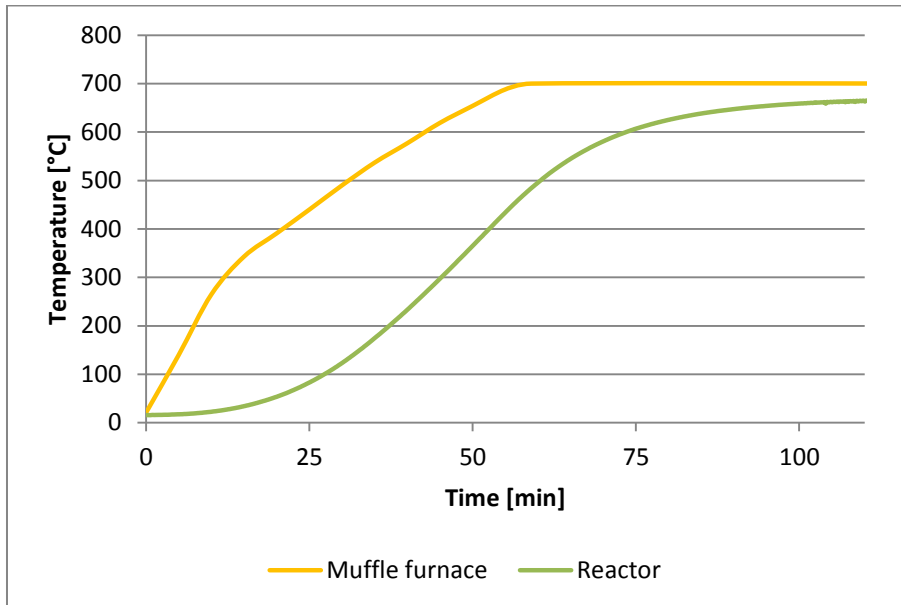


Figure 31 - Temperature curve - pyrolysis at 615 °C

In this measurement the sensor at the heating coil and the sensor inside the oven failed. Only the temperature curve of the muffle furnace and of the reactor could be recorded. The end temperature of this experiment was 667 °C and the average heating rate of the reactor is about 13 K/min between 200 °C and 500 °C. Because two of four sensors failed completely it is possible that the measurements of the other sensors also failed. Therefore the temperature is calculated with the calibration line and the end temperature of the furnace.

3.3 Experimental setup – distillation

As purification step, a distillation is carried out. The distillation is carried out as a single-stage distillation in the same experimental setup in which the pyrolysis is performed (see figure 22). The first collecting container, the pipe heating and the gas analyzer are omitted. The distillate is collected in the second collecting container (see figure 24). The distillation temperature of 250 °C is chosen freely and it does not refer to the distillation temperature of fuels. This temperature is chosen, because most of the reference diesel evaporates at 200 °C and 99.0 % (w/w) evaporate at 250 °C (see table 10). It is expected, that the distillate is similar to diesel after distillation at 250 °C. The temperature of the distillation apparatus is controlled with a PLC, like at the pyrolysis experiments. The distillation is carried out until no more distillate gets into the collection container.

3.4 Gas analyzer



Figure 32 - Rosemount Analytical X-Stream

The pyrolysis gases are analyzed by a “Rosemount Analytical X-Stream”. This device uses different measuring principles like UV- and IR-spectroscopy, TCD (Thermal Conductivity Detector) and electrochemical and paramagnetic principles. The used device can measure the gases CO₂, CO, CH₄, H₂ and O₂. The principle for CO₂, CO and CH₄ is IR-spectroscopy. The principle for H₂ is TCD. O₂ is detected by electrochemical and paramagnetic principles. (ROSEMOUNT ANALYTICAL, 2012)

Before the measurement the device has to be calibrated with test gas. This test gas is a mixture of 25 % (v/v) CO₂, 25 % (v/v) CO, 25 % (v/v) CH₄ and 25 % (v/v) H₂. As zero gas N₂ is used. The test gas for O₂ is ambient air, in which 20.9 % (v/v) are O₂.

The measuring is started online. The gas analyzer needs to be connected via a local area network with a computer where the control panel is called up with a web browser. The gas measuring then runs fully automatically.

3.5 Thermogravimetric analysis with mass spectroscopy

3.5.1 Thermogravimetric analysis

Thermogravimetric analysis is an analytical method in which the mass of a sample is measured while the temperature in the oven of the device is changing. The main parts of a thermogravimetric analyzer are an oven with temperature regulation, an electronic scale and gas supply lines.

To analyse the sample, it is put into a small crucible made of alumina and put on the sample carrier. Parameters like heating rate and gas flow are set and the measurement is started. The used device control heating rate, gas flow and end-temperature fully automatically. It can be chosen between oxidative sample gases and inert sample gases to avoid oxidation.

The used thermogravimetric analyzer is a "NETZSCH STA 409 CD" coupled with a quadrupole mass spectrometer. (NETZSCH THERMAL ANALYSIS, 2017)



Figure 33 - Thermogravimetric analyzer "NETZSCH STA 409 CD" (NETZSCH THERMAL ANALYSIS, 2017)

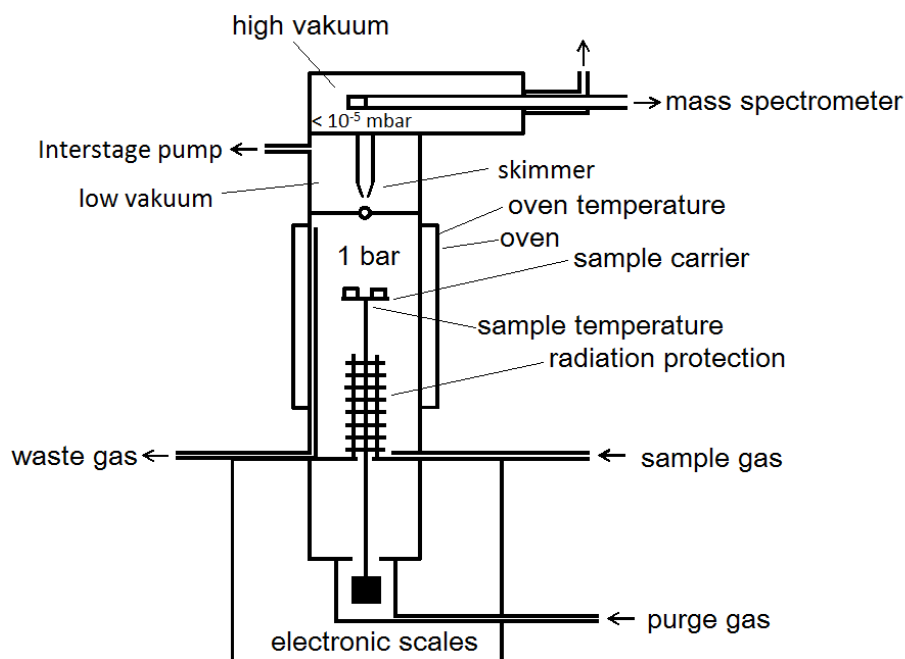


Figure 34 - Construction scheme of a thermogravimetric analyzer

3.5.2 Mass spectrometer

A mass spectrometer is a device for measuring the mass-to-charge (m/z) ratio of atoms and molecules. Therefore the atoms and molecules have to be ionized to get a charge. The main parts of a mass spectrometer are an ion source, where the molecules are ionized, an analyzer, where the ions are sorted based on their mass-to-charge ratio and a detector, where the ions are counted. By ionization most molecules are broken down into smaller pieces and a specific mass spectrum results.

The used device works with electron ionization, a quadrupole mass spectrometer and a secondary electron multiplier.

Thermogravimetric analysis does not separate a mixture of substances into pure substances like other methods like gas chromatography. The substances remain as a mixture when they evaporate and therefore the mass spectrum is a mixture of many substances. The interpretation of the mass spectrum is not done by libraries but specific mass-to-charge ratios are used, that occur very specific in just one molecule or a similar group of substances.

A specific mass-to-charge ratio for water is 18. A specific mass-to-charge ratio for CO_2 is 44. (NETZSCH THERMAL ANALYSIS, 2017)

Expected pyrolysis products are alkanes, alkenes and aromatics. Because these substances break into similar fragments while ionization, leading mass-to-charge ratios are used that occur only in a group of substances. These mass-to-charge ratios are determined empirically and by database analysis.

A strong indicator for alkanes is the mass-to-charge ratio 57 but also long chained alkenes break into this fragment. (WEBBOOK, 2018)

Another indicator for alkanes and alkenes is the mass-to-charge ratio 43 (WEBBOOK, 2018).

A specific mass-to-charge ratio for aromatics is 51 (UNI HEIDELBERG, 2003) (WEBBOOK, 2018).

An indicator for alkenes and branched alkanes is the mass-to-charge ratio 56 (WEBBOOK, 2018).

In this case this method is no quantitative method. There is no possibility to perform a calibration because different substances that evaporate at the same temperature can form the same m/z fragment but in different amounts.

The mass spectra of the products can be taken as a fingerprint to compare the products with the reference substances diesel and petrol and to get extra information of the composition. When this fingerprint of a sample is similar to the fingerprint of the references it is still possible that the composition is different.

3.5.3 Measuring mode

The amount of the sample for the used equipment is about 22 mg. The heating rate is adjusted to 3 K/min in a temperature range from 20 to 700 °C. The sample gas is argon with a total flow rate of 50 mL/min.

Because the standard method for the distillation characteristics of fuels is a volumetric method and the thermogravimetric analysis is a gravimetric method, the samples are compared with the references diesel and petrol. Comparative temperatures for evaporation residues are 70 °C, 100 °C, 150 °C, 250 °C, 350 °C and 360 °C (ÖNORM EM 228:2017-07, Automotive fuels – Unleaded petrol – Requirements and test methods, 2017) (ÖNORM EN 590:2017-11, Automotive fuels – Diesel – Requirements and test methods, 2017).

At the same time a mass spectra with the mass-to-charge ratios 43, 51, 56 and 57 is recorded.

3.6 Determination of quality criteria of fuels and fuel-like pyrolysis products

The standard methods which are described in norms and standards are designed for pure fuels and a certain minimum sample amount is needed for each determination. Because of the small amount and the composition and pollution of the samples, the standard methods have to be adapted. The adapted methods are not as accurate and reproducible as the standard methods but first an overview of the pyrolysis products has to be made.

3.6.1 Appearance

Macroscopic characteristics of the sample like colour, impurities, flow properties and other relevant characteristics of the sample are described visually. Fuels should be clear and bright. (Verordnung des Bundesministers für Land- und Forstwirtschaft, Umwelt und Wasserwirtschaft über die Qualität von Kraftstoffen und die nachhaltige Verwendung von Biokraftstoffen (Kraftstoffverordnung 2012). In: BGBl. II Nr. 398/2012, 2012)

The samples are put into small transparent containers, photos are made and characteristics like clarity, transparency, colour, aggregate state, homogeneity and impurities are described.

3.6.2 Density

Usually density of fuels is determined with the hydrometer method or the oscillation U-tube method. To use these methods, the sample has to be liquid and for the hydrometer method a certain minimum amount of about 200 mL is needed to fill the hydrometer cylinder. (EN ISO 3675:1998, Crude petroleum and liquid petroleum products – Laboratory determination of density – Hydrometer method (ISO 3675:1998), 1998) (EN ISO 12185:1996, Crude petroleum and petroleum products – Determination of density – Oscillation U-tube method, 1996)

Density is defined as mass per volume. Approximately the density is determined by weighing a known volume of the sample and calculating the density by dividing the mass by the volume.

For this work the volume is determined by using 2-mL sample vials. The exact volume has to be determined by weighing the mass of the empty sample vial, filling it up with distilled water and weighing it again. The mass of the water and the volume of the vial can be calculated.

$$V = \frac{m_{water}}{\rho_{water}}$$

V...volume

m_{water}...mass water

ρ_{water}...density water at measuring temperature

The sample vial is emptied, water residues are removed and the vial is filled with the sample. The mass of the sample is determined and the density of the sample is calculated.

$$\rho_{sample} = \frac{m_{sample}}{V}$$

V...volume

m_{sample}...mass sample

ρ_{sample}...density sample at measuring temperature

3.6.3 Cloud point/Pour point

To determine the cloud point, the sample is heated in a heating cabinet until no cloudiness is visible. The temperature of the heating cabinet is lowered in 5°C steps.

The temperature of the sample is measured with an external thermometer in the heating cabinet. In periodic intervals the sample is inspected visually.

The temperature at which the first cloudiness is visible is called cloud point (ISO 23015:1994-05, Petroleum oils; determination of cloud point (ÖNORM ISO 3015:1992), 1994).

At opaque samples and samples with macroscopic impurities the cloud point can not be determined. Instead the pour point, at which the sample solidifies, is determined. The sample is put into a transparent sample container e.g. a 2 mL sample vial. A small space has to remain free to keep an air bubble. The container is closed and heated up in a heating cabinet until the samples are liquid. To determine if a dark coloured and opaque sample is liquid, the vial is slowly turned upside down some times and the air bubble is watched. One can easily see if a sample is liquid or solid. The temperature of the sample is lowered in 5°C steps and the sample is inspected visually by watching the air bubble. The temperature range in which the sample gets solid is noted.

3.6.4 Flash point

Due to the small amount of the sample, no flash point test device can be used. Instead the sample is put into a small container with a cover and it is heated stepwise in a heating cabinet.

The temperature in the heating cabinet is measured with an external thermometer and in periodic intervals each sample is ignited with an ignition source.

The lowest temperature at which the fumes are ignited and the flame spread over the surface of the liquid is called flash point. (EN ISO 2719:2016, Determination of flash point - Pensky-Martens closed cup method (ISO 2719:2016), 2016)

3.6.5 Distillation characteristics

According to norm, distillation characteristics are determined volumetric. Small amounts can not be determined with the available equipment at the institut, instead thermogravimetric analysis is used.

A small amount of the sample (about 22 mg) is weighted in with an analytical scale and put into the thermogravimetric analyser. The sample is heated up with a constant heating rate of 3 K/min at a temperature range of 20 to 700 °C. The loss in weight is recorded simultaneously.

At the same time a mass spectrum is recorded to get information about the substances in the sample.

3.7 Scanning electron microscopy with energy dispersive X-ray spectroscopy – SEM-EDX

3.7.1 Technique

Scanning electron microscopy with energy dispersive X-ray spectroscopy is a widely used surface analytical technic. Primary electrons with a primary energy of 0.5 to 30 kV enter a surface and produce secondary electrons with lower energy. By measuring these secondary electrons an image of the sample can be made. Further it is possible to generate qualitative information of the sample. (WESTERN UNIVERSITY, 2017)

3.7.2 Microscopic images of plastics

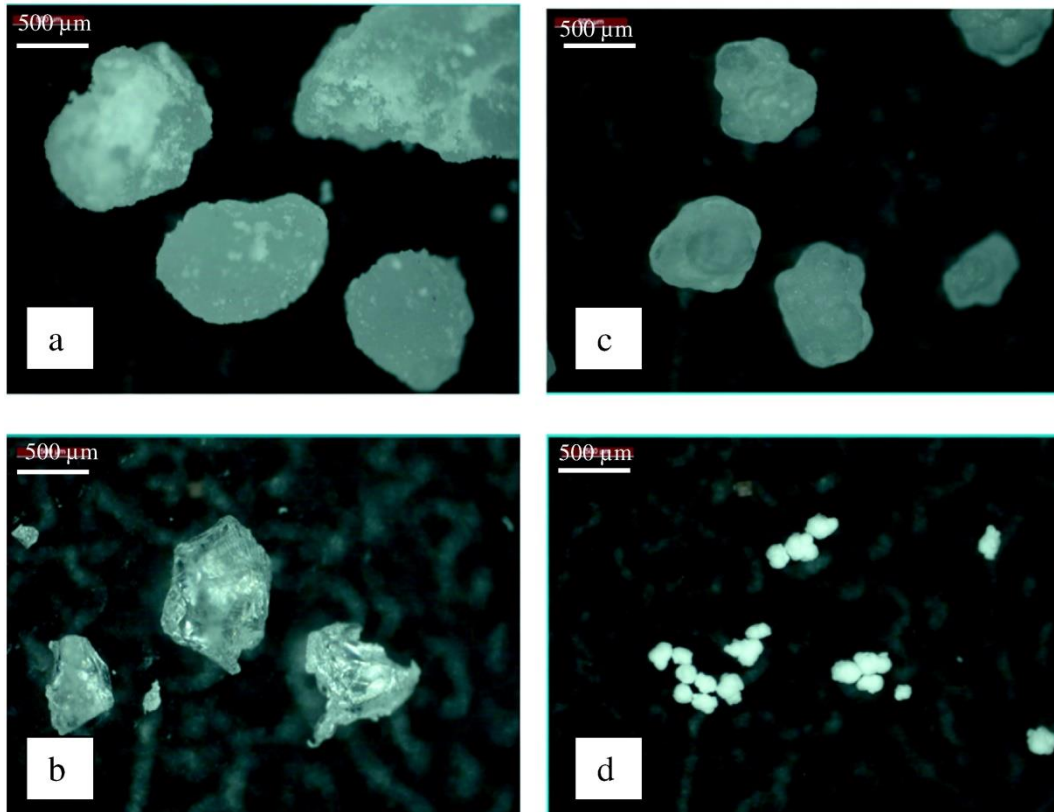


Figure 35 – Optical microscope images of plastic; a) PE b) PET c) PP d) PVC (WANG et al., 2017)

The figure shows pictures of plastic particles under the microscope. The pictures show polyethylene, polyethylene terephthalate, polypropylene and polyvinylchloride. (WANG et al., 2017)

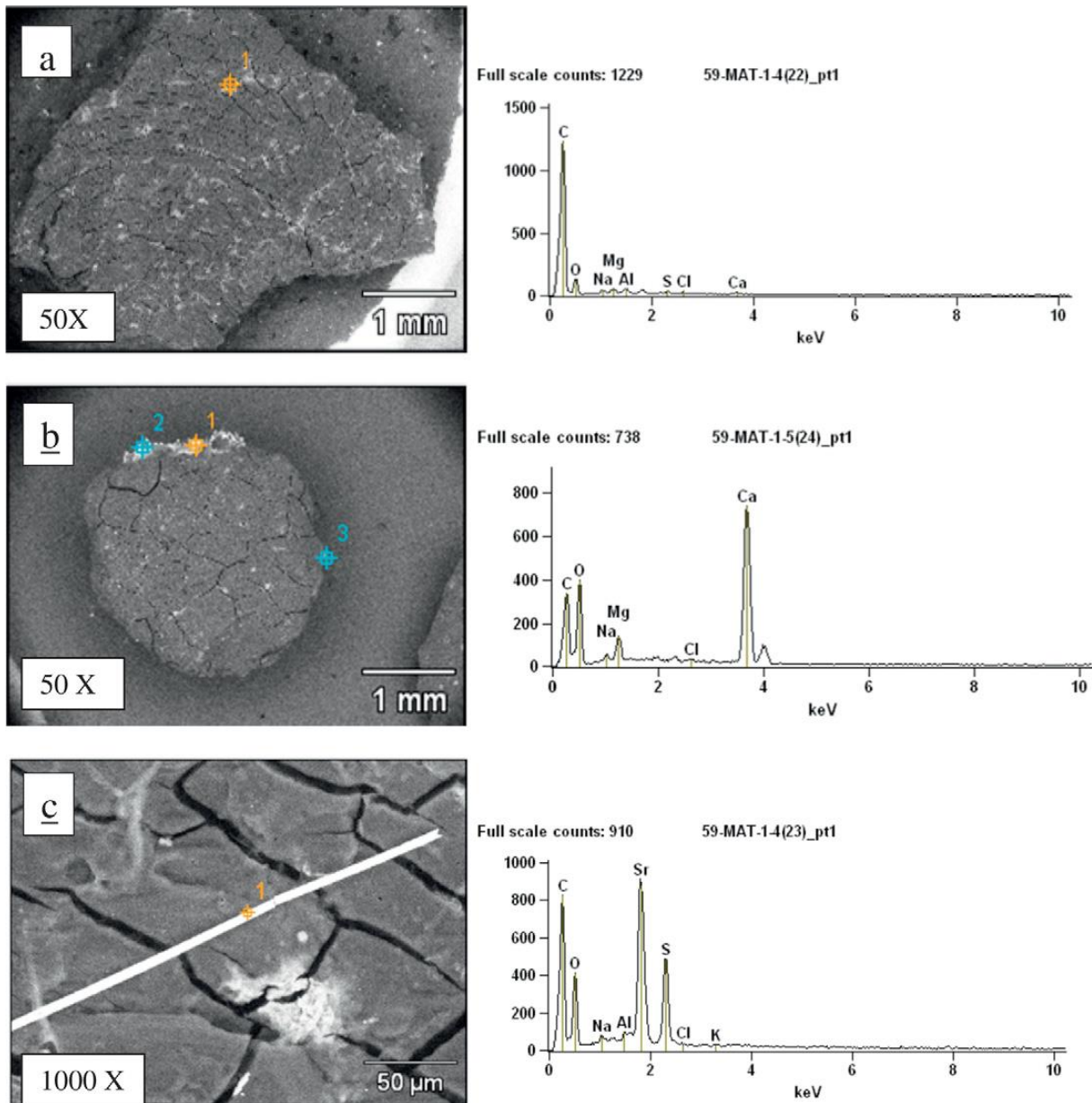


Figure 36 - SEM images of Pacific Ocean trawl micro plastic particles (WANG et al., 2017)

Figure 35 shows SEM images of micro plastic particles from the Pacific Ocean. Due to environmental exposure surface cracks and calcium or magnesium and calcium crusts are visible. (WANG et al., 2017)

4 Results and interpretation

The parameters of the preliminary experiments were chosen by Angelika Pausweg. To get an overview of the process, pyrolysis temperatures from 400 °C to 700 °C were chosen at the muffle furnace. These temperatures correspond to reactor temperatures of 344 °C, 434 °C 525 °C and 615 °C. As reaction time a rather long time of 60 minutes was chosen. (PAUSWEG, 2017)

The parameters of the complementary experiments were based on the results of the preliminary experiments. Because at 344 °C the conversion rate after 60 minutes was rather low, the experiment was repeated with a reaction time of 180 minutes. The experiment at a pyrolysis temperature of 400 °C was carried out because at pyrolysis temperatures from about 400 °C to about 600 °C the waxy product contains a fraction that is solid at room temperature and can block pipes. According to the evaporation curve, this product fraction evaporates at about 400 °C. It is believed that at 400 °C pyrolysis temperature this product does not evaporate and stays in the reactor until it is degraded. Therefore a rather long reaction time of 200 minutes was chosen. A pyrolysis at 615 °C and 60 minutes was carried out to get some product for further experiments like a distillation.

Table 4 - Trial plan for the determination of mass balance and gas composition

Number	Sample	Carried out by
1	Plastic mixture (A) – pyrolyzed at 344 °C and 60 minutes	Angelika Pausweg
2	Plastic mixture (A) – pyrolyzed at 434 °C and 60 minutes	Angelika Pausweg
3	Plastic mixture (A) – pyrolyzed at 525 °C and 60 minutes	Angelika Pausweg
4	Plastic mixture (A) – pyrolyzed at 615 °C and 60 minutes	Angelika Pausweg
5	Sea plastic – pyrolyzed at 344 °C and 60 minutes	Angelika Pausweg
6	Sea plastic – pyrolyzed at 434 °C and 60 minutes	Angelika Pausweg
7	Sea plastic – pyrolyzed at 525 °C and 60 minutes	Angelika Pausweg
8	Sea plastic – pyrolyzed at 615 °C and 60 minutes	Angelika Pausweg
9	Plastic mixture (B) – pyrolyzed at 344 °C and 180 minutes	Josef Holzweber
10	Plastic mixture (B) – pyrolyzed at 400 °C and 200 minutes	Josef Holzweber
11	Plastic mixture (B) – pyrolyzed at 615 °C and 60 minutes	Josef Holzweber

4.1 Mass balance

At the pyrolysis of plastics and plastic mixtures three product fractions are formed: oil or wax, gas and residual substances. To determine the mass balance the input material is weighed before pyrolysis. After pyrolysis the product in the collecting system of the experimental setup is weighed and it is counted as liquid and waxy product. The residue in the pyrolysis reactor is also weighed and counted as ash or residue. The gas is determined by difference calculation. The difference of the mass of the input material and the mass of oil and wax and residues in the reactor is counted as gas.

4.1.1 Pyrolyzed plastic mixture (A) – preliminary experiments

The mass balances and the results of the pyrolysis experiments from the master thesis of Angelika Pausweg are taken over for further calculations and interpretation of the results. The temperatures of the muffle furnace in the diagrams are replaced by the temperatures in the pyrolysis reactor.

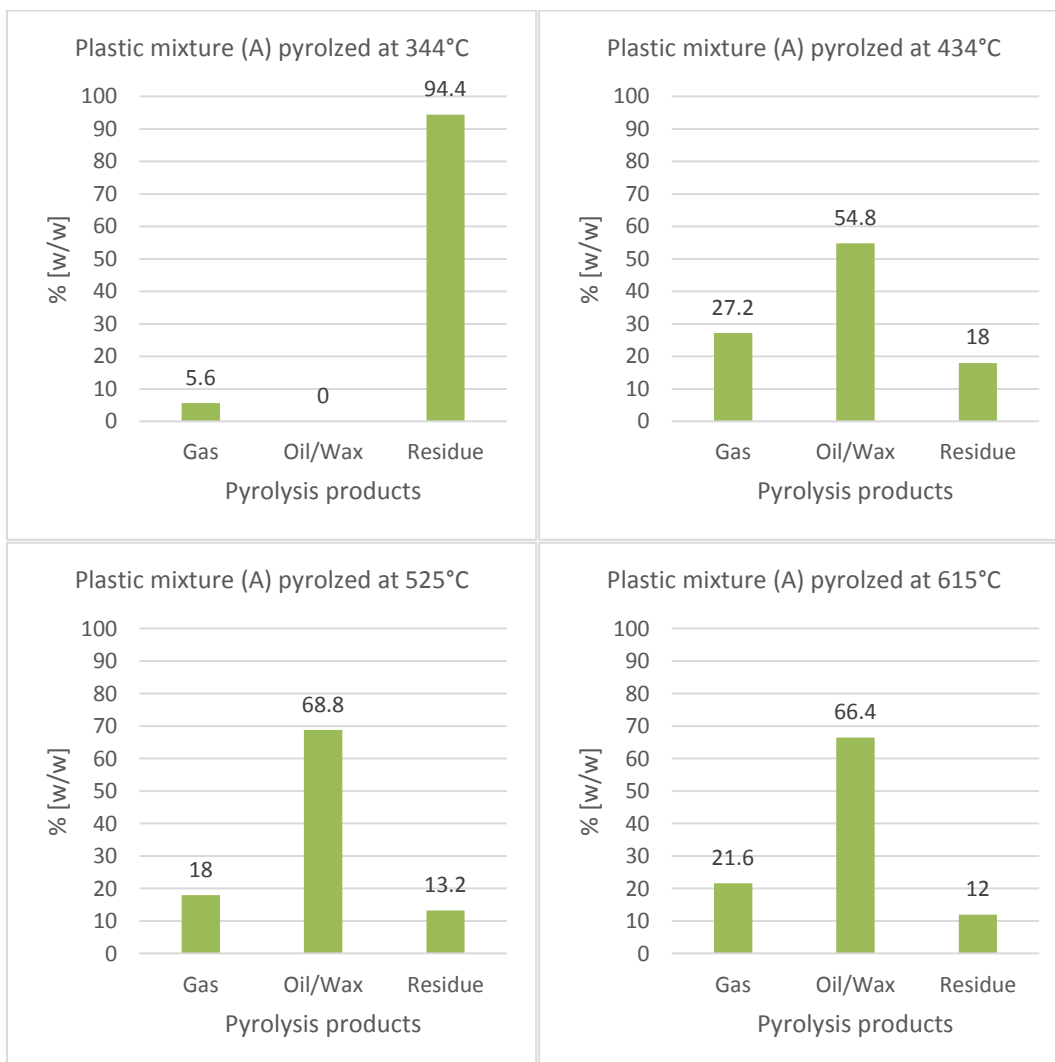


Figure 37 - Mass balances of pyrolysis experiments of the plastic mixture (A) pyrolyzed at 344 °C, 434 °C, 525 °C and 615 °C (PAUSWEG, 2017)

The reaction-time of each experiment was 60 minutes, the reaction temperatures was varied between 344 °C and 615 °C. At 344 °C no oil or wax is produced, the main part is the residue in the reactor. At 434 °C 54.8 % (w/w) of the plastic mixture is converted into oil or wax and only 18 % (w/w) remain as residue, 27.2 % (w/w) are converted into gas. The results of the

two experiments at 525 °C and 615 °C are very similar. The residues and the gas production are also similar in both experiments. (PAUSWEG, 2017)

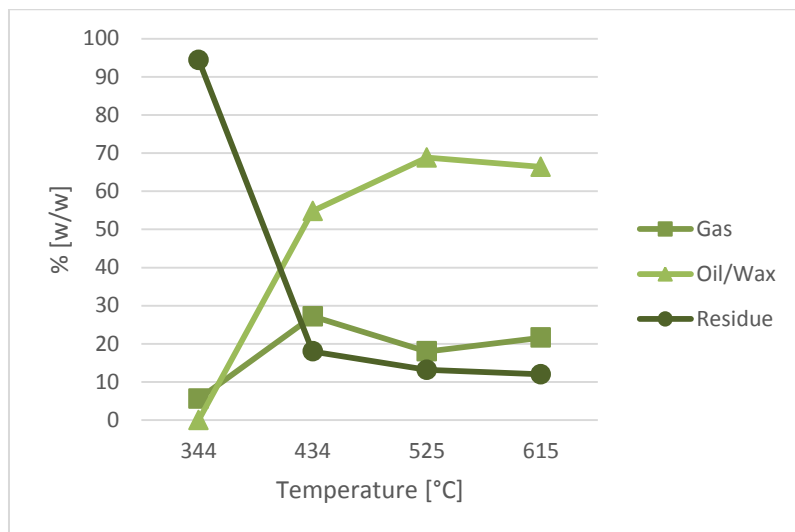


Figure 38 - Comparison of pyrolysis products of the plastic mixture (A) (PAUSWEG, 2017)

With increasing temperature, the amount of the residue in the reactor decreases and the amount of oil and wax increase (PAUSWEG, 2017).

4.1.2 Pyrolyzed sea plastic – preliminary experiments

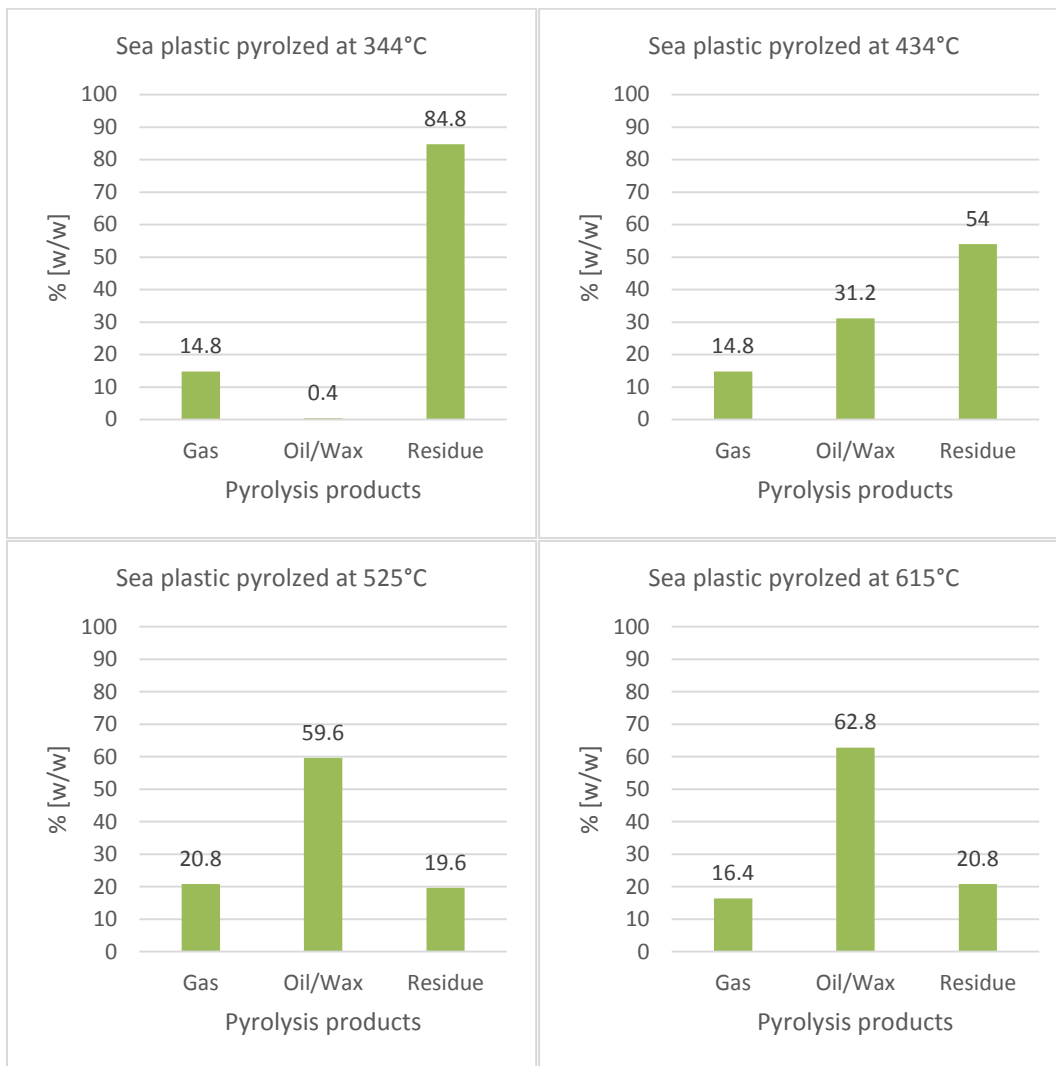


Figure 39 - Mass balances of pyrolysis experiments of sea plastic pyrolyzed at 344 °C, 434 °C, 525 °C and 615 °C (PAUSWEG, 2017)

The reaction-time of each experiment was 60 minutes, the reaction temperatures was varied between 344 °C and 615 °C. At 344 °C only a small amount of liquid product is produced, the main part is again the residue in the reactor. The results of the two experiments at 525 °C and 615 °C are very similar. (PAUSWEG, 2017)

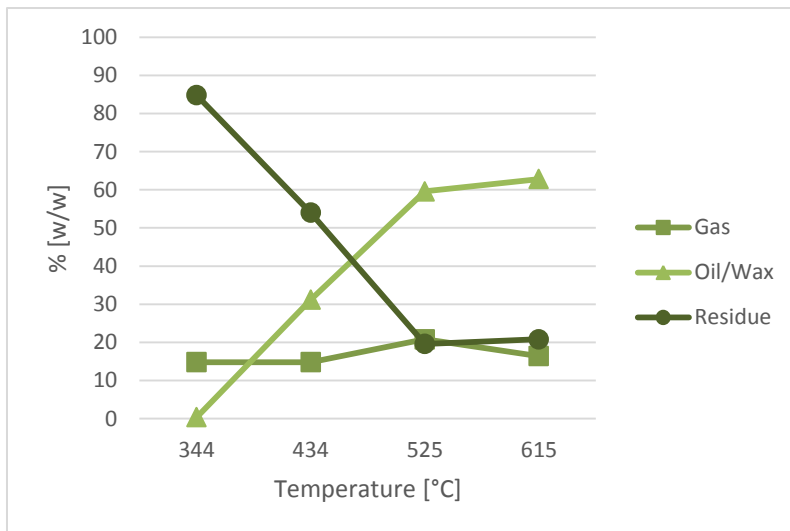


Figure 40 - Comparison of pyrolysis products of sea plastic (PAUSWEG, 2017)

The amount of residue decreases with increasing temperature and the amount of oil and wax increases. The amount of gas remains constant. (PAUSWEG, 2017)

4.1.3 Comparison of plastic mixture (A) and sea plastic

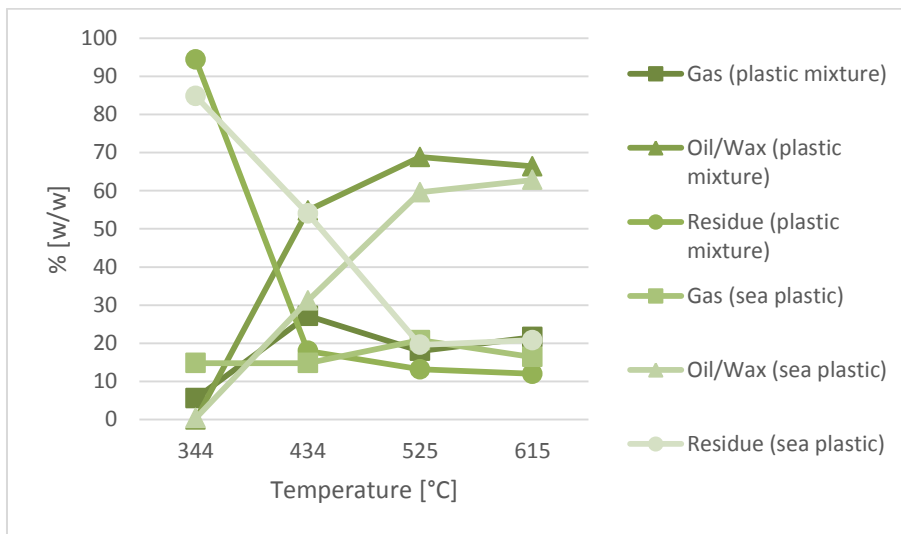


Figure 41 - Comparison of pyrolysis products depending on temperature and feedstock (PAUSWEG, 2017)

Although the sea plastic contains impurities which can't be converted into oil or wax, the results are comparable. With increasing temperature the amount of produced oil/wax and gas increases and the amount of residue decreases. (PAUSWEG, 2017)

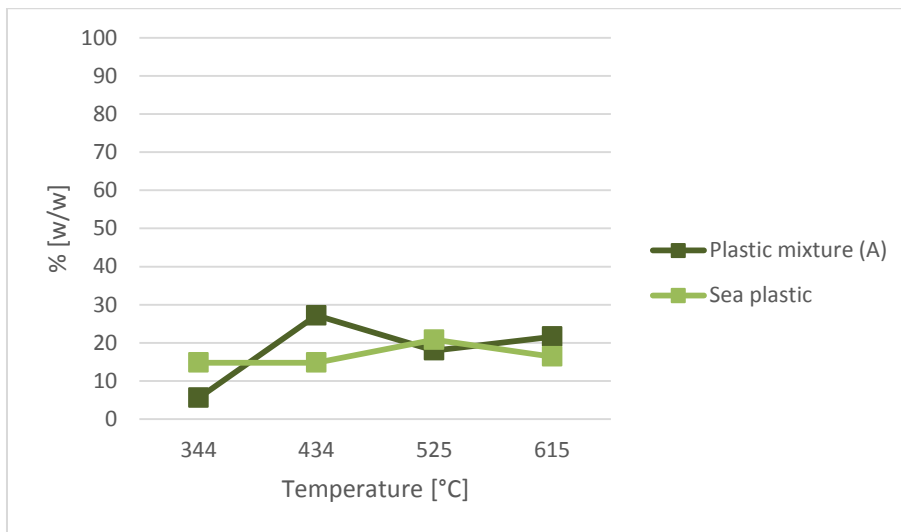


Figure 42 - Comparison of produced gas depending on temperature and feedstock (PAUSWEG, 2017)

The maximal gas production of the plastic mixture is at a reaction temperature of 434 °C. The gas production of the sea plastic varies between 14.8 % (w/w) and 20.8 % (w/w). (PAUSWEG, 2017)

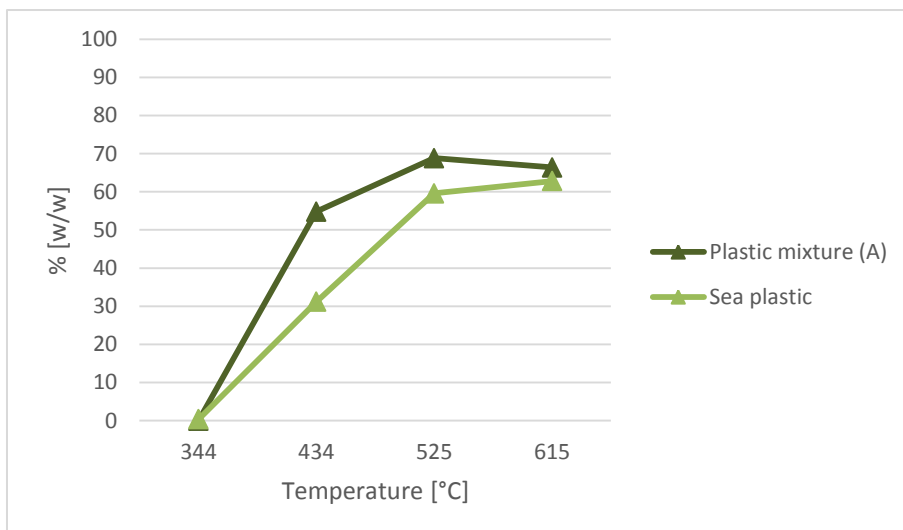


Figure 43 - Comparison of produced oil/wax depending on temperature and feedstock (PAUSWEG, 2017)

Generally nearly no oil or wax is produced at a pyrolysis temperature of 344 °C, neither at the sea plastic nor at the plastic mixture. The wax and oil production increases with an increasing temperature. (PAUSWEG, 2017)

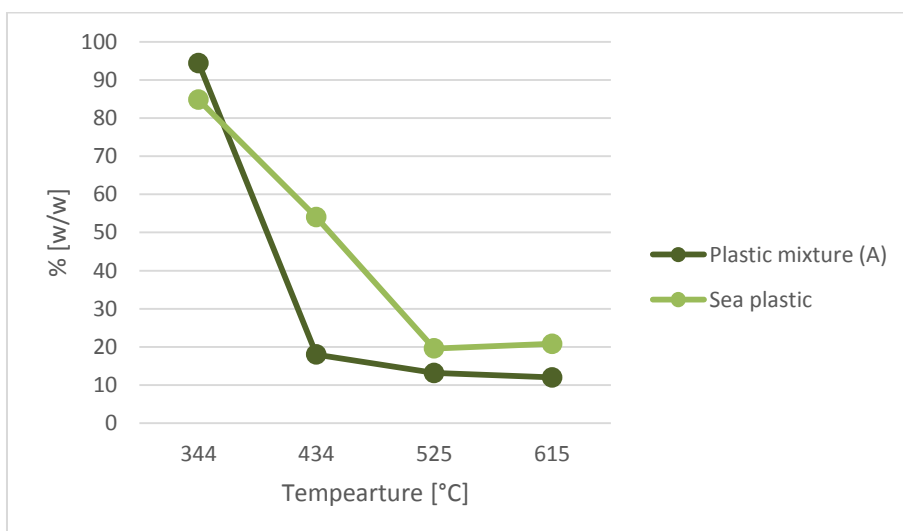


Figure 44 - Comparison of residues depending on temperature and feedstock (PAUSWEG, 2017)

The amount of residue in the reactor decreases with increasing reaction temperature. Generally more residue remains in the reactor at the pyrolysis experiments with the sea plastic due to a higher amount of impurities which can't be converted into pyrolysis gas or oil and wax. (PAUSWEG, 2017)

4.1.3.1 Interpretation

The results show, that higher pyrolysis temperatures lead to a lower amount of residues in the reactor and a higher yield of oil and wax. Higher temperatures than 525 °C do not lead to a significant increase in the amount of oil and wax and higher temperatures do not lead to a significant decrease of residue in the reactor. However the influence of the temperature on the composition of the liquid and gaseous products is not determined.

4.1.4 Pyrolyzed plastic mixture (B) – complementary experiments

4.1.4.1 Plastic mixture (B) pyrolyzed at 344 °C – 180 minutes

Based on the experiments of Angelika Pausweg further experiments were carried out. The preliminary experiments showed that pyrolysis temperatures at about 434 °C and a reaction time of 60 minutes lead to the formation of a solid and brittle product, whose consistency is similar to that of chocolate at room temperature. The evaporation curve of this experiment shows that this fraction evaporates at about 400 °C.

The first experiment was also carried out at a pyrolysis temperature of 344 °C like the preliminary experiments but with a reaction time of 180 minutes.

The assumption was, that a longer reaction time at a lower temperature leads to a degradation of the plastic and the formation of short chained hydrocarbons but no formation of the solid fraction because at this temperature this fraction does not evaporate and stays in the reaction chamber.

High density polyethylene begins to degrade at temperatures around 350 °C (AHMAD et al., 2014) (CZAJCZYNSKA et al., 2017) and polypropylene degrades at 300 °C (AHMAD et al., 2014). The degradation of polyvinylchloride starts at about 200 °C (MA et al., 2002) and the degradation of polystyrene starts at 350 °C (ONWUDILI et al., 2009).

According to literature most plastics start degrading at a temperature of about 350 °C.

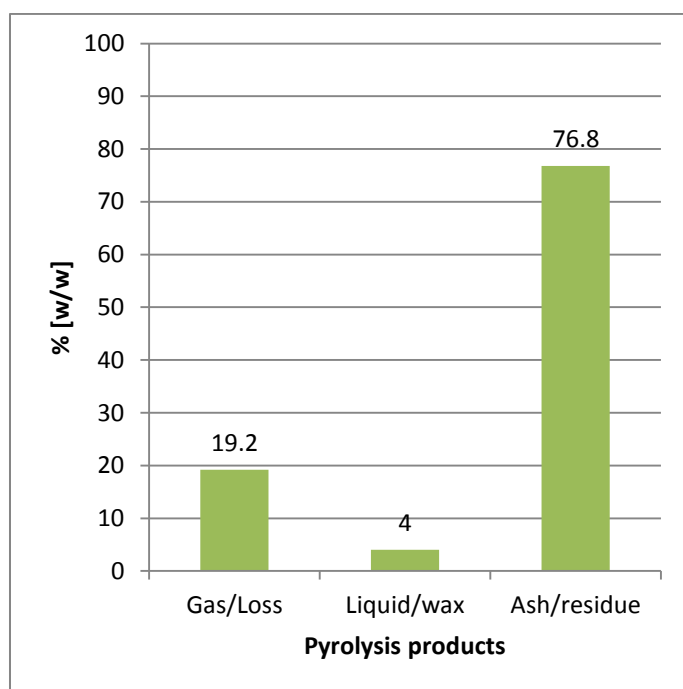


Figure 45 - Mass balance of the plastic mixture (B) pyrolyzed at 344 °C – 180 minutes

The mass balance shows that only 4 % (w/w) of the product are converted into a liquid or waxy fraction, 76.8 % (w/w) are ash or residue and 19.2 % (w/w) are in the gas fraction or get lost because of small leaks in the system and incomplete condensation of the liquid fraction.

Because 94.4 % (w/w) of the plastic mixture is not converted after 60 minutes (PAUSWEG, 2017) and still 76.8 % (w/w) of the plastic mixture is not converted after 180 minutes this temperature seems not to be suitable for pyrolysis.

Because at this temperature no pyrolysis is observed but water evaporates, temperatures of about 110 °C are suitable as drying step.

4.1.4.2 Plastic mixture (B) pyrolyzed at 400 °C – 200 minutes

Because the pyrolysis experiment at 344 °C and 180 minutes reaction time showed, that there is no sufficient product yield observed, the next experiment was carried out at 400°C. This is the boiling temperature of the solid and brittle product fraction. It was assumed, that a higher reaction temperature lead to an increased product yield but that the solid and brittle product fraction does not evaporate at this temperature. The reaction time of this experiment was 200 minutes, whereby the heating of the muffle furnace took 30 minutes, the temperature holding phase took 90 minutes and a cooling phase of 80 minutes was included.

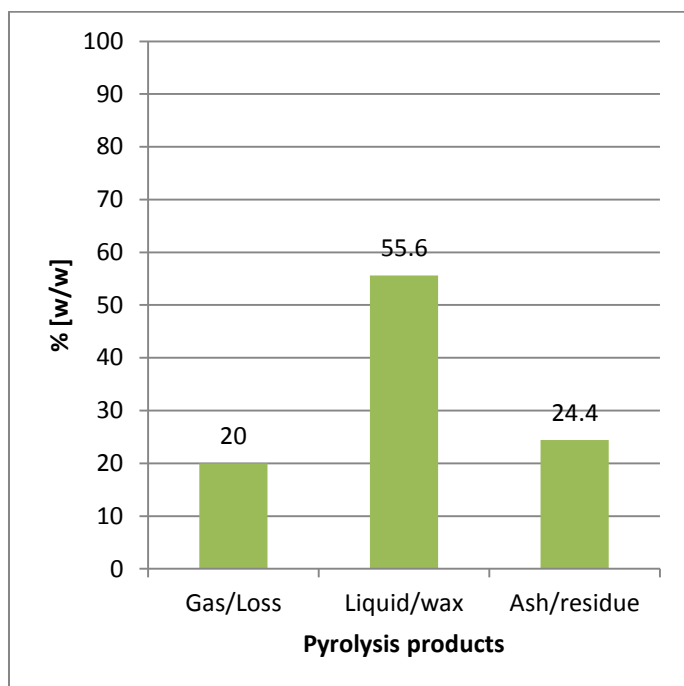


Figure 46 - Mass balance of the plastic mixture (B) pyrolyzed at 400 °C – 200 minutes

At 400 °C 55.6 % (w/w) are converted into a liquid or waxy product, whereby 32.8 % (w/w) of the product are collected in the first collecting tube as a solid product and 22.8 % (w/w) are collected in the second collecting vessel as a waxy or liquid product. 24.4 % (w/w) remain as ash or residue in the reactor and 20 % (w/w) are gas or loss.



Figure 47 - Plastic mixture (B) pyrolyzed at 344 °C - solid/brittle fraction (left), waxy/liquid fraction (right)

4.1.4.3 Plastic mixture (B) pyrolyzed at 615 °C

Because at the pyrolysis at 400 °C still 24.4 % (w/w) remained as ash or residue after 200 minutes in the reactor, this temperature is not suitable for the pyrolysis of the plastic mixture. Further a high amount of the product was a chocolate-like substance with a rather high boiling point of about 400 °C according to the evaporation curve (see point 4.7.4.2).

The assessment of products of the preliminary experiments of Angelika Pausweg showed that at a pyrolysis temperature of 434 °C also a high amount of a chocolate-like high boiling fraction was produced. At a pyrolysis temperature of 525 °C there was still a small amount of this fraction in the liquid and waxy product. Because this high boiling fraction causes problems due to blockage of the pipes of the reactor, no experiments with these temperatures were performed.

At a pyrolysis temperature of 615 °C there is no high boiling product fraction formed according to the evaporation curve (see point 4.7.3.4). The pyrolysis experiment at a temperature of 615 °C and 60 minutes was repeated with the plastic mixture (B) to compare the two plastic mixtures and to measure the temperature profile of the experiment.

According to the evaporation curve of the pyrolysis of the plastic mixture (A) at a pyrolysis temperature of 615 °C it is possible to simply distil the liquid and waxy product fraction and get a high grade product.

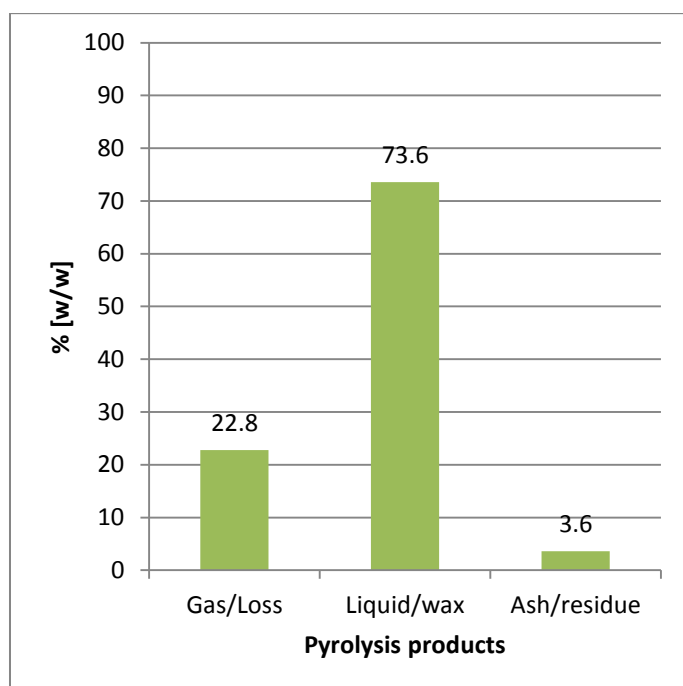


Figure 48 - Mass balance of the plastic mixture (B) pyrolyzed at 615 °C – 60 minutes

The results of the pyrolysis of the plastic mixture (B) at 615 °C are similar to the results of the pyrolysis of the plastic mixture (A) at 615 °C. The amount of ash and residue is clearly lower and the amount of the liquid or waxy fraction is higher.

Only 3.6 % (w/w) remain as ash or residue in the reactor and 22.8 % (w/w) are converted into gas or get lost. 73.6 % (w/w) of the plastic mixture (B) are converted into a liquid or wax.

4.2 Gas composition

The gas composition of the pyrolysis gas was analysed during the pyrolysis experiment with an online gas measuring device. The recorded gases were CO₂, CO and CH₄.

Note: Theoretically, the device can also detect hydrogen, but negative values were displayed. It is assumed that there are disturbances of the detector due to other pyrolysis gases.

4.2.1 Pyrolyzed plastic mixture (A) – preliminary experiments

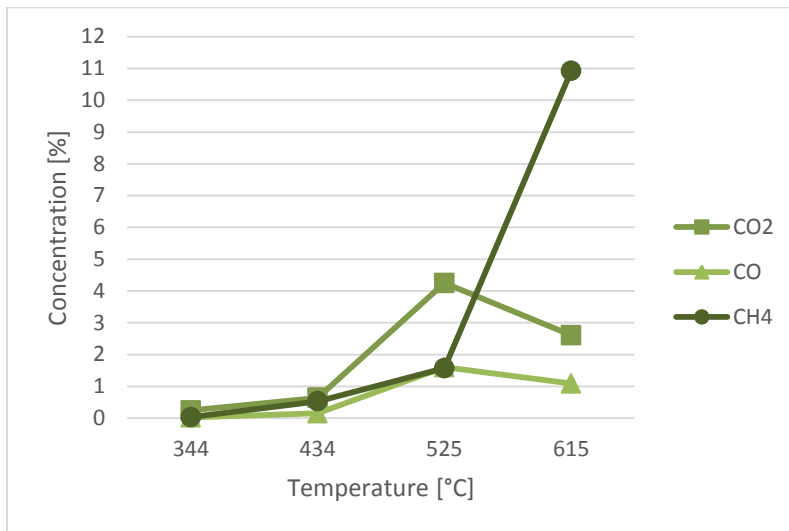


Figure 49 - Gas composition of the pyrolyzed plastic mixture (A) (PAUSWEG, 2017)

With increasing temperatures, the gas concentrations increase. At 615 °C the CH₄-concentration increases rapidly by a decreasing CO₂- and CO-concentration. (PAUSWEG, 2017)

4.2.2 Pyrolyzed sea plastic – preliminary experiments

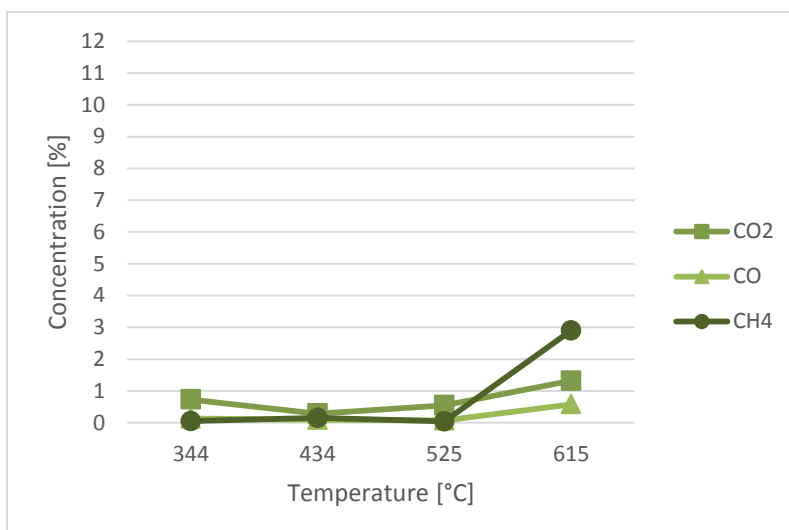


Figure 50 - Gas composition of pyrolyzed sea plastic (PAUSWEG, 2017)

Like at the experiments with the plastic mixture the CH₄-concentration increases at 615 °C (PAUSWEG, 2017).

4.2.3 Pyrolyzed plastic mixture (B) – complementary experiments

At the complementary experiments additionally to the concentration of the pyrolysis gases, the amount of produced gas was recorded with a gas flowmeter. By multiplying the gas concentration and the gas flow and dividing the result by the mass of the feedstock, the standard cubic meters per kg feedstock are calculated.

4.2.3.1 Plastic mixture (B) pyrolyzed at 344 °C – 180 minutes

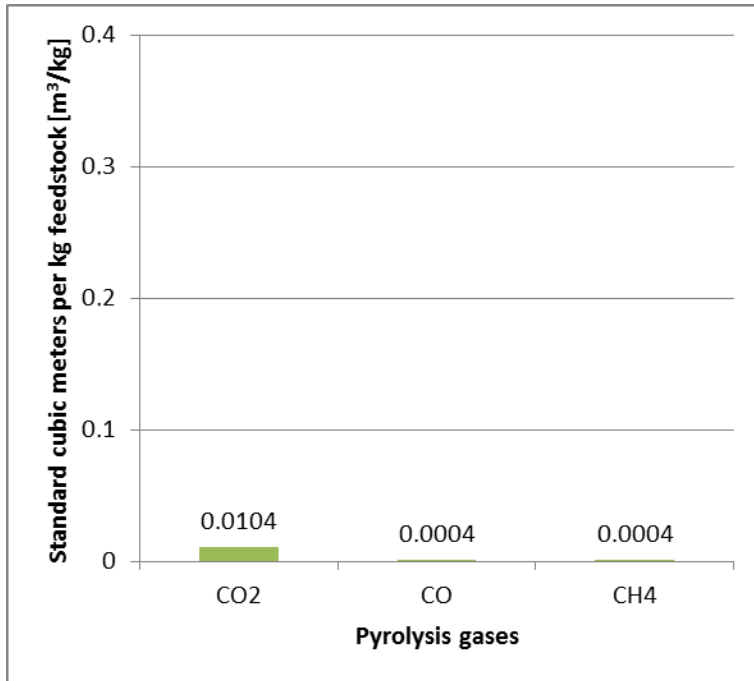


Figure 51 - Gas composition of the plastic mixture (B) pyrolyzed at 344 °C

At a pyrolysis temperature of 344 °C and a reaction time of 180 minutes 0.0104 standard cubic meters of CO₂, 0.0004 standard cubic meters of CO and 0.0004 standard cubic meters of CH₄ are produced per kg feedstock. It is possible that other gases are produced, but they can not be detected by the gas measuring device.

4.2.3.2 Plastic mixture (B) pyrolyzed at 400 °C – 200 minutes

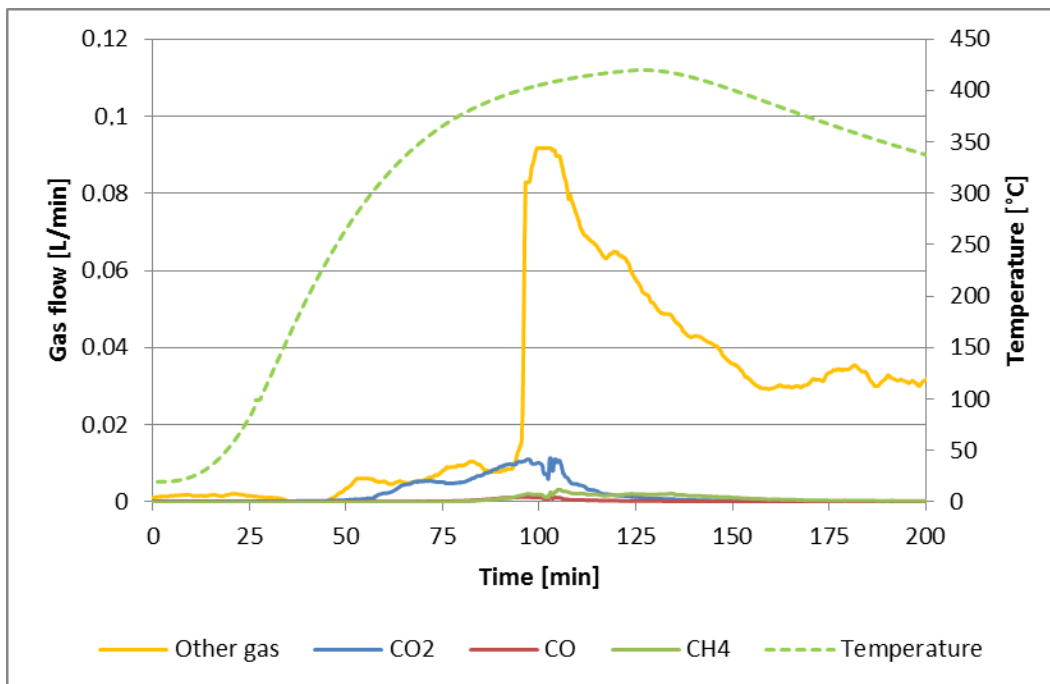


Figure 52 - Gas composition real time measurement – plastic mixture (B) pyrolyzed at 400 °C

The diagram shows a real time measurement of the produced gases. The dotted green line shows the temperature curve inside the reactor. The blue line shows produced CO₂, the red line CO and the green line CH₄. The yellow line shows the volume flow of other gases that are produced but can not be detected by the gas measuring device like short chained hydrocarbons. This curve is calculated by subtracting the gas volume flow of the detectable gases from the total gas volume flow.

Because the reactor takes some time to heat up, the gas production also starts delayed. The figure shows, that only small amounts of CO and CH₄ are produced. The production of CO₂ starts after 55 minutes and ends after 110 minutes. The production of undetectable gas starts after 45 minutes but it rises suddenly after 95 minutes. At this time the temperature reaches nearly 400 °C in the reactor. This could be an indicator that some kind of reaction starts at 400 °C or any substance evaporates at this temperature and releases a high amount of gas.

The production of gas still goes on after 200 minutes. This indicates that the reaction has not finished yet.

In this case a batch reactor is used. In a continuous reactor the temperature and the gas composition will reach an equilibrium state, in which they remain constant.

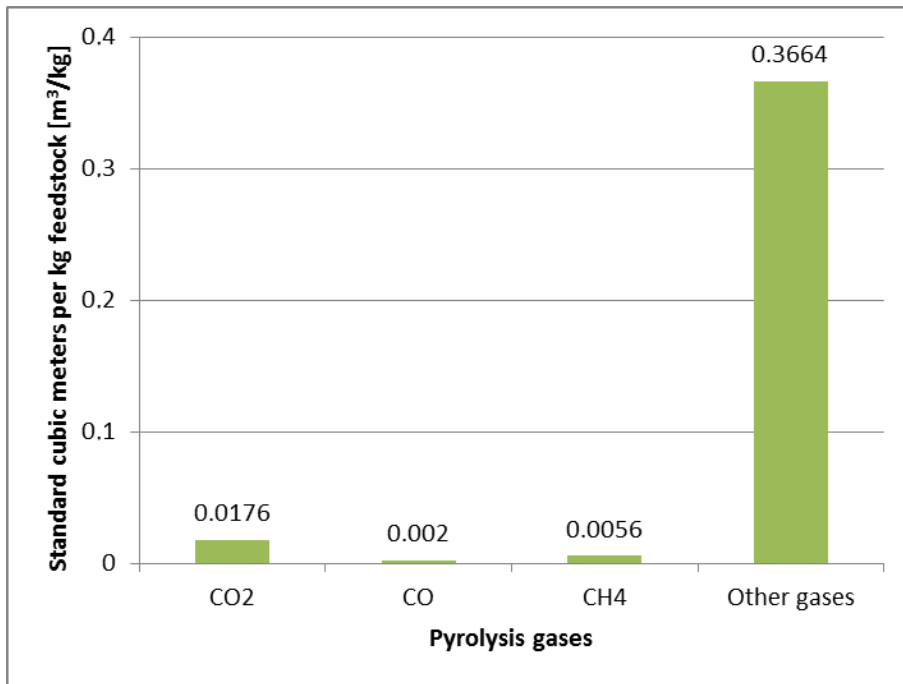


Figure 53 - Gas composition of the plastic mixture (B) pyrolyzed at 400 °C

At a pyrolysis temperature of 400 °C and a total reaction time of 200 minutes 0.0176 standard cubic meters of CO₂, 0.002 standard cubic meters of CO, 0.0056 standard cubic meters of CH₄ and 0.3664 standard cubic meters of other gas, that can not be detected by the gas measuring device, are produced per kg feedstock.

4.2.3.3 Plastic mixture (B) pyrolyzed at 615 °C

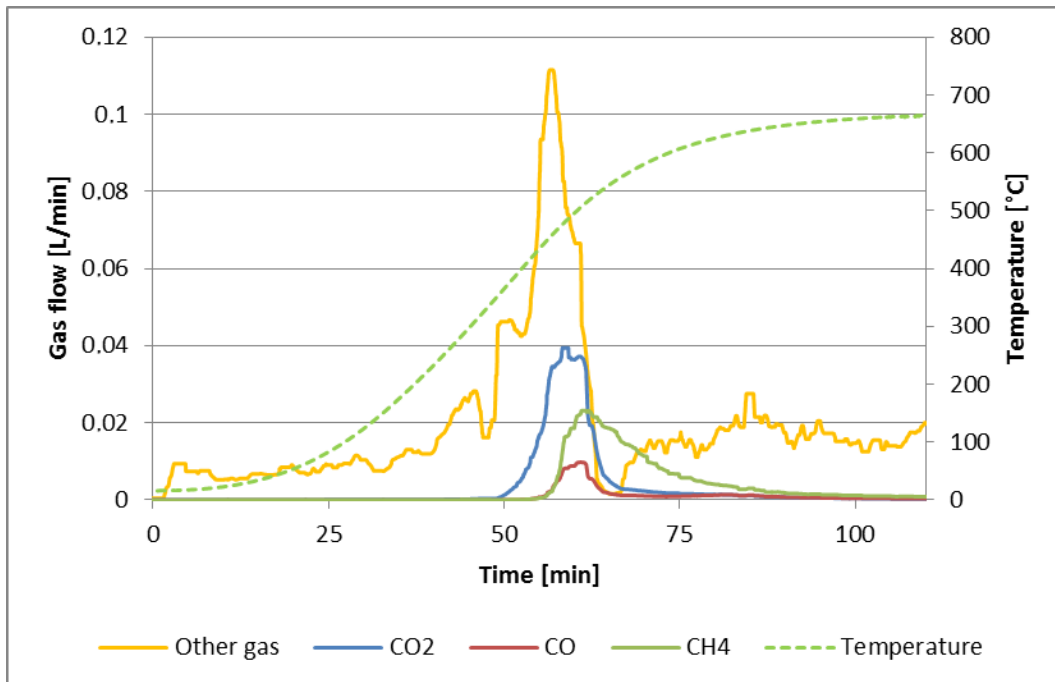


Figure 54 - Gas composition real time measurement – plastic mixture (B) pyrolyzed at 615 °C

The diagram shows that the production of CO₂ starts after 50 minutes and ends after about 65 minutes. At this time the reactor temperature is between 400 °C and 550 °C. The release of CO₂ indicates the decomposition of PET. The production of CO and CH₄ starts after 55 minutes. Again the production of undetectable gas starts very early but rises suddenly after about 53 minutes. At this time the reactor reaches the 400 °C mark. The production of other gas goes down to a minimum at 62 minutes and then goes on again. At this time the temperature of the reactor is about 520 °C.

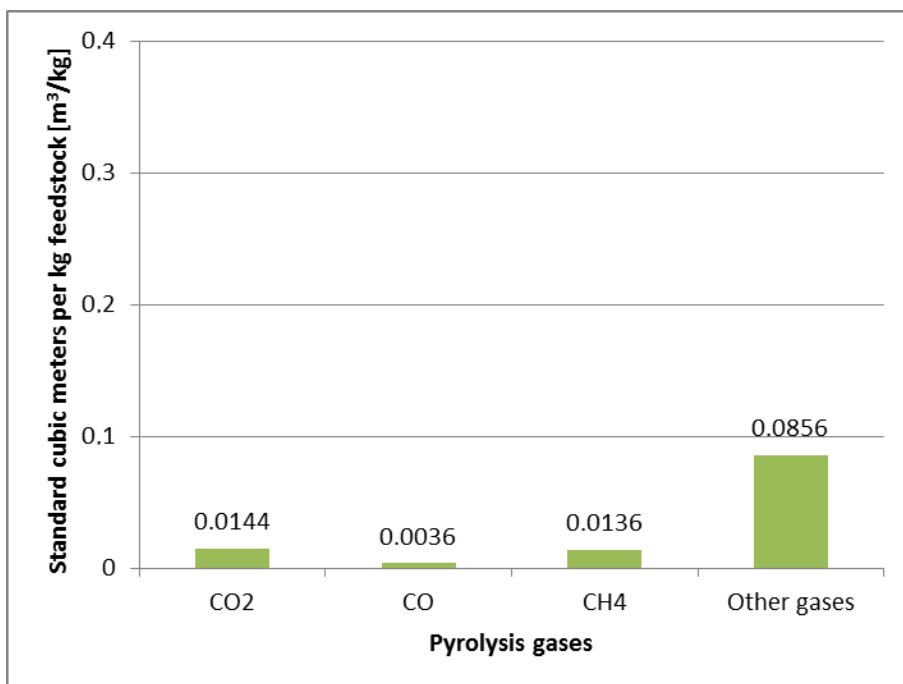


Figure 55 - Gas composition of the plastic mixture (B) pyrolyzed at 615 °C

At a pyrolysis temperature of 615 °C 0.0144 standard cubic meters of CO₂ are produced per kg feedstock, 0.0036 standard cubic meters of CO, 0.0136 standard cubic meters of CH₄ and 0.0856 standard cubic meters of other gas.

The production of CO₂ and CO is nearly the same as in the experiment with a pyrolysis temperature of 400 °C. The amount of produced CH₄ has gone up and the amount of produced other gases that can not be detected has gone down.

Compared with the experiment at 400 °C the total volume of produced gas goes down at a pyrolysis temperature of 615 °C but according to the mass balances of these two experiments the mass of the produced gas has gone up at pyrolysis temperature of 615 °C. This indicates that the average molar mass of the produced gases at 615 °C has become higher.

4.3 Appearance

The appearance is an easy determinable characteristic, which can give a lot of information like the colour, macroscopically visible impurities, water inclusions, particles and the aggregate state at room temperature. The determination was carried out visually after transferring the sample into a sample vessel. For comparison diesel and petrol are used as reference.

Generally, fuels should be clear and bright. (Verordnung des Bundesministers für Land- und Forstwirtschaft, Umwelt und Wasserwirtschaft über die Qualität von Kraftstoffen und die nachhaltige Verwendung von Biokraftstoffen (Kraftstoffverordnung 2012). In: BGBl. II Nr. 398/2012, 2012)

Table 5 - Trial plan for the determination of appearance

Number	Sample	Note	Sample-ID
1	Petrol (Reference)		
2	Diesel (Reference)		
3	Plastic mixture (A) – pyrolyzed at 344 °C and 60 minutes	no sample available	V19-20171017-PP
4	Plastic mixture (A) – pyrolyzed at 434 °C and 60 minutes		V18-20171019-PP
5	Plastic mixture (A) – pyrolyzed at 525 °C and 60 minutes		V20-20171018-PP
6	Plastic mixture (A) – pyrolyzed at 615 °C and 60 minutes		V14-20171012-PP
7	Sea plastic– pyrolyzed at 344 °C and 60 minutes	no sample available	V21-20171019-MP
8	Sea plastic– pyrolyzed at 434 °C and 60 minutes		V27-20171031-MP
9	Sea plastic– pyrolyzed at 525 °C and 60 minutes		V26-20171031-MP
10	Sea plastic– pyrolyzed at 615 °C and 60 minutes		V25-20171030-MP
11	Plastic mixture (B) – pyrolyzed at 344 °C and 180 minutes		HV3-20171220-liquid/wax
12	Plastic mixture (B) – pyrolyzed at 400 °C and 200 minutes	mixture of solid/hard and liquid/waxy product	HV4-20180110-liquid/wax_3
13	Plastic mixture (B) – pyrolyzed at 400 °C and 200 minutes	solid/hard product	HV4-20180110-liquid/wax_1
14	Plastic mixture (B) – pyrolyzed at 400 °C and 200 minutes	liquid/waxy product	HV4-20180110-liquid/wax_2
15	Plastic mixture (B) – pyrolyzed at 615 °C and 60 minutes		HV5-20180116-liquid/wax
16	Plastic mixture (B) – pyrolyzed at 615 °C and 60 minutes	distilled at 250 °C	HV5-20180116-distillate_oil

4.3.1 Petrol and diesel – references



Figure 56 - Petrol (left) and Diesel (right)

Petrol (left) is crystal clear and transparent. It is slightly yellowish, liquid and homogenous. There are no visible impurities in it.

Diesel (right) is crystal clear and transparent. It is yellow, liquid and homogenous. There are no visible impurities.

4.3.2 Pyrolyzed plastic mixture (A) – preliminary experiments



Figure 57 - Plastic mixture (A) pyrolyzed at 434 °C (left), 525°C (middle) and 615°C (right)

The plastic mixture (A) pyrolyzed at 434 °C (left) is opaque, light brown and not liquid at room temperature. The consistency is pasty and inhomogenous. The sample contains visible impurities and lumps.

The plastic mixture (A) pyrolyzed at 525 °C (middle) is opaque, dark brown and not liquid at room temperature. The consistency is pasty and homogenous. There are no visible impurities in it.

The plastic mixture (A) pyrolyzed at 615 °C (right) is identical with the plastic mixture pyrolyzed at 525 °C. It is opaque, dark brown and not liquid at room temperature. The consistency is pasty and homogenous. There are no visible impurities in it.

4.3.3 Pyrolyzed sea plastic – preliminary experiments



Figure 58 - Sea plastic pyrolyzed at 434°C (left), 525°C (middle) and 615°C (right)

The sea plastic pyrolyzed at 434 °C (left) is opaque, brown and not liquid at room temperature. The consistency is pasty and inhomogenous. The sample contains visible impurities like black particles and liquid inclusions.

The sea plastic pyrolyzed at 525 °C (middle) is opaque, brown and not liquid at room temperature. The consistency is pasty and inhomogenous. The sample contains visible liquid inclusions.

The sea plastic pyrolyzed at 615 °C (right) is identical with the sea plastic pyrolyzed at 525 °C. It is opaque, brown and not liquid at room temperature. The consistency is pasty and inhomogenous. The sample contains visible liquid inclusions.

4.3.4 Pyrolyzed plastic mixture (B) – complementary experiments

4.3.4.1 Plastic mixture (B) – pyrolyzed at 344 °C and 180 minutes

Ash/residue



Figure 59 - Residue of the plastic mixture (B) pyrolyzed at 344 °C and 180 minutes

The pyrolysis residue of the plastic mixture (B) pyrolyzed at 344 °C and 180 minutes is solid and dark brown. It consists mainly of molten plastic. The feedstock is not completely converted.

Liquid/waxy product

The liquid or waxy product of this experiment is separated into two phases. One phase is liquid, yellow and transparent and the other phase is tarry, brown and opaque.

4.3.4.2 Plastic mixture (B) – pyrolyzed at 400 °C and 200 minutes

Ash/residue



Figure 60 - Residue of the plastic mixture (B) pyrolyzed at 400 °C and 200 minutes

The pyrolysis residue of the plastic mixture (B) pyrolyzed at 400 °C and 200 minutes is waxy and brown. The feedstock is not completely converted.

Liquid/waxy product

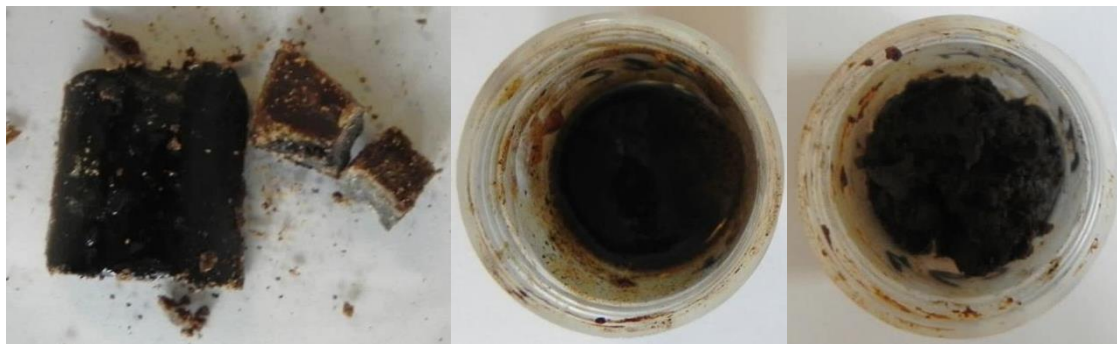


Figure 61 - Plastic mixture (B) pyrolyzed at 400 °C and 200 minutes - solid/hard product fraction (left), liquid/waxy product fraction (middle), mixture of both fractions (right)

At the pyrolysis of the plastic mixture (B) at 400 °C and 200 minutes two fractions are produced. One fraction is solid and hard and the other fraction is liquid and waxy. The solid fraction is opaque, brown, brittle and not wax-like. The liquid/waxy fraction is viscous, brown and opaque. It contains black lumps and other impurities.

For further characterization, the two fractions are mixed. The mixture of these two fractions is brown, opaque and pasty.

4.3.4.3 Plastic mixture (B) – pyrolyzed at 615 °C and 60 minutes

Ash/residue



Figure 62 - Residue of plastic mixture (B) pyrolyzed at 615 °C and 60 minutes

The pyrolysis residue of the plastic mixture (B) pyrolyzed at 615 °C and 60 minutes is black, brittle and porous. It seems that the feedstock is completely converted into a gaseous or liquid and waxy product but the black colour of the residue indicates that it still contains a lot of carbon, which could be used as fuel.

Liquid/waxy product



Figure 63 - Liquid/waxy product of plastic mixture (B) pyrolyzed at 615 °C

The liquid/waxy product of the plastic mixture (B) pyrolyzed at 615 °C is dark brown, opaque and not liquid at room temperature. The consistency is pasty and homogenous. There are no visible impurities in it.

4.3.4.4 Plastic mixture (B) – pyrolyzed at 615 °C and 60 minutes, distilled at 250 °C



Figure 64 - Plastic mixture (B) pyrolyzed at 615 °C, distilled at 250 °C

At the pyrolysis at 615 °C 73.6 % (w/w) of the feedstock could be recovered as liquid/waxy product. This fraction is distillation at 250 °C. At the distillation 13.4 % (w/w) of the liquid/waxy product could be recovered as oil and 67.2 % (w/w) remained as wax. The rest (19.4 % (w/w)) could not be recovered. (see point 4.8.2)

After distillation of the pyrolyzed plastic mixture (B) at 250 °C, the sample is yellow, liquid, clear and transparent and there are no visible impurities in it. At the bottom of the sample vial water has separated.

4.4 Density

The density is an important material property. It is related with the composition of a material. The density of the samples is determined by weighing a defined volume and calculation. The density is compared with the two references diesel and petrol.

Table 6 - Determination of density

Number	Sample	Density	Sample-ID
1	Petrol (Reference)	0.749 kg/L	V19-20171017-PP
2	Diesel (Reference)	0.831 kg/L	V18-20171019-PP
3	Plastic mixture (A) – pyrolyzed at 344 °C and 60 minutes	no sample available	V20-20171018-PP
4	Plastic mixture (A) – pyrolyzed at 434 °C and 60 minutes	0.890 kg/L	V14-20171012-PP
5	Plastic mixture (A) – pyrolyzed at 525 °C and 60 minutes	0.872 kg/L	V21-20171019-MP
6	Plastic mixture (A) – pyrolyzed at 615 °C and 60 minutes	0.849 kg/L	V27-20171031-MP
7	Sea plastic – pyrolyzed at 344 °C and 60 minutes	no sample available	V26-20171031-MP
8	Sea plastic – pyrolyzed at 434 °C and 60 minutes	0.826 kg/L	V25-20171030-MP
9	Sea plastic – pyrolyzed at 525 °C and 60 minutes	0.843 kg/L	V19-20171017-PP
10	Sea plastic – pyrolyzed at 615 °C and 60 minutes	0.842 kg/L	V18-20171019-PP

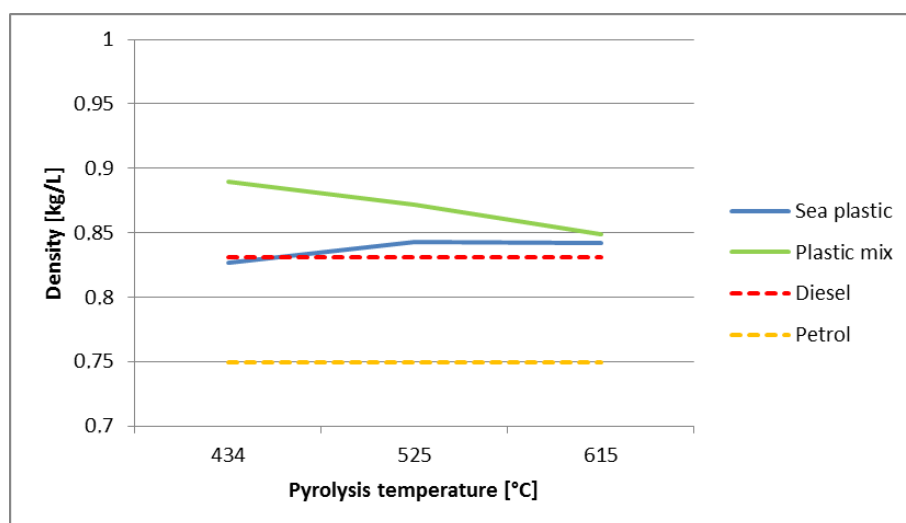


Figure 65 - Density of pyrolyzed plastic products

The results show that the density of the pyrolyzed plastic mixture (A) decreases with increasing pyrolysis temperature. At a pyrolysis temperature of 615 °C the density of the product is very close to the density of diesel.

The density of the pyrolyzed sea plastic is lowest at a pyrolysis temperature of 434 °C. The density at a pyrolysis temperature of 525 °C and 615 °C is nearly the same and it is very close to the density of diesel.

The results show, that the density of the oil/wax product fraction gets very close to the density of diesel at a pyrolysis temperature of 615 °C. It seems that there is a difference in the composition of the pyrolysis products at 525 °C and 615 °C although they are macroscopically identical.

4.5 Pour point

The pour point indicates at which temperature the sample solidifies. This is an important material characteristic of fuels because if it is too high it can lead to a blockage of fuel pipes. Furthermore, it is related to the composition of the fuel. The pour point is determined by heating the sample, cooling it down stepwise and determining the pour point visually.

Table 7 - Determination of pour point

Number	Sample	Pour Point	Sample-ID
1	Diesel (Reference)	-15 – -35 °C (SONG et al., 2000)	V19-20171017-PP
2	Plastic mixture (A) – pyrolyzed at 344 °C and 60 minutes	no sample available	V18-20171019-PP
3	Plastic mixture (A) – pyrolyzed at 434 °C and 60 minutes	> 85 °C	V20-20171018-PP
4	Plastic mixture (A) – pyrolyzed at 525 °C and 60 minutes	> 85 °C	V14-20171012-PP
5	Plastic mixture (A) – pyrolyzed at 615 °C and 60 minutes	50 – 55 °C	V21-20171019-MP
6	Sea plastic – pyrolyzed at 344 °C and 60 minutes	no sample available	V27-20171031-MP
7	Sea plastic – pyrolyzed at 434 °C and 60 minutes	50 – 55 °C	V26-20171031-MP
8	Sea plastic – pyrolyzed at 525 °C and 60 minutes	60 – 70 °C	V25-20171030-MP
9	Sea plastic – pyrolyzed at 615 °C and 60 minutes	> 85 °C	V19-20171017-PP

The pour point of common diesel is about -15 to -35 °C to avoid freezing in fuel pipes (SONG et al., 2000).

All samples are pasty at room temperature. At the pyrolyzed plastic mixture (A) the pour point goes down with increasing pyrolysis temperature, at the pyrolyzed sea plastic it goes up with increasing pyrolysis temperature. In this case the composition of the feedstock seems to have a big influence on the pour point.

Nevertheless all pyrolysis products have to be further worked up to suitable as fuels.

4.6 Flash point

The flash point indicates at which temperature flammable gases are formed. As reference the flash point of diesel is determined. The flash point is determined by heating the sample stepwise and igniting it, the temperature at which flammable gases are formed is the flash point.

Table 8 - Determination of flash point

Number	Sample	Flash point	Sample-ID
1	Diesel (Reference)	65 – 70 °C	V19-20171017-PP
2	Plastic mixture (A) – pyrolyzed at 344 °C and 60 minutes	no sample available	V18-20171019-PP
3	Plastic mixture (A) – pyrolyzed at 434 °C and 60 minutes	> 85 °C	V20-20171018-PP
4	Plastic mixture (A) – pyrolyzed at 525 °C and 60 minutes	75 – 80 °C	V14-20171012-PP
5	Plastic mixture (A) – pyrolyzed at 615 °C and 60 minutes	65 – 75 °C	V21-20171019-MP
6	Sea plastic – pyrolyzed at 344 °C and 60 minutes	no sample available	V27-20171031-MP
7	Sea plastic – pyrolyzed at 434 °C and 60 minutes	75 – 80 °C	V26-20171031-MP
8	Sea plastic – pyrolyzed at 525 °C and 60 minutes	75 – 85 °C	V25-20171030-MP
9	Sea plastic – pyrolyzed at 615 °C and 60 minutes	70 – 75 °C	V19-20171017-PP

Generally the flashpoint of the samples goes down with increasing pyrolysis temperature. The flash point of the pyrolyzed plastic mixture (A) pyrolyzed at 615 °C is very similar to the flashpoint of diesel.

4.7 Evaporation curve and qualitative valuation by mass spectrometry

The evaporation curve shows the evaporation characteristics of the sample. It allows an estimate of the efficiency of the pyrolysis because short chained hydrocarbons evaporate earlier than long chained hydrocarbons. Additionally a mass spectrum is recorded, that shows specific mass-to-charge ratios of alkanes, alkenes, branched alkanes and aromatics.

According to the quality criteria of fuels (see point 2.4) the evaporation residues at 70 °C, 100 °C and 150 °C are of interest at petrol and the evaporation residues at 250 °C, 350 °C and 360 °C are of interest at diesel. Therefore the evaporation residues at these temperatures are listed. A direct comparison of the evaporation residues according to the quality criteria of fuels and the results of the evaporation curve can not be done because the quality criteria of fuels deals with volume percent and the results are in mass percent.

Table 9 - Determination of evaporation curve and mass spectrum

Number	Sample	Note	Sample-ID
1	Petrol (Reference)		
2	Diesel (Reference)		
3	Plastic mixture (A) – pyrolyzed at 344 °C and 60 minutes	no sample available	V19-20171017-PP
4	Plastic mixture (A) – pyrolyzed at 434 °C and 60 minutes		V18-20171019-PP
5	Plastic mixture (A) – pyrolyzed at 525 °C and 60 minutes		V20-20171018-PP
6	Plastic mixture (A) – pyrolyzed at 615 °C and 60 minutes		V14-20171012-PP
7	Sea plastic– pyrolyzed at 344 °C and 60 minutes		V21-20171019-MP
8	Sea plastic– pyrolyzed at 434 °C and 60 minutes		V27-20171031-MP
9	Sea plastic– pyrolyzed at 525 °C and 60 minutes		V26-20171031-MP
10	Sea plastic– pyrolyzed at 615 °C and 60 minutes		V25-20171030-MP
11	Plastic mixture (B) – pyrolyzed at 344 °C and 180 minutes		HV3-20171220-liquid/wax
12	Plastic mixture (B) – pyrolyzed at 400 °C and 200 minutes	mixture of solid/hard and liquid/waxy product	HV4-20180110-liquid/wax_3
13	Plastic mixture (B) – pyrolyzed at 400 °C and 200 minutes	solid/hard product	HV4-20180110-liquid/wax_1
14	Plastic mixture (B) – pyrolyzed at 400 °C and 200 minutes	liquid/waxy product	HV4-20180110-liquid/wax_2
15	Plastic mixture (B) – pyrolyzed at 615 °C and 60 minutes		HV5-20180116-liquid/wax
16	Plastic mixture (B) – pyrolyzed at 615 °C and 60 minutes	distilled at 250 °C	HV5-20180116-distillate_oil

4.7.1 Evaporation curve and mass spectrum of the references

4.7.1.1 Evaporation curve and mass spectrum of diesel

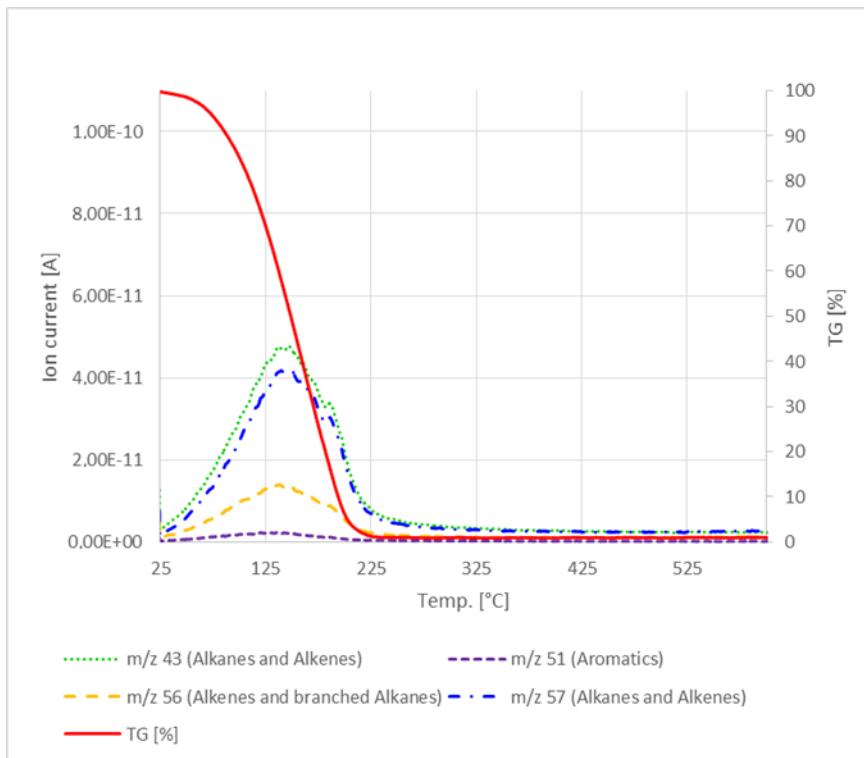


Figure 66 - Evaporation curve and mass spectrum of diesel

Table 10 - Evaporation residue of diesel

Temperature	Evaporation residue
70 °C	95.6 % (w/w)
100 °C	85.2 % (w/w)
150 °C	49.1 % (w/w)
250 °C	1.0 % (w/w)
350 °C	0.9 % (w/w)
360 °C	0.9 % (w/w)

The diagram shows the evaporation curve of diesel (red line). At 150 °C 50.9 % (w/w) of the sample are evaporated and at 250 °C 99.0 % (w/w) are evaporated.

All four indicator mass-to-charge ratios show a clear signal.

The signal of the mass-to-charge ratio 43 (green line) and 57 (blue line) both indicate the presence of alkanes and alkenes. The signal of the mass-to-charge ratio 56 (yellow line) which indicate alkenes and branched alkanes is about one-third as high as the signal m/z 43 and m/z 57. The signal of the mass-to-charge ratio 51 (purple line) which indicates aromatics is very low. This indicates a low amount of aromatics.

4.7.1.2 Evaporation curve and mass spectrum of petrol

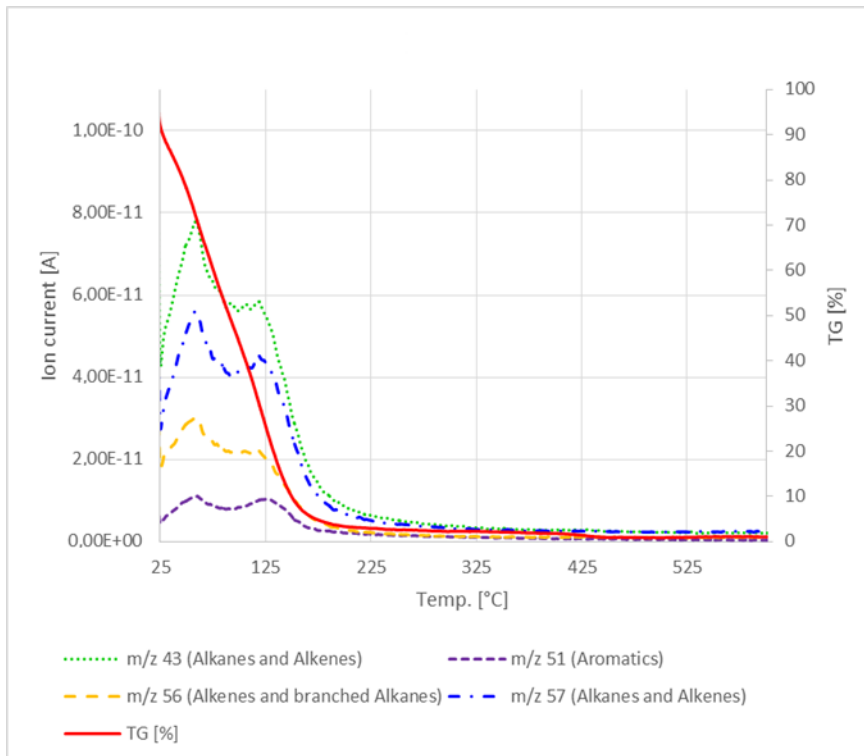


Figure 67 - Evaporation curve and mass spectrum of petrol

Note: The evaporation curve of petrol does not start at 100 % (w/w) because petrol is a very volatile substance which partially evaporates at room temperature. The samples are weighed in at 20 °C (room temperature) and the TGA has a starting temperature of 25 °C. Therefore a certain part of the sample has evaporated when the device starts the measurement.

Table 11 - Evaporation residue of petrol

Temperature	Evaporation residue
70 °C	64.0 % (w/w)
100 °C	44.0 % (w/w)
150 °C	9.9 % (w/w)
250 °C	2.6 % (w/w)
350 °C	2.1 % (w/w)
360 °C	2.0 % (w/w)

This diagram shows the evaporation curve of petrol (red line). At 100 °C already 56.0 % (w/w) of the sample are evaporated. At 150 °C 90.1 % (w/w) are evaporated and at 250 °C 97.6 % (w/w) are evaporated.

In this case of petrol the signal of the mass-to-charge ratio 43 (green line) is clearly higher than the signal of the mass-to-charge ratio 57 (blue line). The signal of the mass-to-charge ratio 56 (yellow line) is about one half as high as the signal of m/z 57. The signal of the mass-to-charge ratio 51 (purple line) is much higher than the signal of diesel, which indicates a higher amount of aromatics in petrol.

4.7.2 Evaporation curve and mass spectrum of the pyrolyzed plastic mixture (A) – preliminary experiments

4.7.2.1 Evaporation curve and mass spectrum of the liquid/waxy product of the plastic mixture (A) pyrolyzed at 344 °C

There has not formed enough liquid/waxy product from the pyrolysis experiment of the plastic mixture (A) at a pyrolysis temperature of 344 °C to record an evaporation curve. Therefore the experiment is repeated at the complementary experiments with a longer reaction time.

4.7.2.2 Evaporation curve and mass spectrum of the liquid/waxy product of the plastic mixture (A) pyrolyzed at 434 °C

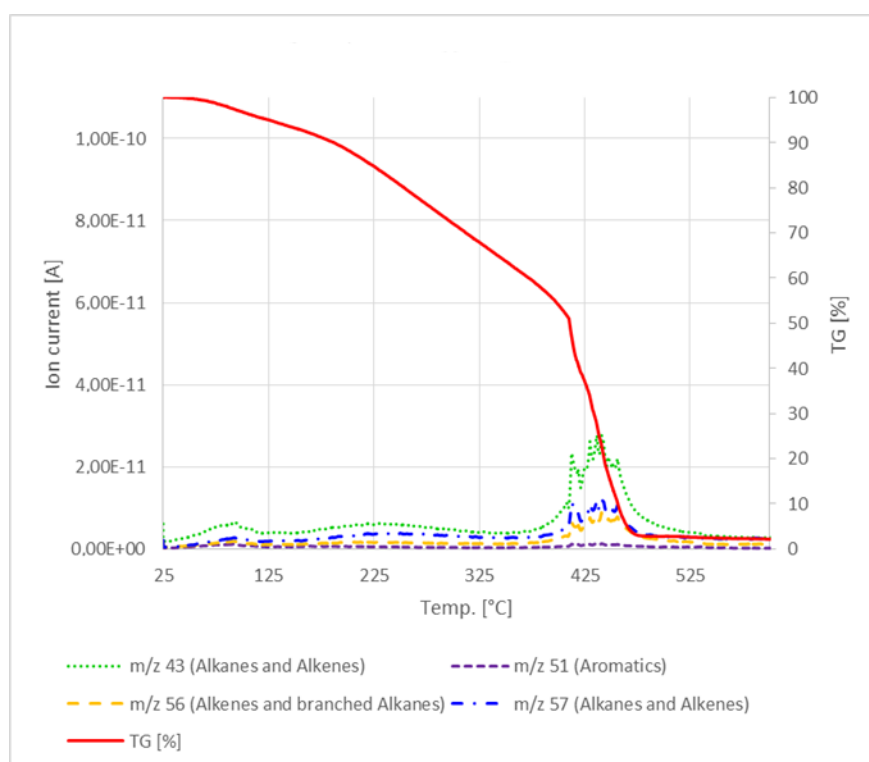


Figure 68 - Evaporation curve and mass spectrum of the liquid/waxy product of the plastic mixture (A) pyrolyzed at 434 °C

Table 12 - Evaporation residue of the liquid/waxy product of the plastic mixture (A) pyrolyzed at 434 °C

Temperature	Evaporation residue
70 °C	99.0 % (w/w)
100 °C	96.8 % (w/w)
150 °C	93.2 % (w/w)
250 °C	80.6 % (w/w)
350 °C	63.7 % (w/w)
360 °C	62.1 % (w/w)

The evaporation curve of the plastic mixture (A) pyrolyzed at 434 °C (red line) shows that only a small amount of the sample has been converted into volatile substances. At 150 °C

only 6.8 % (w/w) are evaporated and at 250 °C only 19.4 % (w/w) are evaporated. At 400 °C the sample evaporates abruptly.

All four indicator mass-to-charge ratios show a clear signal. The signals rise abruptly as the sample evaporates at 400 °C. This shows that the non-volatile fraction of the sample still contains hydrocarbons.

4.7.2.3 Evaporation curve and mass spectrum of the liquid/waxy product of the plastic mixture (A) pyrolyzed at 525 °C

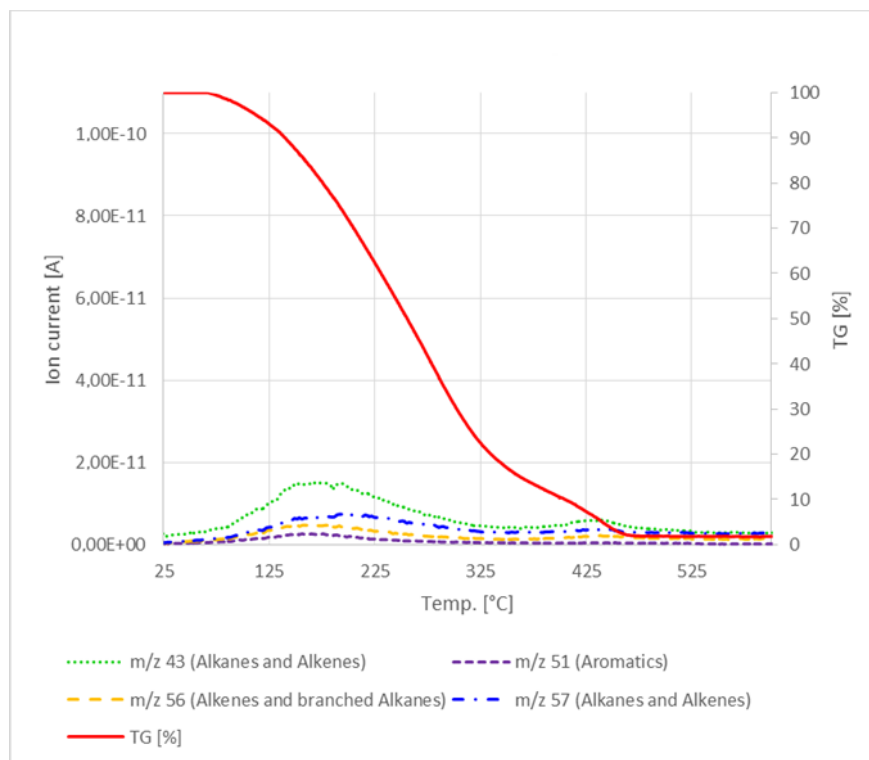


Figure 69 - Evaporation curve and mass spectrum of the liquid/waxy product of the plastic mixture (A) pyrolyzed at 525 °C

Table 13 - Evaporation residue of the liquid/waxy product of the plastic mixture (A) pyrolyzed at 525 °C

Temperature	Evaporation residue
70 °C	96.7 % (w/w)
100 °C	90.8 % (w/w)
150 °C	79.1 % (w/w)
250 °C	40.9 % (w/w)
350 °C	5.3 % (w/w)
360 °C	3.8 % (w/w)

At a pyrolysis temperature of 525 °C the evaporation curve of the pyrolysis product (red line) is nearly evenly distributed. There is only a small amount with an evaporation temperature higher than 400 °C. At 150 °C 20.9 % (w/w) of the sample are evaporated and at 250 °C 59.9 % (w/w) are evaporated.

All four indicator mass-to-charge ratios show a clear signal but the signal is much lower than the signal of diesel or petrol.

4.7.2.4 Evaporation curve and mass spectrum of the liquid/waxy product of the plastic mixture (A) pyrolyzed at 615 °C

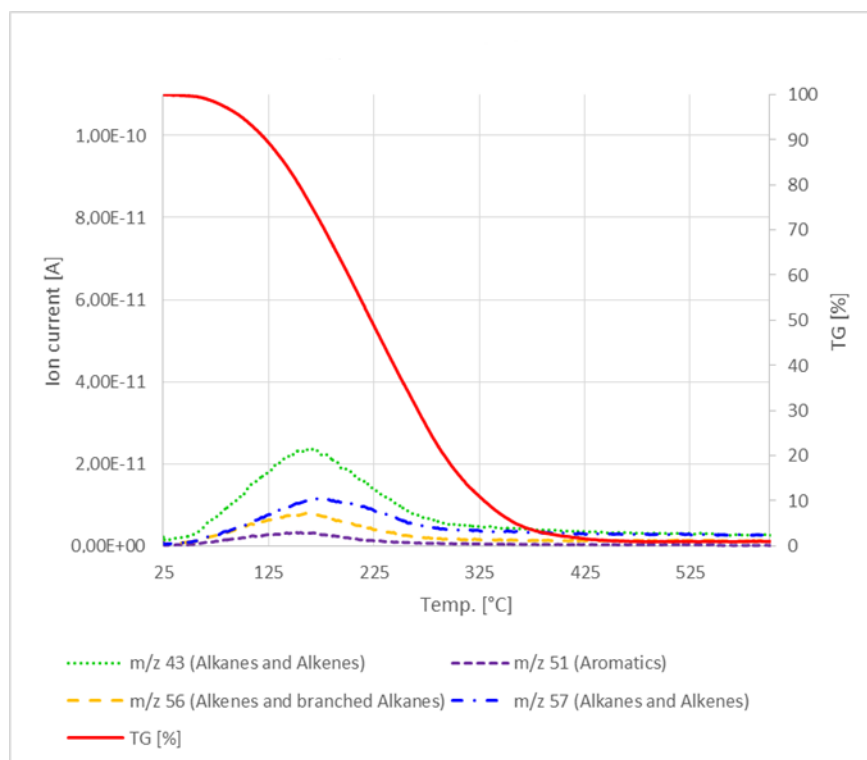


Figure 70 - Evaporation curve and mass spectrum of the liquid/waxy product of the plastic mixture (A) pyrolyzed at 615 °C

Table 14 - Evaporation residue of the liquid/waxy product of the plastic mixture (A) pyrolyzed at 615 °C

Temperature	Evaporation residue
70 °C	98.7 % (w/w)
100 °C	94.9 % (w/w)
150 °C	81.5 % (w/w)
250 °C	37.3 % (w/w)
350 °C	6.3 % (w/w)
360 °C	4.9 % (w/w)

At a pyrolysis temperature of 615 °C the evaporation curve of the pyrolysis product (red line) is evenly distributed. Nearly the whole sample is evaporation at 400 °C. At 150 °C 18.5 % (w/w) of the sample are evaporated and at 250 °C 63.7 % (w/w) are evaporated.

All four indicator mass-to-charge ratios show a clear signal. With increasing pyrolysis temperature the signals of the indicator mass-to-charge ratios increase too. The ratios of the signals to each other are similar to the ratios of the signals to each other of petrol. Compared with diesel the mass-to-charge ratio 57 (blue line) is much lower. This signal indicates alkanes and long chained alkenes.

4.7.2.5 H₂O (m/z 18) in the liquid/waxy product of the pyrolyzed plastic mixture (A)

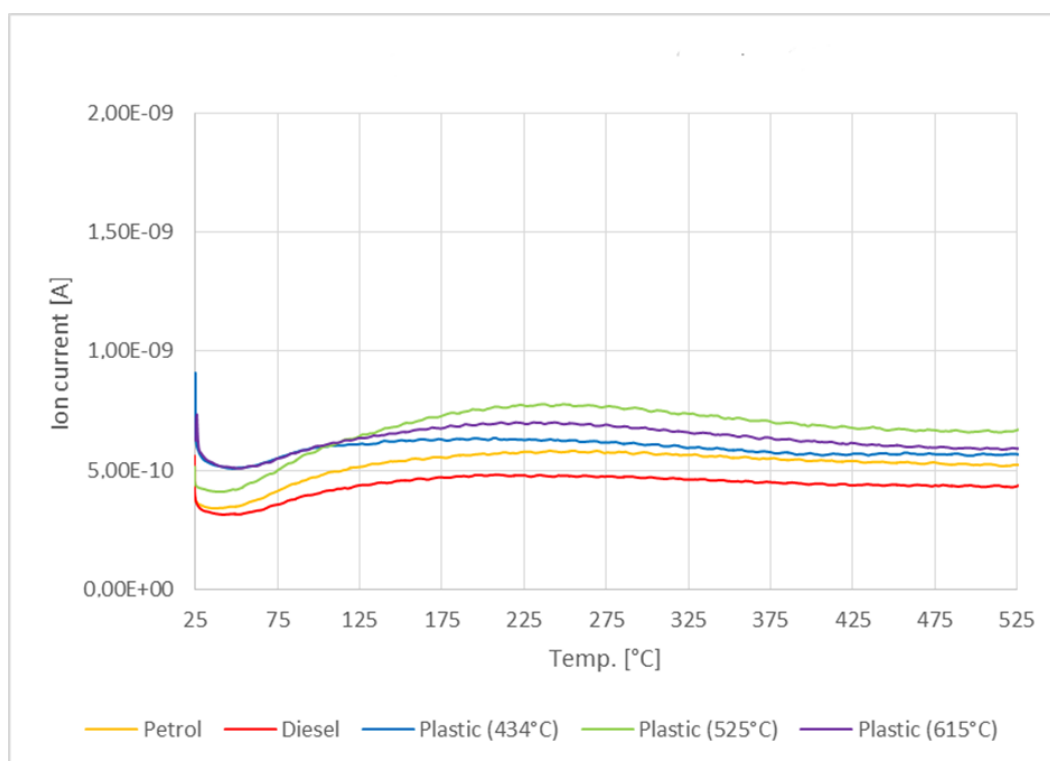


Figure 71 - H₂O (m/z 18) in the liquid/waxy product of the pyrolyzed plastic mixture (A)

This diagram shows the signal of the mass-to-charge ratio 18 of petrol, diesel and the liquid/waxy product of the plastic mixture (A) pyrolyzed at 434 °C, 525 °C and 615 °C. The mass-to-charge ratio 18 indicates water. There is no peak visible in the signals, which means there is no water expected in the samples.

4.7.3 Evaporation curve and mass spectrum of the pyrolyzed sea plastic – preliminary experiments

4.7.3.1 Evaporation curve and mass spectrum of the liquid/waxy product of the sea plastic pyrolyzed at 344 °C

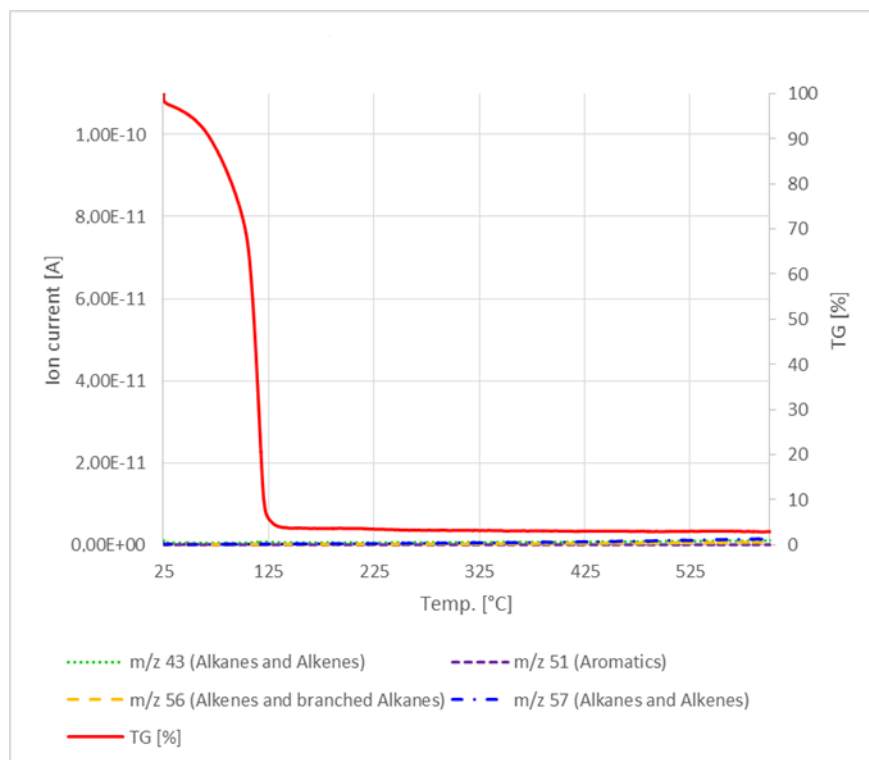


Figure 72 - Evaporation curve and mass spectrum of the liquid/waxy product of the sea plastic pyrolyzed at 344 °C

Table 15 - Evaporation residue of the liquid/waxy product of the sea plastic pyrolyzed at 344 °C

Temperature	Evaporation residue
70 °C	89.9 % (w/w)
100 °C	72.8 % (w/w)
150 °C	3.7 % (w/w)
250 °C	3.3 % (w/w)
350 °C	3.1 % (w/w)
360 °C	3.1 % (w/w)

The diagram shows the evaporation curve of the liquid/waxy product of the sea plastic that was pyrolyzed at 344 °C (red line). At 100 °C 23.2 % (w/w) are evaporated, at 150 °C 96.3 % (w/w) are evaporated.

There is no mass-to-charge ratio visible that indicate the presence of alkanes, alkenes or aromatics. This and the fact, that most of the sample is evaporated at about 110 °C indicate that the sample consists mainly of water.

4.7.3.2 Evaporation curve and mass spectrum of the liquid/waxy product of the sea plastic pyrolyzed at 434 °C

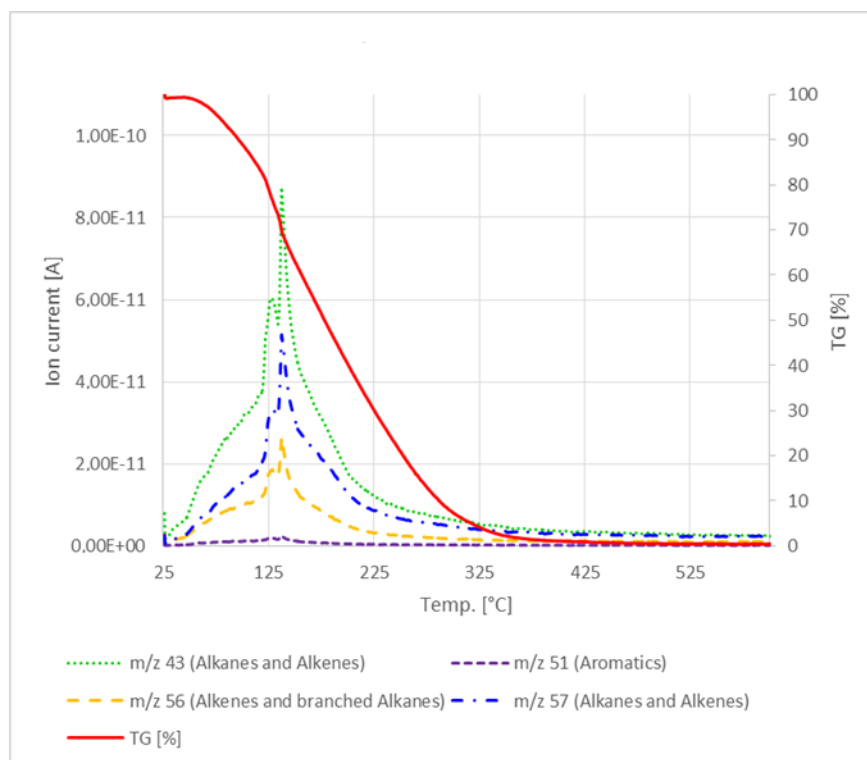


Figure 73 - Evaporation curve and mass spectrum of the liquid/waxy product of the sea plastic pyrolyzed at 434 °C

Table 16 - Evaporation residue of the liquid/waxy product of the sea plastic pyrolyzed at 434 °C

Temperature	Evaporation residue
70 °C	96.8 % (w/w)
100 °C	89.0 % (w/w)
150 °C	63.0 % (w/w)
250 °C	21.0 % (w/w)
350 °C	2.2 % (w/w)
360 °C	1.8 % (w/w)

Unlike the plastic mixture (A) pyrolyzed at 434 °C, the pyrolyzed sea plastic does not contain a fraction that evaporates at 400 °C according to the evaporation curve (red line). At 150 °C 37 % (w/w) are evaporated. At 250 °C 79 % (w/w) are evaporated.

The mass-to-charge ratios 43 (green line), 57 (blue line) and 56 (yellow line) show a strong signal, which indicate the presence of alkanes, branched alkanes and alkenes. The mass-to-charge ratio 51 (purple line) shows only a low signal compared with petrol and diesel. This indicates that only a small amount of aromatics is contained in the pyrolysis product.

4.7.3.3 Evaporation curve and mass spectrum of the liquid/waxy product of the sea plastic pyrolyzed at 525 °C

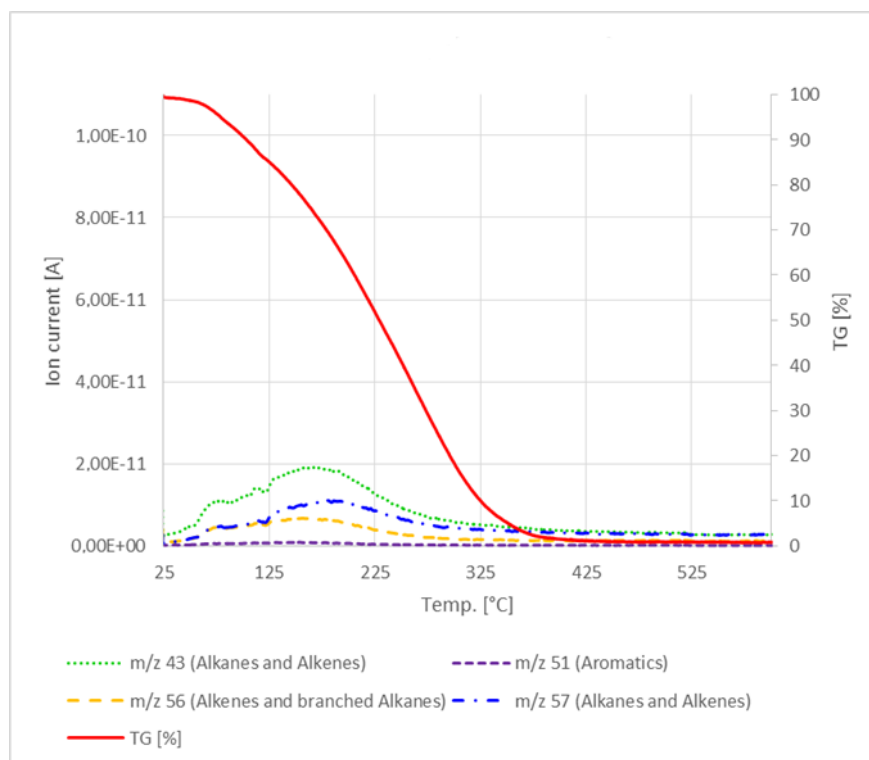


Figure 74 - Evaporation curve and mass spectrum of the liquid/waxy product of the sea plastic pyrolyzed at 525 °C

Table 17 - Evaporation residue of the liquid/waxy product of the sea plastic pyrolyzed at 525 °C

Temperature	Evaporation residue
70 °C	96.7 % (w/w)
100 °C	90.8 % (w/w)
150 °C	79.1 % (w/w)
250 °C	40.9 % (w/w)
350 °C	5.3 % (w/w)
360 °C	3.8 % (w/w)

At a pyrolysis temperature of 525 °C nearly the whole sample is evaporation at 400 °C. At 150 °C 20.9 % (w/w) of the sample are evaporated and at 250 °C 59.1 % (w/w) are evaporated. The evaporation curve is similar to the evaporation curve of the pure plastic mixture (A) at 615 °C. There is no high-boiling fraction that starts evaporating at 400 °C

The mass-to-charge ratios 43 (green line), 57 (blue line) and 56 (yellow line) show a strong signal, which indicate the presence of alkanes, branched alkanes and alkenes. The mass-to-charge ratio 51 (purple line) shows only a low signal. This indicates that only a small amount of aromatics is contained in the pyrolysis product, like at a pyrolysis temperature of 434 °C. It seems that the content of aromatic hydrocarbons is strongly influenced by the feedstock and that the sea plastic does not contain plastics that form aromatics like polystyrene.

4.7.3.4 Evaporation curve and mass spectrum of the liquid/waxy product of the sea plastic pyrolyzed at 615 °C

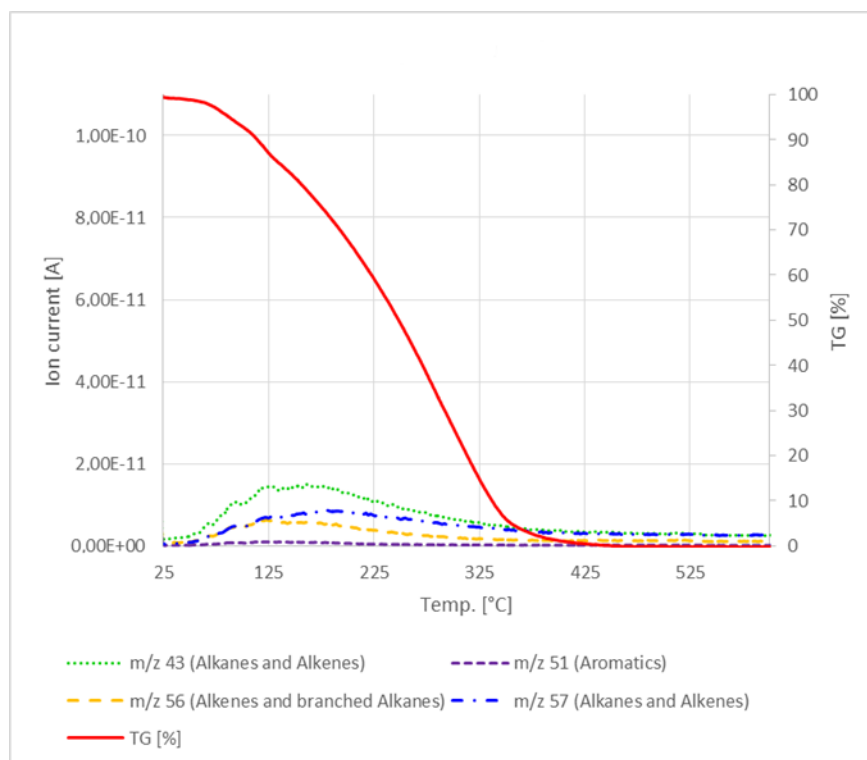


Figure 75 - Evaporation curve and mass spectrum of the liquid/waxy product of the sea plastic pyrolyzed at 615 °C

Table 18 - Evaporation residue of the liquid/waxy product of the sea plastic pyrolyzed at 615 °C

Temperature	Evaporation residue
70 °C	97.6 % (w/w)
100 °C	92.9 % (w/w)
150 °C	81.6 % (w/w)
250 °C	49.4 % (w/w)
350 °C	6.0 % (w/w)
360 °C	4.3 % (w/w)

At a pyrolysis temperature of 615 °C the evaporation curve (red line) of sea plastic is very similar to the evaporation curve of sea plastic that was pyrolyzed at 525 °C. At 150 °C 18.4 % (w/w) are evaporated and at 250 °C 50.6 % (w/w) are evaporated. Both values are a bit lower than at a pyrolysis temperature of 525 °C.

The indicator mass-to-charge ratios are similar to the signals at a pyrolysis temperature of 525 °C. The mass-to-charge ratio 51 (purple line) shows again a low signal, which indicates that the content of aromatics is very low.

4.7.3.5 H₂O (m/z 18) in the liquid/waxy product of the pyrolyzed sea plastic

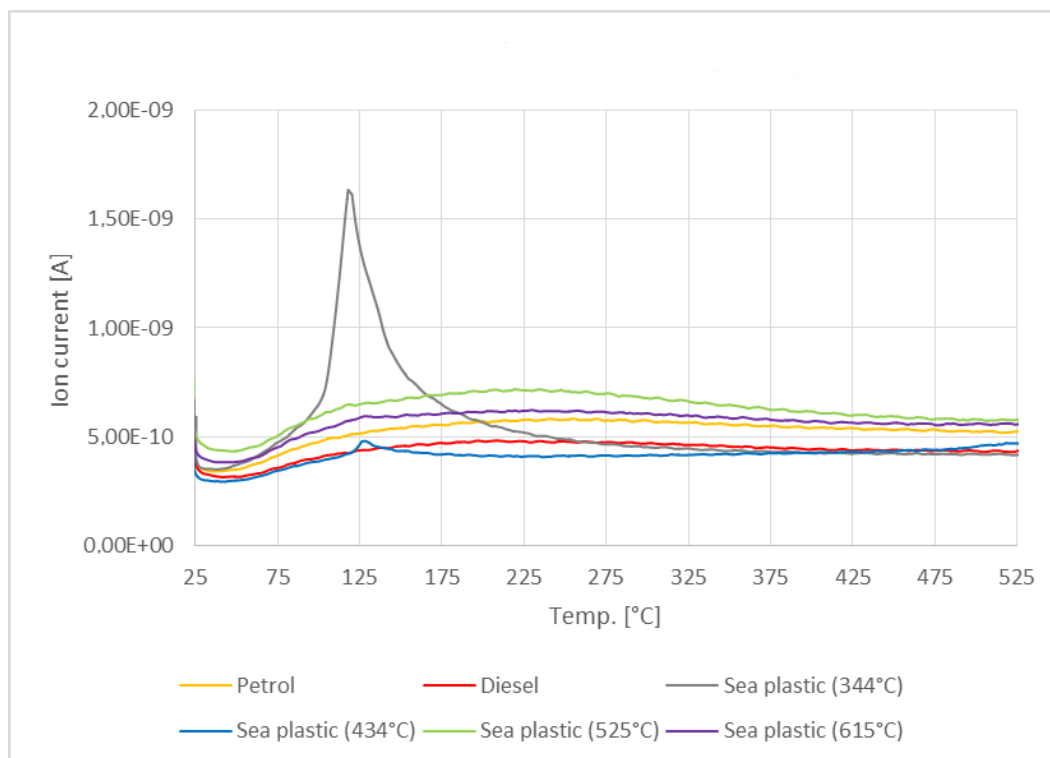


Figure 76 - H₂O (m/z 18) in the liquid/waxy product of the pyrolyzed sea plastic

This diagram shows the mass-to-charge ratio 18 of pyrolyzed sea plastic at different pyrolysis temperatures, which indicates the presence or absence of water in the sample. The sample with a pyrolysis temperature of 344 °C shows a strong peak. The sample with a pyrolysis temperature of 434 °C also shows a peak.

Because the sea plastic that was pyrolyzed at 344 °C did not show a signal at the mass-to-charge ratios that indicate alkanes, alkenes and aromatics but a strong signal at the mass-to-charge ratio that indicates water it is very likely that the sample mainly consists of water and no hydrocarbons.

This means that a pyrolysis temperature of about 344 °C could be used as drying temperature because no pyrolysis is observed at this temperature.

4.7.4 Evaporation curve and mass spectrum of the pyrolyzed plastic mixture (B) – complementary experiments

4.7.4.1 Evaporation curve and mass spectrum of the liquid/waxy product of the plastic mixture (B) pyrolyzed at 344 °C – 180 minutes

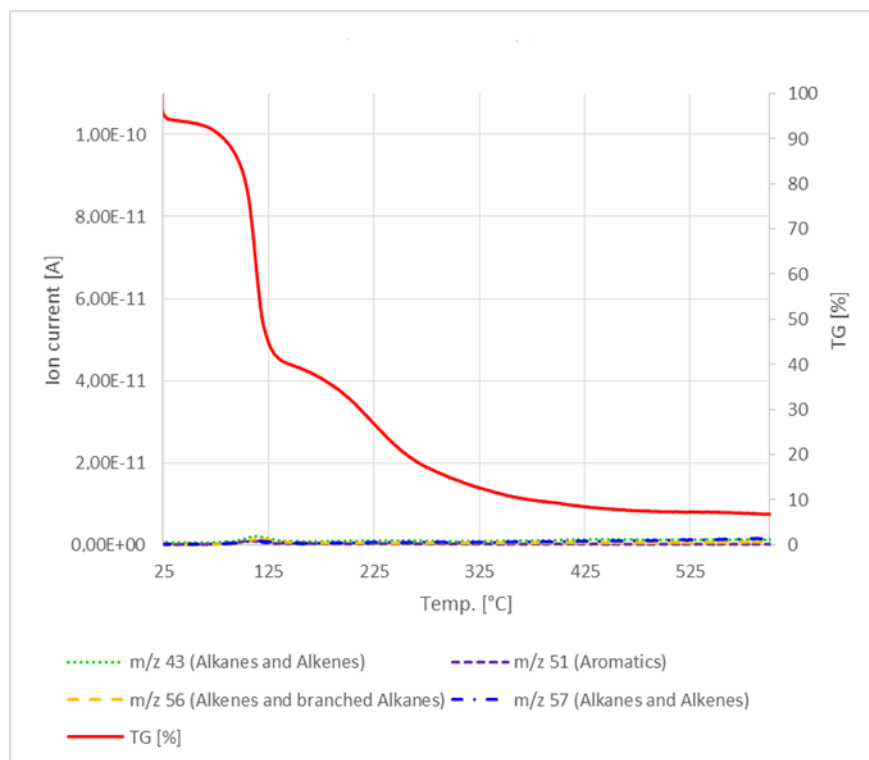


Figure 77 - Evaporation curve and mass spectrum of the liquid/waxy product of the plastic mixture (B) pyrolyzed at 344 °C – 180 minutes

Table 19 - Evaporation residue of the liquid/waxy product of the plastic mixture (B) pyrolyzed at 344 °C – 180 minutes

Temperature	Evaporation residue
70 °C	92.3 % (w/w)
100 °C	83.0 % (w/w)
150 °C	39.6 % (w/w)
250 °C	21.1 % (w/w)
350 °C	11.0 % (w/w)
360 °C	10.6 % (w/w)

Because at a pyrolysis temperature of 344 °C and a reaction time of 60 minutes no product has formed, the experiment was repeated with the plastic mixture (B) and a reaction time of 180 minutes. At this experiment a small amount of product has been formed.

The evaporation curve (red line) shows that the sample evaporates at about 100 °C. At 150 °C 60.4 % (w/w) are evaporated. The evaporation curve indicates that the sample consists of two fractions, a fraction that evaporates at about 100 °C and a high boiling fraction.

There are nearly no signals in the mass spectrum that indicate hydrocarbons, this indicates that the liquid fraction consists mainly of water.

4.7.4.2 Evaporation curve and mass spectrum of the liquid/waxy product of the plastic mixture (B) pyrolyzed at 400 °C – 200 minutes

The collecting system of the experimental setup consists of the first collecting container where a rather hard and brittle product fraction is collected and a second collecting container, where a liquid and waxy product fraction is collected. These product fractions were collected separately and both fractions were analyzed. Because the product fraction in the second collecting container is rather liquid, it is called “liquid product fraction”. The product fraction in the first collection container is rather solid, therefore it is called “solid product fraction”. Because there is no clear demarcation between the two collection containers a third sample was created, which is a mixture of the “liquid product fraction” and the “solid product fraction”. It is called “mixture of solid and liquid product” and it is also analyzed.

Liquid product fraction

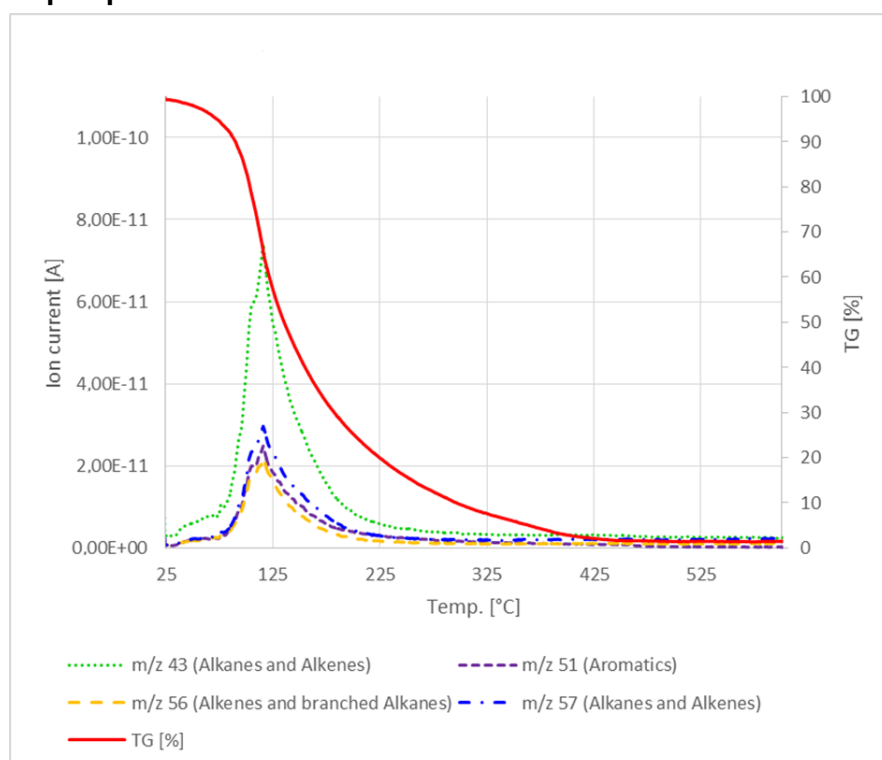


Figure 78 - Evaporation curve and mass spectrum of the liquid/waxy product of the plastic mixture (B) pyrolyzed at 400 °C – 200 minutes, liquid product fraction

Table 20 - Evaporation residue of the liquid/waxy product of the plastic mixture (B) pyrolyzed at 400 °C – 200 minutes, liquid product fraction

Temperature	Evaporation residue
70 °C	95.5 % (w/w)
100 °C	83.6 % (w/w)
150 °C	42.5 % (w/w)
250 °C	25.3 % (w/w)
350 °C	5.9 % (w/w)
360 °C	5.3 % (w/w)

This diagram shows the evaporation curve of the liquid product fraction of the plastic mixture (B) pyrolyzed at 400 °C. At 150 °C 57.5 % (w/w) are evaporated and at 250 °C 74.7 % (w/w) are evaporated.

The mass-to-charge ratios of hydrocarbons show a strong signal. The mass-to-charge ratio 51 is very strong which indicates that a high amount of aromatics is in the sample.

A pyrolysis temperature of 400 °C could possibly be useful to remove aromatics.

Solid product fraction

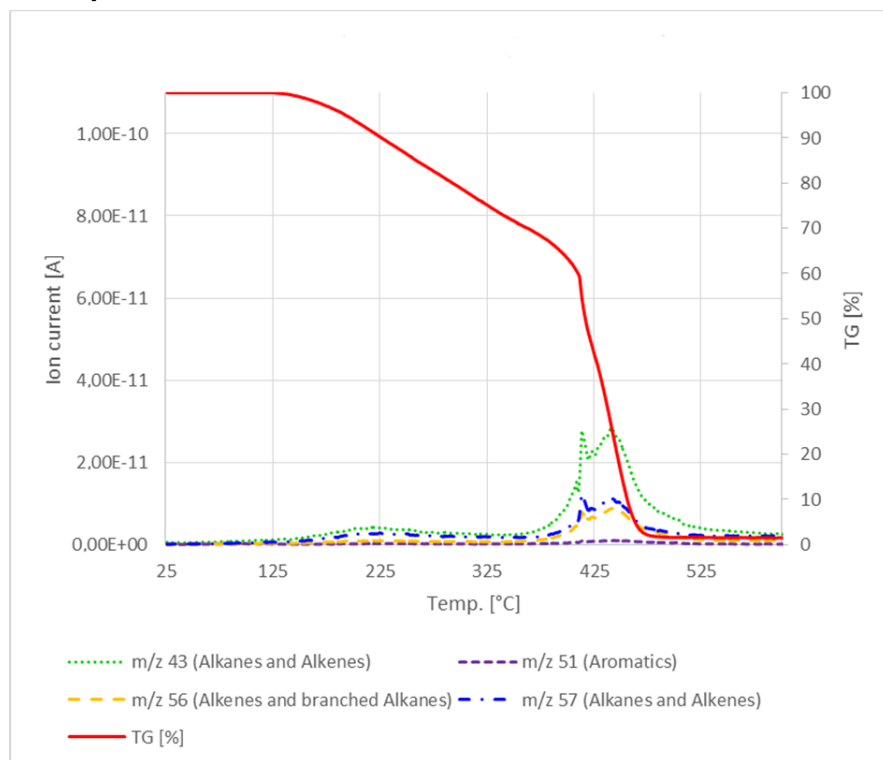


Figure 79 - Evaporation curve and mass spectrum of the liquid/waxy product of the plastic mixture (B) pyrolyzed at 400 °C – 200 minutes, solid product fraction

Table 21 - Evaporation residue of the liquid/waxy product of the plastic mixture (B) pyrolyzed at 400 °C – 200 minutes, solid product fraction

Temperature	Evaporation residue
70 °C	100.0 % (w/w)
100 °C	100.0 % (w/w)
150 °C	99.1 % (w/w)
250 °C	86.5 % (w/w)
350 °C	71.7 % (w/w)
360 °C	70.3 % (w/w)

This diagram shows the evaporation curve of the solid product fraction of the plastic mixture (B) pyrolyzed at 400 °C. It is similar to the evaporation curve of the mixture of liquid and solid product but at the beginning no sample evaporates.

Mixture of solid and liquid product

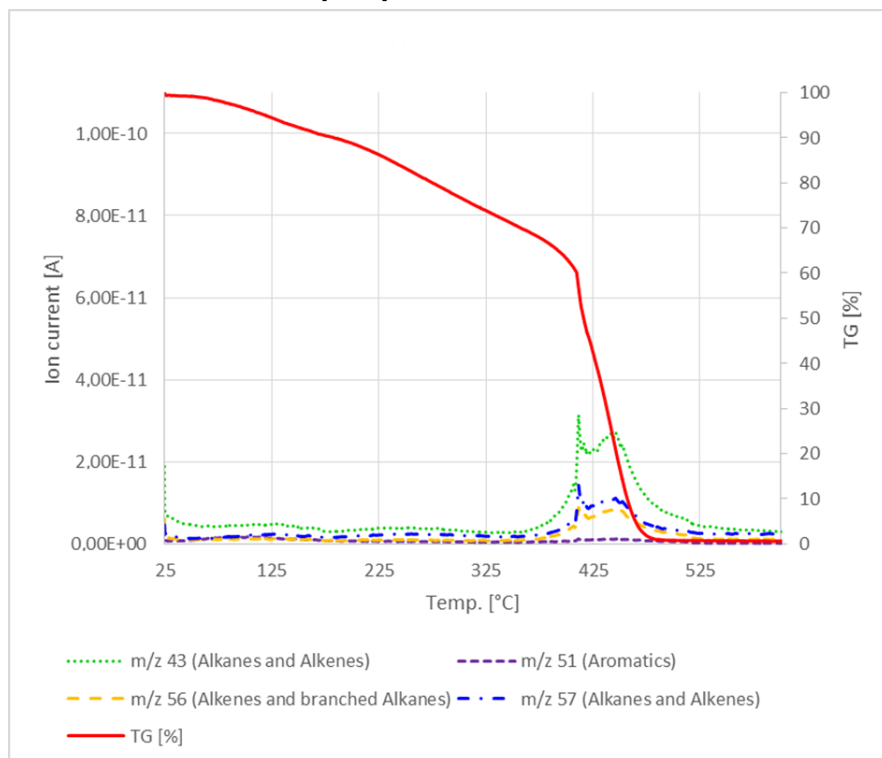


Figure 80 - Evaporation curve and mass spectrum of the liquid/waxy product of the plastic mixture (B) pyrolyzed at 400 °C – 200 minutes, mixture of solid and liquid product fraction

Table 22 - Evaporation residue of the liquid/waxy product of the plastic mixture (B) pyrolyzed at 400 °C – 200 minutes, mixture of solid and liquid product fraction

Temperature	Evaporation residue
70 °C	98.4 % (w/w)
100 °C	96.5 % (w/w)
150 °C	92.3 % (w/w)
250 °C	83.2 % (w/w)
350 °C	70.9 % (w/w)
360 °C	69.7 % (w/w)

The diagram shows the evaporation curve of the liquid/waxy product of the plastic mixture (B) pyrolyzed at 400 °C. The evaporation curve of the plastic mixture (B) pyrolyzed at 400 °C is similar to the plastic mixture (A) pyrolyzed at 434 °C. A high boiling fraction has formed that evaporates at about 400 °C.

4.7.4.3 Evaporation curve and mass spectrum of the liquid/waxy product of the plastic mixture (B) pyrolyzed at 615 °C

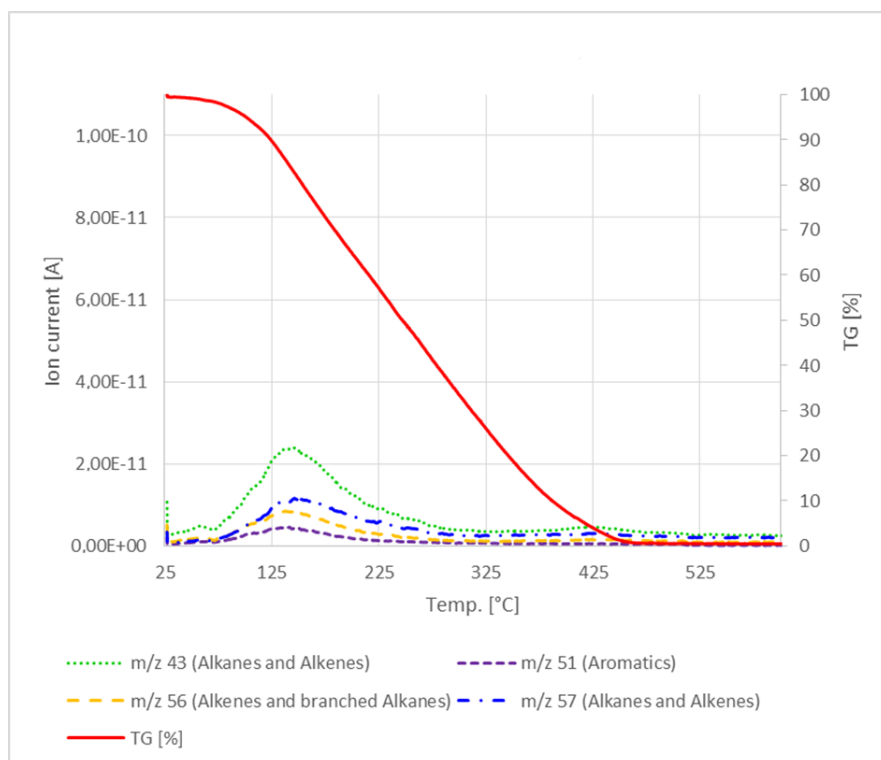


Figure 81 - Evaporation curve and mass spectrum of the liquid/waxy product of the plastic mixture (B) pyrolyzed at 615 °C

Table 23 - Evaporation residue of the liquid/waxy product of the plastic mixture (B) pyrolyzed at 615 °C

Temperature	Evaporation residue
70 °C	98.5 % (w/w)
100 °C	95.2 % (w/w)
150 °C	81.4 % (w/w)
250 °C	49.1 % (w/w)
350 °C	18.9 % (w/w)
360 °C	16.3 % (w/w)

This diagram shows the evaporation curve of the plastic mixture (B) pyrolyzed at 615 °C. It is similar to the evaporation curve of the plastic mixture (A) pyrolyzed at 615 °C. This experiment was carried out to compare the two plastic mixtures and continue working with this sample.

At 150 °C 18.6 % (w/w) of the sample are evaporated and at 250 °C 50.9 % (w/w) are evaporated.

All indicator mass-to-charge ratios show a signal.

4.7.4.4 H₂O (m/z 18) in the liquid/waxy product of the pyrolyzed plastic mixture (B)

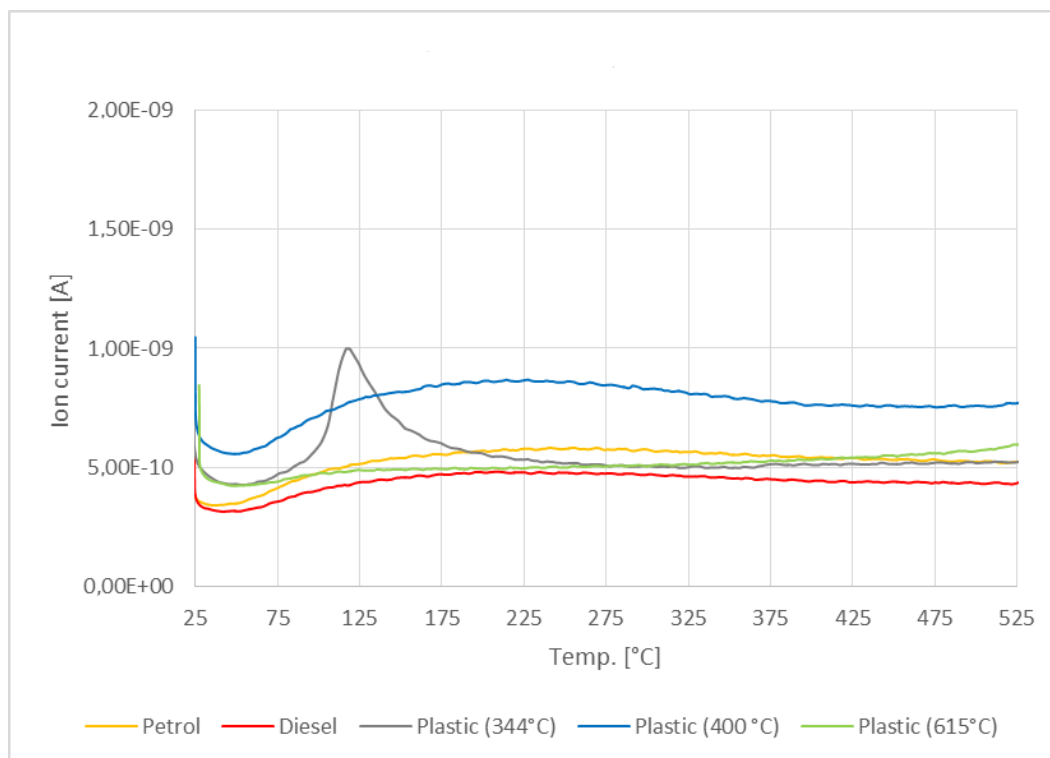


Figure 82 - H₂O (m/z 18) in the liquid/waxy product of the pyrolyzed plastic mixture (B)

The mass-to-charge ratio 18 of the plastic mixture (B), pyrolyzed at 344 °C and 180 minutes, shows a peak at about 100 °C. This indicates that the sample contains water.

Because the sample was dry before pyrolysis it seems that water is formed at a pyrolysis temperature of 344 °C after a long reaction time. This could possibly lead to a decrease of the product yield.

The samples at higher pyrolysis temperatures (400 °C and 615 °C) do not show any peaks that indicate water in the samples. The signal at 400 °C is generally higher, which can be attributed to small differences while the measurement, like a higher vacuum in mass spectrometer.

4.7.4.5 Evaporation curve and mass spectrum of the liquid/waxy product of the plastic mixture (B) pyrolyzed at 615 °C and distilled at 250 °C

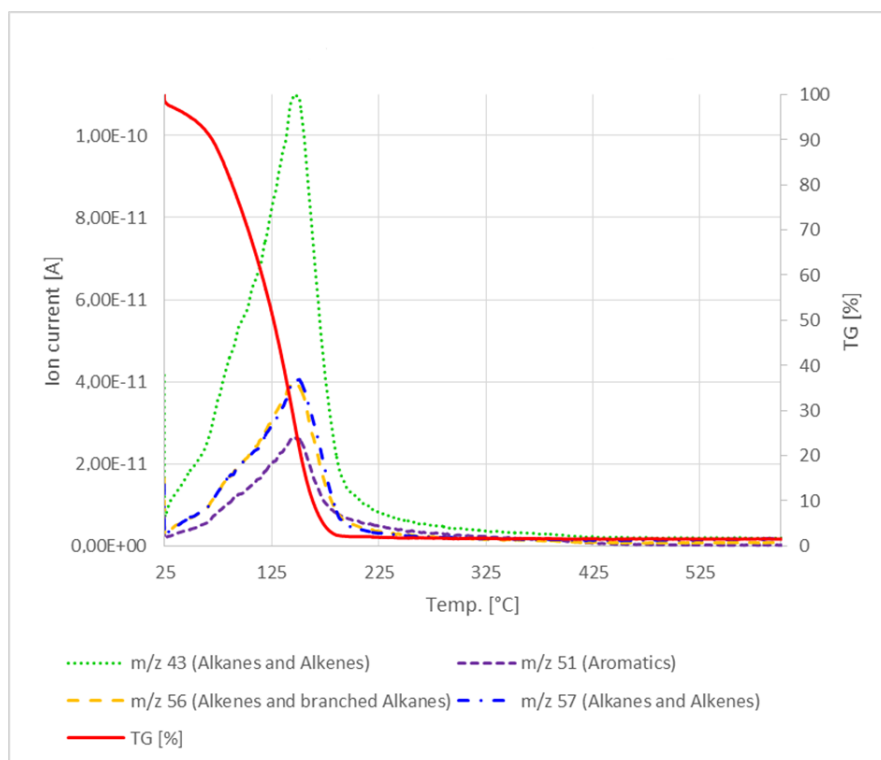


Figure 83 - Evaporation curve and mass spectrum of the liquid/waxy product of the plastic mixture (B) pyrolyzed at 615 °C and distilled at 250 °C, distillate

Table 24 - Evaporation residue of the liquid/waxy product of the plastic mixture (B) pyrolyzed at 615 °C and distilled at 250 °C, distillate

Temperature	Evaporation residue
70 °C	89.8 % (w/w)
100 °C	72.2 % (w/w)
150 °C	22.7 % (w/w)
250 °C	1.8 % (w/w)
350 °C	1.6 % (w/w)
360 °C	1.6 % (w/w)

The diagram shows the evaporation curve (red line) of the plastic mixture (B) pyrolyzed at 615 °C after distillation at 250 °C.

Most of the sample is evaporated at 175 °C. At 150 °C 77.3 % (w/w) of the sample are evaporated and at 250 °C 98.2 % (w/w) are evaporated.

Compared with diesel at 150 °C 50.9 % (w/w) are evaporated and at 250 °C 99.0 % (w/w) are evaporated.

The mass-to-charge ratios 43, 56 and 57 which indicate alkanes and alkenes show a very strong signal. The mass-to-charge ratio 51 which indicates aromatics also shows a very strong signal compared with diesel. This indicates a high amount of aromatics.

The residue after distillation is a brown wax-like substance. Since the main focus was on the distillate, no evaporation curve was recorded from the residue, which probably mainly consists of hydrocarbons. It would be interesting, if the distillation residue contains aromatic compounds. If the concentration of aromatic compounds is noticeable lower in the residue than in the distillate, a two stage pyrolysis could be a possibility to separate aromatics from the pyrolysis products.

4.8 Expected total yield after distillation at 250 °C

As a purification step distillation can be applied. In this case a distillation at 250 °C was assumed. This temperature was chosen freely and does not refer to usual distillation temperatures of fuels. It was chosen because most of the reference diesel evaporates at 200 °C and 99.0 % (w/w) evaporate at 250 °C according to the evaporation curve of diesel (see point 4.7.1.1). It is expected that the evaporation curve of the product after distillation at 250 °C is similar to the evaporation curve of the reference diesel.

4.8.1 Calculation

For calculating the expected total oil yield from the feedstock after distillation at 250 °C, the percentages of the liquid/waxy products which were produced at the pyrolysis and the percentages of how much has evaporated at 250 °C according to the evaporation curves are multiplied. The percentage of liquid/waxy product is taken from the mass balances of the associated experiments (PAUSWEG, 2017). The percentage of the evaporated mass of the liquid/waxy product at 250 °C is from the evaporation curves of the respective experiments (see point 4.7).

$$Y_{250} = \frac{L}{100\%} * \frac{E_{250}}{100\%} * 100\%$$

Y₂₅₀...expected total oil yield from the feedstock after distillation at 250 °C [% (w/w)]

L...percentage of liquid/waxy product after pyrolysis [% (w/w)]

E₂₅₀...percentage of the evaporated mass of liquid/waxy product at 250 °C [% (w/w)]

Table 25 - Expected yield after pyrolysis and distillation at 250 °C

Feedstock	Pyrolysis temperature	% (w/w) liquid/waxy product	% (w/w) evaporated at 250 °C	Expected total oil yield from the feedstock after distillation at 250 °C	Sample-ID
Plastic mixture (A)	344 °C	0.0 % (w/w)	0.0 % (w/w)	0.0 % (w/w)	V19-20171017-PP
Plastic mixture (A)	434 °C	54.8 % (w/w)	19.4 % (w/w)	10.6 % (w/w)	V18-20171019-PP
Plastic mixture (A)	525 °C	68.8 % (w/w)	59.1 % (w/w)	40.7 % (w/w)	V20-20171018-PP
Plastic mixture (A)	615 °C	66.4 % (w/w)	62.7 % (w/w)	41.6 % (w/w)	V14-20171012-PP
Sea plastic	344 °C	0.4 % (w/w)	96.7 % (w/w)	3.9 % (w/w)	V21-20171019-MP
Sea plastic	434 °C	31.2 % (w/w)	79.0 % (w/w)	24.6 % (w/w)	V27-20171031-MP
Sea plastic	525 °C	59.6 % (w/w)	59.1 % (w/w)	35.2 % (w/w)	V26-20171031-MP
Sea plastic	615 °C	62.8 % (w/w)	50.6 % (w/w)	31.8 % (w/w)	V25-20171030-MP
Plastic mixture (B)	344 °C	4.0 % (w/w)	78.9 % (w/w)	3.2 % (w/w)	HV3-20171220-liquid/wax
Plastic mixture (B)	400 °C	55.6 % (w/w)	16.8 % (w/w)	9.3 % (w/w)	HV4-20180110-liquid/wax_3
Plastic mixture (B)	615 °C	73.6 % (w/w)	50.9 % (w/w)	37.5 % (w/w)	HV5-20180116-liquid/wax

The table shows the expected yields of the pyrolysis products after a distillation at 250 °C. The value was calculated from the proportion of liquid or waxy product after pyrolysis according to the mass balances and the proportion that has evaporated at 250 °C according to the evaporation curves.

Some samples contain macroscopically visible immiscible drops of water according to the visual investigation (see point 4.3). This water also evaporates and increases the expected yield but this error was not considered in this table.

According to this table a total oil yield of about 40 % (w/w) from the feedstock can be expected after pyrolysis at 525 °C in a batch reactor and distillation at 250 °C. The expected yield of the plastic mixture (A) pyrolyzed at 615 °C is marginally higher than the expected yield of the plastic mixture (A) pyrolyzed at 525 °C. The yield of sea plastic is a bit lower but impurities and variations in the feedstock must be considered. The yield of the plastic mixture (B) is also a bit lower than 40 % (w/w) which can be caused by the different plastic mixture.

4.8.2 Implementation

The pyrolysis product of the plastic mixture (B) pyrolyzed at 615 °C was distilled at 250 °C. The sample was distilled in the same experimental setup in which the pyrolysis was performed because the laboratory distillation devices available at the institute did not reach the required temperature.

In the distillation 13.4 % (w/w) could be recovered as oil, 67.2 % (w/w) remained as wax and 19.4 % (w/w) got lost.

Because after pyrolysis 73.6 % (w/w) liquid/waxy product could be recovered and 13.4 % (w/w) of this product could be recovered as oil after distillation, the resulting total oil yield from the feedstock is 9.9 % (w/w) (see calculation point 4.8.1). This is rather low and it seems that the pyrolysis reactor is not suitable as distillation device, because a big amount of the sample got lost or didn't evaporate although it was expected according to the evaporation curve.

Higher oil yields can be expected, if the waxy residue that remains after distillation is pyrolyzed and distilled again.

4.9 Analysis of pyrolysis residues with SEM-EDX

4.9.1 Sample

For the analysis of the pyrolysis residue with SEM-EDX the residue of sea plastic pyrolyzed at 344 °C was selected. It was selected because it contains a lot of unpyrolyzed molten plastic and impurities like stones and pieces of wood which can influence the reaction. Unfortunately only one sample could be examined because the SEM-EDX device had an error.



Figure 84 - Pyrolysis residue of sea plastic pyrolyzed at 344 °C

The sample is nearly black and contains macroscopic visible impurities like stones and wooden pieces. It is hard and brittle and consists mainly of molten plastic.

4.9.2 Qualitative elementary analysis

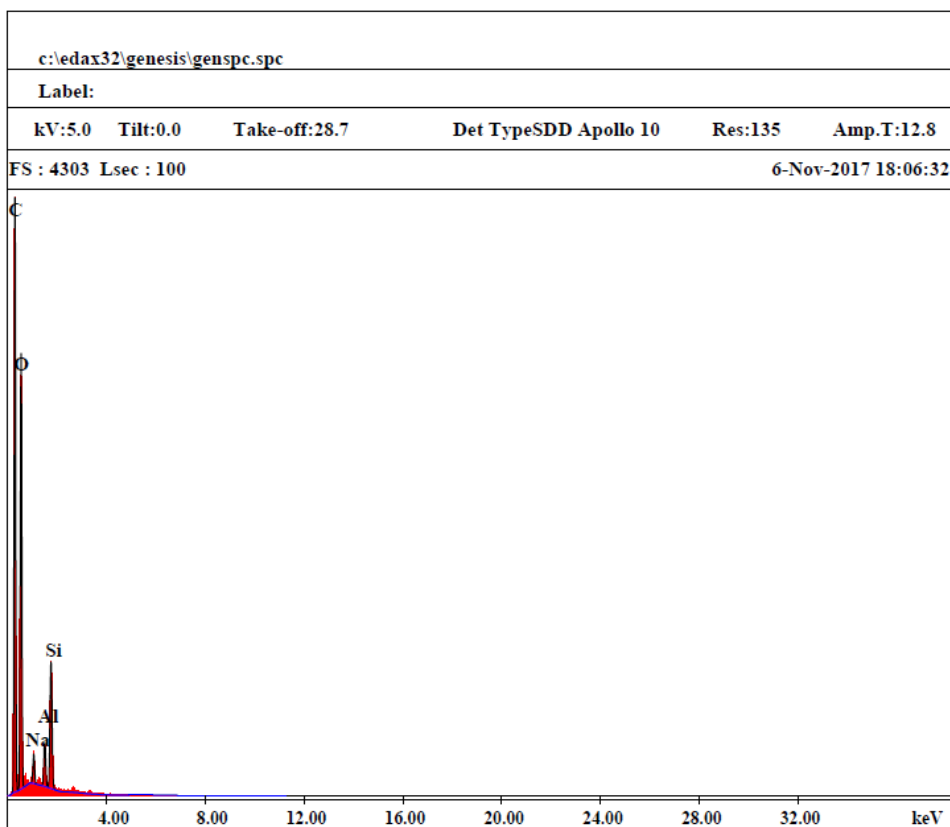


Figure 85 - Qualitative SEM-EDX elementary analysis of pyrolysis residue of sea plastics pyrolysed at 344°C

Table 26 - Qualitative SEM-EDX elementary analysis of pyrolysis residue of sea plastic pyrolysed at 344°C

EDAX ZAF Quantification (Standardless)			
Element Normalized			
SEC Table : User C:\Savecalib_Install_24-03-2010\SEC\CBFON.sec			
Element	Wt %	At %	K-Ratio
C K	45.72	58.64	0.2963
O K	26.94	25.94	0.1926
NaK	2.45	1.64	0.0207
AlK	5.49	3.13	0.0488
SiK	19.41	10.65	0.1766
Total	100.00	100.00	

Because small atoms are not detectable with SEM-EDX, elements like hydrogen are not detected. 45.72 % (w/w) of the detectable elements are carbon, 26.94 % (w/w) are oxygen and 19.41 % (w/w) are silicone. Little amounts of sodium and aluminium are also detected.

Due to the low reaction temperature of about 344°C the sample is not completely converted into the liquid or waxy products. A high amount of carbon is still present in the residue, with indicates a low conversion rate from plastic to oil or wax at this temperature.

Further the high amount of silicone and oxygen is notable. Usually silicone is in the form of quartz present. Quartz has the sum formula SiO_2 . Converted into atomic percent 25.94 % are oxygen and 10.65 % are silicone. That means, that about 21.3 atomic percent of oxygen are bound as quartz. The rest is probably present as aluminium oxide or as a part of the plastic residue.

4.9.3 SEM-EDX images

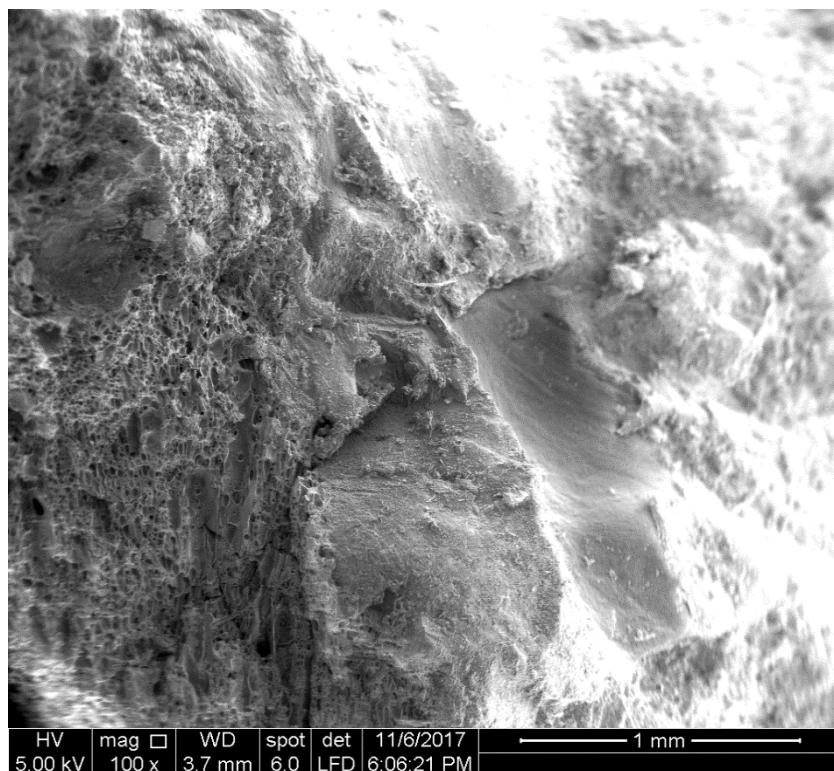


Figure 86 - SEM-EDX image of pyrolysis residue of sea plastics pyrolysed at 344°C (100x)

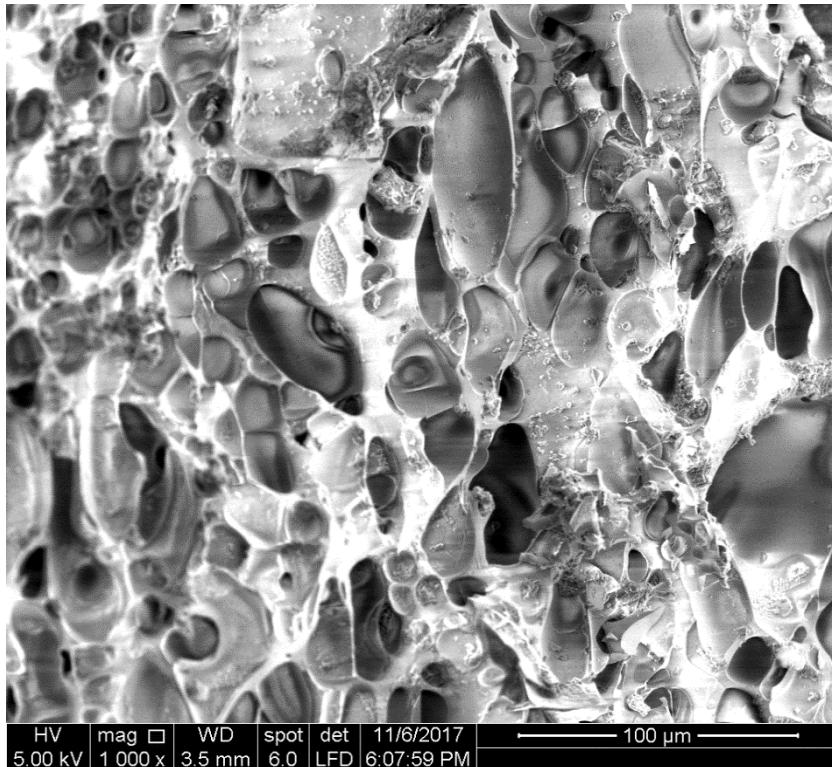


Figure 87 - SEM-EDX image of pyrolysis residue of sea plastics pyrolysed at 344°C (1000x)

Figure 86 and 87 show SEM-EDX images of the pyrolysis residue of sea plastics which were pyrolysed at 344°C.

Microscope images of pure plastic samples (figure 35) do not show hollow spaces. Microscope images of sea plastics from the Pacific Ocean (figure 36) show cracks on the surface due to environmental exposure and calcium or magnesium and calcium crusts.

The pyrolysis residue shows a lot of hollow spaces. These are probably formed by the formation of gas from the plastic inside the sample. While cooling down the plastic sample solidifies and the hollow spaces are conserved.

4.9.4 Remaining samples

From the other samples no SEM-EDX recording could be made due to technical difficulties. Instead, an estimation is made by visual assessment.

Pyrolysis residues of the plastic mixture (A)



Figure 88 - Residues of the plastic mixture (A) pyrolyzed at 344 °C, 434 °C, 525 °C and 615 °C

At a pyrolysis temperature of 344 °C the pyrolysis residue of the plastic mixture (A) is light-brown and it mainly consists of molten plastic. Macroscopically, no pores are visible.

At a pyrolysis temperature of 434 °C and 525 °C the pyrolysis residues are similar. The samples are brown and there is no plastic visible. The visible pieces are remains of PVC and slag. In the slag pores are visible. The brown colour may indicate the formation of coal dust.

At a pyrolysis temperature of 615 °C the pyrolysis residue of the plastic mixture (A) is black and there is no plastic visible. In the slag pores are visible. The black colour indicates the formation of coal.

Pyrolysis residues of the sea plastic



Figure 89 - Residues of the sea plastic pyrolyzed at 344 °C, 434 °C, 525 °C and 615 °C

At a pyrolysis temperature of 344 °C the pyrolysis residue of the sea plastic is nearly black and it contains impurities like stones and wooden pieces. The sample mainly consists of molten plastic.

At a pyrolysis temperature of 434 °C the pyrolysis residue is black and there is no plastic visible. The residue consists of char, stones and slag.

The pyrolysis residues at a pyrolysis temperature of 525 °C and 615 °C are similar. There is no plastic visible and the residue consists of char, stones and slag. In the slag pores are visible. The pyrolysis residues are black, which indicates high carbon content.

5 Evaluations of the results

The mass balances show that temperatures below 400 °C are not suitable for the pyrolysis of plastic, because only a small amount of the feedstock is converted into oil or wax and pyrolysis gases. At a pyrolysis temperature of 400 °C the feedstock is partially converted and at about 525 °C the feedstock is completely converted.

At a pyrolysis temperature of 400 °C the product contains a solid fraction which can solidify in pipes and valves. This can lead to failures in a continuous system or even damages. This solid fraction decomposes more and more at higher temperatures and at a pyrolysis temperature of 615 °C it seems to be decomposed completely according to the evaporation curves.

According to visual evaluation of the liquid and waxy pyrolysis products, they look more homogenous at higher pyrolysis temperatures whereby there is no macroscopic difference between the liquid and waxy pyrolysis products at a pyrolysis temperature of 525 °C and 615 °C.

The density of the pyrolysis products of the plastic mixture decreases with increasing pyrolysis temperature and it gets very close to the density of diesel. At the pyrolyzed sea plastic the density increases with increasing pyrolysis temperature.

The pour point of the pyrolyzed plastic mixtures goes down with increasing pyrolysis temperature. At the pyrolyzed sea plastic the pour point goes up with increasing pyrolysis temperature.

The flash point of the pyrolysis products goes down with increasing pyrolysis temperature.

The evaporation curves of the liquid/waxy products of pyrolyzed plastic mixtures show that no hydrocarbons are produced below a pyrolysis temperature of 400 °C but mainly water according to the mass spectrum (see figure 76 and 82). At a pyrolysis temperature above 400 °C a high boiling fraction is formed which evaporates at about 400 °C. This fraction is fully degraded at a pyrolysis temperature of 615 °C. The pyrolyzed sea plastic does not contain such a high boiling fraction. With increasing pyrolysis temperatures the evaporation curves of the different feedstock become more similar.

Generally the characteristics of the pyrolyzed plastic mixture are more similar to the characteristics of diesel and petrol at higher pyrolysis temperatures. The characteristics of pyrolyzed sea plastic are more similar to the characteristics of diesel and petrol at lower pyrolysis temperatures. The difference between the characteristics of the pyrolyzed sea plastic and the pyrolyzed plastic mixtures becomes less at higher pyrolysis temperatures. This can be beneficial at a two-stage pyrolysis plant because the process is more controllable if the feedstock does not vary.

The evaporation curves show that temperatures of up to 344 °C mainly lead to an evaporation of water which is collected as liquid product fraction. Thus temperatures of about 110 °C can be used as drying step. Temperatures of about 300 °C are suitable as dechlorination step (YUAN et al., 2014).

The expected yield after pyrolysis and distillation at 250 °C is about the same at 525 °C and 615 °C pyrolysis temperature at the pyrolyzed plastic mixtures.

According to the results a pyrolysis temperature between 400 °C and 525 °C is not practical because of the formation of a solid high boiling fraction, a low conversion rate and a low product yield. Because a small amount of a high boiling fraction is still produced at a pyrolysis temperature of 525 °C, a temperature of about 600 °C or higher should be used. However, a compromise from an economic and ecological point of view must be found. Higher temperatures lead to higher energy consumption and higher demands on the reactor material.

6 Concept for a pyrolysis reactor

Based on the results obtained, a concept for a continuous pyrolysis reactor is elaborated and a sketch is made. Important points in this concept are a conveyor system for the entry of the feedstock and the discharge of residues, removal of water, heating- and reaction chambers and a collecting system for the pyrolysis products.

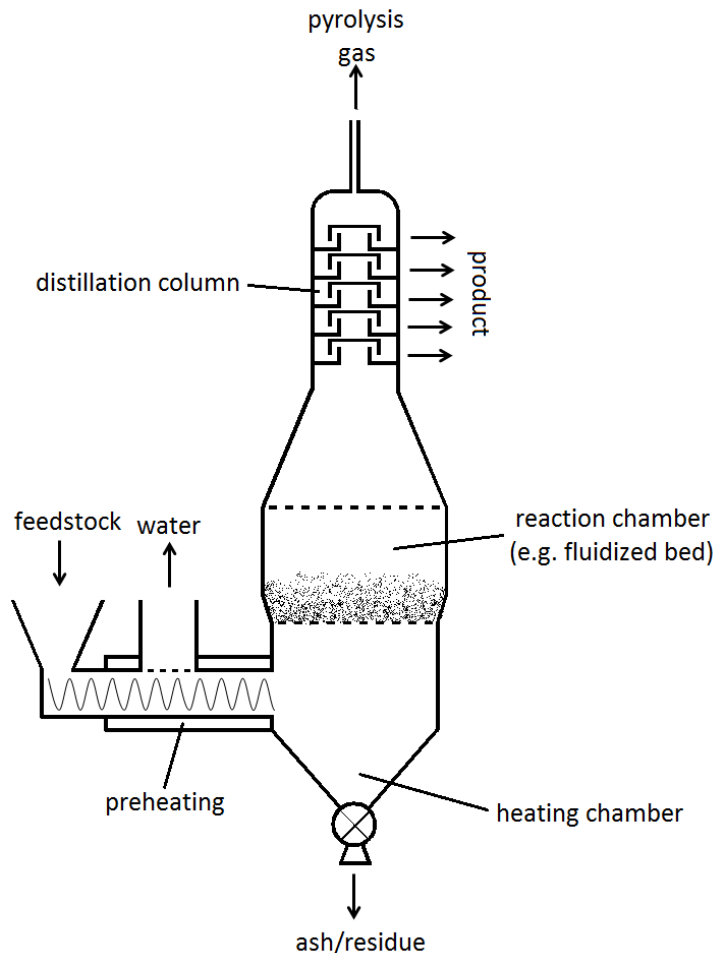


Figure 90 - Concept for a pyrolysis reactor

To transport the feedstock into the heating chamber, a screw conveyor is used. The feedstock is preheated to remove water and reduce the temperature difference of the feedstock and the heating chamber. The recommend temperature for the drying step is about 110 °C. After drying the temperature should be increased up to 300 °C. At this temperature most of the plastics melt and it is also suitable as dechlorination temperature (YUAN et al., 2014). By dechlorinating the plastic hydrochloric acid and other chlorine-containing compounds are vaporized. This vapour has to be handled carefully because it can be toxic and damage the reactor. By melting the plastic it seals the heating chamber, so that no vapour can escape and the oxygen input is reduced.

In the heating chamber the temperature should be over 600 °C, so that the formation of the solid and high boiling product fraction and the risk of blockage are reduced. Ash, stones, residues and carbon are transported out thru a valve at the bottom of the heating chamber. This residue possibly can be used as fuel as well.

The gaseous and partially cracked feedstock goes thru a sieve bottom into a reaction chamber. To increase the reaction rate a fluidized bed reactor can be used.

After cracking the product is condensed fractionally in a tray column.

7 Outlook and further experiments

The results show that it is possible to produce fuel-like oil out of waste plastic and a general temperature zone for the pyrolysis of waste plastic is determined. By further experiments the optimal temperature of this process should be determined more precisely.

To increase the yield after distillation a suitable distillation apparatus has to be constructed and the conditions for this distillation have to be optimized.

Because the feedstock of an industrial plant will contain contaminations like water, stones, wood, metals and dust but also proteins, carbohydrates and fat the influence of these substances on the process have to be investigated.

Furthermore, the composition of the feedstock will vary enormously. Therefore the influence of the individual types of plastic and the robustness of the process has to be investigated.

According to literature the solid and high boiling fraction is caused by polyethylene terephthalate (RICARDO-AEA Ltd, 2013).

Pyrolysis is only one possibility to degrade PET, another way is hydrolysis. The advantages would be that terephthalic acid could be recovered. (GRAUSE, 2003)

Hydrolysis of PET as a previous step of pyrolysis should be considered if the feedstock contains a lot of PET.

The energy efficiency of the process has to be investigated and the possibility, if the pyrolysis gases could be used as fuel for the process itself, has to be checked. It is likely that the residue in the pyrolysis reactor also could be burned and used as fuel for the pyrolysis.

As a further step a continuous plant has to be constructed to determine the process parameters of a continuous process.

8 List of abbreviations

[A]	amps
Al	aluminum
aPP	atactic polypropylene
at %	atomic percent
c	concentration
C	carbon
CH ₄	methane
Cl	chlorine
cm	centimetre
CO	carbon monoxide
CO ₂	carbon dioxide
FAME	fatty acid methyl ester
FI	flow indication
FIC	flow indication and control
g	gram
H ₂	hydrogen
HCl	hydrochloric acid
HD-PE	high density polyethylene
H ₂ O	water
iPP	isotactic polypropylene
IR	infrared
K	Kelvin
kg	kilogram
kJ	kilojoule
KOH	potassium hydroxide
kPa	kilopascal
kV	kilovolt
L	liter
LD-PE	low density polyethylene
m	mass
m ³	cubic meter
mg	milligram
min	minute
mL	millilitre
mm ²	square millimetre
m/z	mass to charge
N ₂	nitrogen
Na	sodium
O	oxygen
O ₂	oxygen
p	pressure
PE	polyethylene
PE-HD	high density polyethylene
PE-LD	low density polyethylene
PET	polyethylene terephthalate
PLC	Programmable Logic Controller
PP	polypropylene
PS	polystyrene
PUR	polyurethane
PVC	polyvinylchloride
s	second
SEM-EDX	scanning electron microscopy with energy dispersive X-ray spectroscopy
Si	silicon
SiO ₂	silicon oxide
sPP	syntactic polypropylene
t	mean flow time
T	temperature
Temp	temperature
TG	thermogravimetry (weight loss)

TI.....	temperature indication
TIC.....	temperature indication and control
V.....	volume
wt %.....	weight percent
η	dynamic viscosity
ρ	density
μm	micrometre
ν	kinematic viscosity
$^{\circ}\text{C}$	centigrade
% (v/v).....	volume percent
% (w/w).....	weight percent

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12 Appendix – Sample ID

Designation	Sample-ID	feedstock	pyrolysis temperature	Description
plastic mixture (A) pyrolyzed at 344 °C	V19-20171017-PP	plastic mixture (A)	344 °C	
plastic mixture (A) pyrolyzed at 434 °C	V18-20171019-PP	plastic mixture (A)	434 °C	
plastic mixture (A) pyrolyzed at 525 °C	V20-20171018-PP	plastic mixture (A)	525 °C	
plastic mixture (A) pyrolyzed at 615 °C	V14-20171012-PP	plastic mixture (A)	615 °C	
sea plastic pyrolyzed at 344 °C	V21-20171019-MP	sea plastic	344 °C	
sea plastic pyrolyzed at 434 °C	V27-20171031-MP	sea plastic	434 °C	
sea plastic pyrolyzed at 525 °C	V26-20171031-MP	sea plastic	525 °C	
sea plastic pyrolyzed at 615 °C	V25-20171030-MP	sea plastic	615 °C	
liquid/waxy product of the plastic mixture (B) pyrolyzed at 344 °C	HV3-20171220-liquid/wax	plastic mixture (B)	344 °C	Liquid/waxy product collected in both collecting containers
residue of the plastic mixture (B) pyrolyzed at 344 °C	HV3-20171220-residue	plastic mixture (B)	344 °C	Residue which remained in the pyrolysis reactor
liquid/waxy product of the plastic mixture (B) pyrolyzed at 400 °C, solid product fraction	HV4-20180110-liquid/wax_1	plastic mixture (B)	400 °C	Liquid/waxy product collected in the first collecting container
liquid/waxy product of the plastic mixture (B) pyrolyzed at 400 °C, liquid product fraction	HV4-20180110-liquid/wax_2	plastic mixture (B)	400 °C	Liquid/waxy product collected in the second collecting container
liquid/waxy product of the plastic mixture (B) pyrolyzed at 400 °C, mixture of solid and liquid product fraction	HV4-20180110-liquid/wax_3	plastic mixture (B)	400 °C	Mixture of the liquid/waxy product collected in the both collecting containers
residue of the plastic mixture (B) pyrolyzed at 400 °C	HV4-20180110-residue	plastic mixture (B)	400 °C	Residue which remained in the pyrolysis reactor
liquid/waxy product of the plastic mixture (B) pyrolyzed at 615 °C	HV5-20180116-liquid/wax	plastic mixture (B)	615 °C	Liquid/waxy product collected in both collecting containers
residue of the plastic mixture (B) pyrolyzed at 615 °C	HV5-20180116-residue	plastic mixture (B)	615 °C	Residue which remained in the pyrolysis reactor
liquid/waxy product of the plastic mixture (B) pyrolyzed at 615 °C and distilled at 250 °C, distillate	HV5-20180116-distillate_oil	plastic mixture (B)	615 °C	Distillate
liquid/waxy product of the plastic mixture (B) pyrolyzed at 615 °C and distilled at 250 °C, residue	HV5-20180116-distillate_residue	plastic mixture (B)	615 °C	Residue which remained in the distillation apparatus