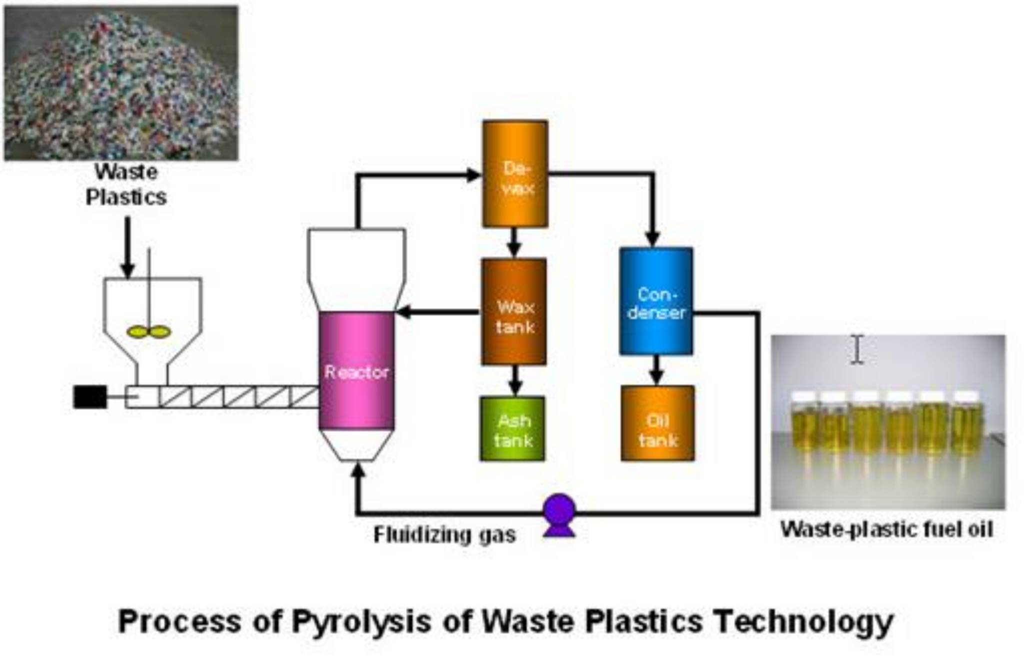
Plastic waste recycling and valorisation via dedicated pyrolysis approaches
Final report (FR)



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Abstract:

Pyrolysis of plastic waste is a new and mostly unimplemented technology. This research provides an analysis of the current technology and an analysis of which parts of this technology are mature and profitable enough to be considered to be implemented. Pyrolysis of mixed plastic waste is possible but unlikely to be profitable. Pyrolysis of most pure plastic waste flows can be profitable but more research is needed and other recycling method are most likely more suitable. Pyrolysis of Poly(methyl methacrylate) (PMMA) has a high potential to be profitable and the technology is mature enough to be implemented.

Contents

1. Introduction

1.1 Plastic waste

"In 2011, the total world plastic waste production was around 280 million tons"[1]. "The current process routes for plastic waste management in the EU are ~26% recycling, ~35% used for energy recovery (mainly incineration) and ~38% disposed to landfill"[2]. Landfilling of plastic waste is unsustainable and undesirable, and incineration of plastic waste for energy is suboptimal and costs are much higher than the revenue created by selling the energy[25].
Pyrolysis of plastic waste is a promising alternative to deal with plastic waste flows, and implementation within the plastic waste processing system should be researched and considered. However, it is yet unclear which kinds of plastics are suitable for recycling via pyrolysis, which reactors and processes are needed, which products can be created and if the revenue of these products exceed the costs of the process.

1.2 Principles of pyrolysis

Pyrolysis is a thermal decomposition process that occurs in the absence of oxygen. Pyrolysis is an age-old process already used by the ancient Egyptians. Historically it was mainly used to make charcoal out of wood. As the iron age started, charcoal was needed to heat fires hot enough to melt iron and charcoal kilns became commonplace. Later as the industrial revolution started the demand for coal increased sharply. In spite of the dangers of coal mining due to risk of mine collapse, suffocation from gases and gas explosions, coal mining became more prevalent for economic reasons and charcoal creation via pyrolysis became obsolete.

Figure 1: Creating charcoal from wood can be done by stacking wood and covering it with sand or brick and lighting it. The layer of sand prevents oxygen from reaching the wood. Only the oxygen already present in the wood is burned, therefore the combustion of the wood is incomplete and charcoal is created.

$$\underset{\text{(wood)}}{6C_{10}H_{15}O_7} + \text{Heat} \rightarrow \underset{\text{(charred wood)}}{C_{50}H_{10}O} + \underset{\text{(gas)}}{10CH_2O}$$

Figure 2: Chemical process of charcoal creation As the wood reaches a temperature of 270°C an exothermic reaction takes place converting the wood into charcoal.

Nowadays pyrolysis is used in biofuel production processes, which are comparable to charcoal creation processes. Pyrolysis is also used in the crude oil cracking industry, where long hydrocarbon chains are broken down to smaller chains and simultaneously separated trough distillation. This process is called destructive distillation.

Plastics are synthetic polymers most of which consist of long hydrocarbon chains. These hydrocarbon chains can also be broken down using pyrolysis processes, this process has the potential to create fuel and other products from plastics. Most plastic waste pyrolysis processes focus on creating liquid hydrocarbons. This liquid fuel mixture is called pyrolysis oil and often has to be upgraded and purified to create dedicated fuels such as diesel or gasoline. Liquid fuel is generally more valuable than solid or gaseous fuels, because it is easier to handle, but dependent on the temperature, catalysts and reactor type pyrolysis processes can have high fractions in the gaseous and solid phase. The solid phase is called char. Other plastic waste pyrolysis processes focus on recovering monomers from polymers. The suitability of these processes depends on the plastic type.

The chemical reactions that take place in a typical pyrolysis reactor are very complex and consists of many stages[18]. Pyrolysis can be executed in many different reactors such as batch reactors, fixed bed reactors, rotary kiln reactors and fluidized bed reactors. Catalysts can be used to influence the pyrolysis process. The majority of pyrolysis processes are carried out at temperatures of 300°C to 1000°C[19].

2. Problem analysis

2.1 Problem statement

Traditional plastic waste recycling methods are inefficient and expensive. It is unclear if pyrolysis of plastic waste is a suitable, cost effective and environmental friendly alternative.

2.2 Problem owner

The problem owner is Paul de Wild from the Energy Research Centre of the Netherlands (ECN). He is a researcher of biorefinery, pyrolysis of biomass and plastic waste. He is interested in the potential of plastic waste pyrolysis.

2.3 Stake-holder analysis

The stakeholders, their goals, constraints, power and interest in this research are listed in table 1.

Stakeholder	Goals	Constraints	Power and Interest
Energy research centre Netherlands (ECN)	To develop new technology and conduct pioneering research into innovative solutions to facilitate the transition to sustainable energy management	Limited resources	Low power high interest (Show consideration)
European plastic waste processing centres and organizations	To process waste and make profit	Government regulations; the need to make profit and the need of a continuous waste flow	High power and High interest (Key player)
National Government	To reduce plastic waste in landfills and the environment and reduce carbon footprint	Limited available financial resources and political vigor	High power and Low interest (Meet their needs)
European Union	To reduce plastic waste in landfills and the environment and reduce carbon footprint	Limited international waste infrastructure and slow to adopt new technologies	High power and Low interest (Meet their needs)

Table 1: Stakeholder analysis

2.4 System description

The system considered in this research is depicted in figure 3.
This research will consider the recycling of mixed plastic waste. Therefore, both the waste processing and separation plant and the plastic waste pyrolysis and purification plant will be considered. One has to take the input of the pyrolysis step into account because this greatly influences the output. When considering mixed plastic waste, the proportions of different plastics within the plastic waste flow can differ greatly within and between different flows. To create a process with a reliable product output, the different proportions of plastics in the input of the pyrolysis step should be controlled and consistent. To exert this level of control and provide the needed proportional consistency over the plastic waste streams, the plastic waste processing and separation plant is within the system boundary.
The recycling and incineration plants will be considered too, so a comparison in sustainability and cost effectiveness between the pyrolysis recycling methods and the traditional recycling methods can be made. Landfilling plastic waste is undesirable and unsustainable and will, therefore, not be within the system boundary.
The input of the pyrolysis step (plastic waste proportions) and the pyrolysis process (temperature, pressure and catalyst) will be configured to create valuable products. After the pyrolysis step, the pyrolysis oil has to be purified. Valuable created products will be extracted from the oil and will be sold separately.
These valuable products will most likely be monomers, for example ethylene or styrene, which can be used to create new plastics.

2.5 System efficacy

This system will contribute to the higher order European waste processing system by processing plastic waste in a cost effective and environmentally friendly manner. This system will also create raw materials that can be used in other processes and products. This contributes to improve European waste processing.

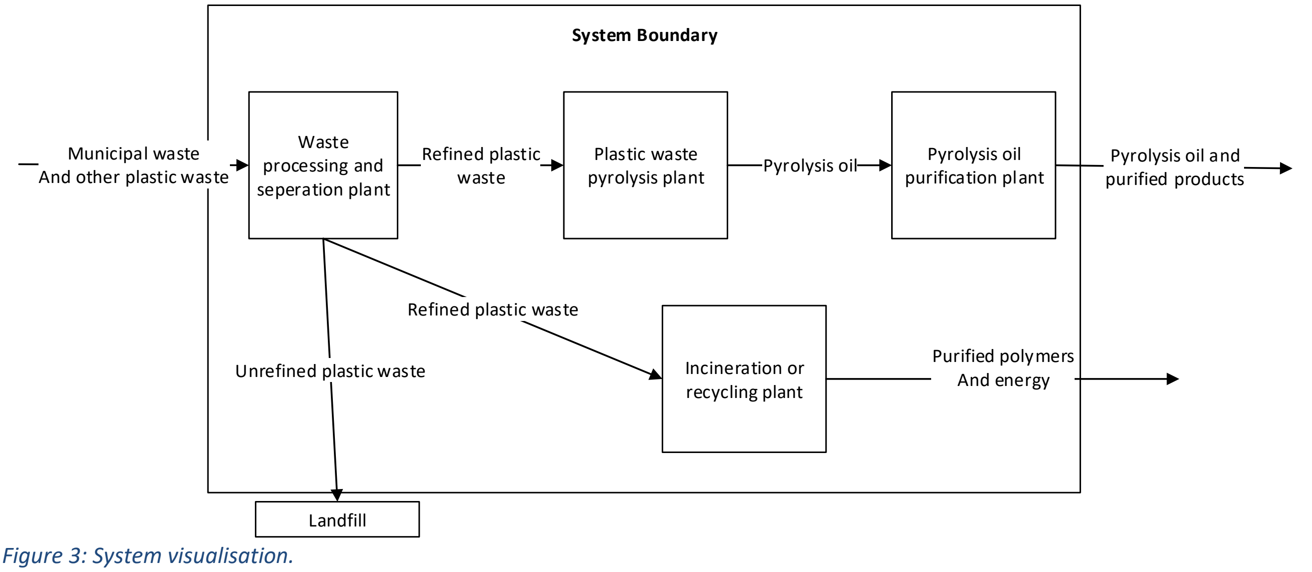


Figure 3: System visualisation.

3. Goal

The goal of this research is to deliver one scenario for a promising mixed plastic waste pyrolysis system and one scenario for a promising pure plastic waste pyrolysis system. Their feasibility will be judged in terms of environmental friendliness, sustainability and overall cost effectiveness.

These scenario's will give insight if pyrolysis is a suitable process for recycling both mixed and pure plastic waste or if other recycling methods are more suitable. The scenario's will consist of a technical process outline design and a limited economic analysis of the raw resources and the products of the processes. This economic analysis will give an indication of the potential profitability of the scenarios.

3.1 Scope

- Only European plastic waste streams and plastic waste processing systems will be considered
- Both the plastic waste pyrolysis and the plastic waste processing and separation plant will be considered because the input of the pyrolysis step greatly influences the output.
- The current recycling and incineration methods will be considered to compare it in cost effectiveness to plastic waste pyrolysis
- Landfilling and emptying landfills will not be considered because landfilling is unsustainable.
- Pure plastic waste streams will not be considered because pure plastic recycling processes are currently more optimized.
- The processes within the incineration or recycling plant will not be taken into account, only their cost and environmental friendliness.
- Plastic biomass co-pyrolysis will not be taken into account because this will unnecessarily complicate the system.
- Both thermal and catalytic pyrolysis processes will be taken into account to maximize the chances of finding a cost-effective process configuration which creates valuable products.
- Possible subsidies will not be taken into account.
- Implementation issues such as plant location, building dates and abiding governmental regulations will not be taken into account.
- Process initial investment and process exploitation costs will not be considered in the proposed scenarios because this is out of the scope of this research. If a specific process appears to be very promising an extensive economic analysis can be done in further research.

3.2 Main research question

Is pyrolysis of plastic waste a cost effective and environmentally friendly alternative to traditional plastic separation and processing?

3.3 Sub questions

1. How does plastic waste pyrolysis work?
2. How suitable are the differences in plastic types for pyrolysis?
3. What are suitable waste streams and do these waste streams need pre-processing (separation of certain plastic types, cleaning or crushing/shredding)?

4. What valuable products can be created from plastic waste pyrolysis of these waste streams?
5. How cost efficient is plastic waste pyrolysis when compared to traditional plastic waste recycling and incineration?

4. Research design

For the first sub question an overview of the different plastic waste pyrolysis techniques will be made with their respective pros and cons.
For the second sub question, an overview of pure plastics and their respective suitability for pyrolysis as mixture or as pure plastic will be made.
For the third sub question, the plastic waste streams will be listed with their respective chemical compositions, this information will be found in the literature and on the sites of plastic waste processing companies.
For the fourth sub question, the value plastic waste pyrolysis products will be estimated.
For the fifth sub question, the cost effectiveness and environmental friendliness of one or multiple proposed scenarios will be judged.

4.1 Cycle choice

All three cycles of the design science research method as described in Hevner et al, (2007) will be used.
The relevance cycle starts with the need to clean up plastic waste.
The rigor cycle starts with the question if pyrolysis is a suitable technology to clean up this plastic waste.
The design cycle starts with the goal to clean up plastic waste in a cost effective and environmentally friendly manner.
With the help of these 3 cycles, an outline design for integration of plastic waste pyrolysis within the European plastic waste processing system can be made.

4.2 Data acquisition and literature

The information used in this research will mostly be acquired by using articles on plastic waste pyrolysis. The plastic waste composition will be determined by checking the specifications of the available plastic waste streams and by interviewing managers of the plastic waste processing and separation plant. The prices of both the input and exit products of the system will be acquired using the sites of the respective wholesalers.
There is much literature available regarding the pyrolysis of plastic waste.
Five review articles[8-11 and 21] were found about plastic waste pyrolysis and will be used intensively as information source. All these review articles are about how plastic waste pyrolysis works and which methods and technologies are available within this field. These articles also discuss the different kinds of plastics, different pyrolysis techniques and the respective product yields.

4.3 Risk analysis and contingency plan

There are four main risks when considering this system. These risks arise in a certain step in the system as depicted in figure 3. These risks and their respective contingency plan are depicted in table 2.

Risk	System step	Contingency plan
1. Refining plastic waste in the waste processing and separation plant is technically unfeasible or very costly	Waste processing and separation plant	Bypass waste processing and separation plant step by searching for already more refined plastic waste flows or do not refine plastic waste flow at all
2. Mixed plastic waste pyrolysis is technically unfeasible or exit products are useless	Plastic waste pyrolysis plant	Refine input more so more contol on the exit products can be exerted
3. Purification of the pyrolysis oil is technically unfeasible or very costly	pyrolysis purification plant	Skip pyrolysis oil purification and sell the pyrolysis oil directly
4. The pyrolysis oil is contaminated with undesirable products	pyrolysis oil output	Refine plastic waste so no undesirable products are created or scrub the pyrolysis oil to remove undesirable products

Table 2: risk analysis and contingency plan

4.4 Activity plan

Every week one sub question will be answered. The 3 weeks will be used to answer the main question and write the preliminary and final report.

Week	Actions	Deliverables
16	read literature	
17	answer sub question 1	
18	answer sub question 2 + write IR	
19	answer sub question 3 + make presentation	Intermediate Report **(IR)** (8 may 12:00)
20	answer sub question 4	
21	answer sub question 5	
22	answer main question + write PR	
23	write PR + summary page	Preliminary report **(PR)** (5 jun 12:00) + Summary for page in symposium booklet (8 jun 12:00)
24	revise PR	
25	write FR + make Poster	**Final Report** (18 jun 12:00) + Poster (22 jun 15:00)
26	Make presentation symposium	Presentation symposium (26 jun)

Table 3: Activity plan of this research

5. Types of reactors for plastic waste pyrolysis

5.1 Batch and semi-batch reactor

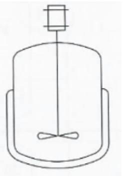


Figure 4: Batch reactor

A batch or semi-batch reactor as depicted in figure 4, is often used in research of plastic waste pyrolysis due to its simplicity, small size, easily controllable parameters and low cost. Mostly because of labour intensity a batch or semi-batch reactor becomes less suitable when the process is scaled up to higher volumes in which it is generally more cost efficient when a continuous flow is created. Temperatures range from 300° to 900°C and reaction time 30 to 90 minutes[9].

5.2 Fluidized bed reactor

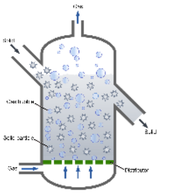


Figure 5: Fluidized bed reactor

In a fluidized bed reactor as depicted in figure 5, pressurized gas flow from the bottom up to the top trough the solid particles. This fluidizes the solid particles which creates good mixing properties and heat transfer for solid particles. A fluidized bed reactor is more suitable to develop continuous pyrolysis processes, which are less labour intensive. A narrower and more uniform spectrum of products can be produced as opposed to a batch reactor because the polymer waste can be bed into the reactor at a constant temperature[9]. Nevertheless, fluidized bed reactors are uncommon for municipal solid waste pyrolysis because of the problems that arise when separating the coke from the bed material[21]. It should also be noted that external heating, recirculation and the choice of the fluidizing agent are complicated and expensive.

5.3 Conical spouted bed reactor (CSBR)

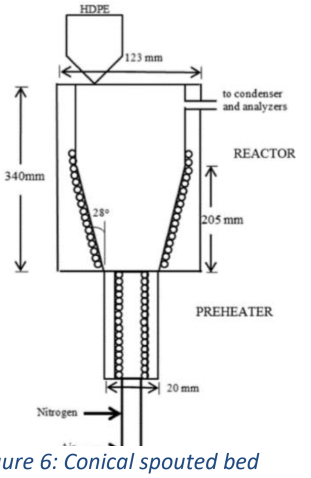


Figure 6: Conical spouted bed reactor

The conical spouted bed reactor was proposed to avoid defluidization in a fluidized bed reactor by melted plastic and to avoid troublesome coke separation from packing material. The very short residence time (~20ms) and the collision between particles reduces the chance of particle accumulation in the bed materials. Another advantage is the low pressure drop. Due to the lower residence time CSBR's tend to create more waxy products with a low polydispersity index (narrow range of polymer lengths). This suggests the existence of secondary and tertiary reactions during thermal pyrolysis. The produced waxes are suitable to be upgraded into gasoline, naphtha and other commercial hydrocarbon products[9]. Although plastic waste pyrolysis in CSBR's is promising not much research is done in this field.

5.4 Fixed bed reactor

A fixed bed reactor as depicted in figure 6, is a tube filled with catalyst pellets. The reactants flow through the bed and are converted into products. The catalyst can be configured into one large bed or multiple beds. If the catalyst is fixed in place it is called packing and the reactor is called a packed reactor. A fixed bed reactor has a low heating rate, as result of its low heat transfer coefficient. Therefore, the temperature is not uniform within the reactor when considering large volumes[21]. Temperature uniformity is desirable because it creates a narrower range of products.

5.5 Rotary kiln reactor

A rotary kiln reactor is a heated rotating tube, as depicted in figure 7, which is often inclined. Due to its rotating motion a rotary kiln reactor has good mixing properties. Heating is uniform but relatively slow (max 100°C/min), because only the reactor wall transports heat. Rotary kiln reactors are widely used for plastic waste pyrolysis due to the flexibility of the residence time and easy maintenance. Rotary kiln reactors also possess the ability to handle heterogeneous materials and

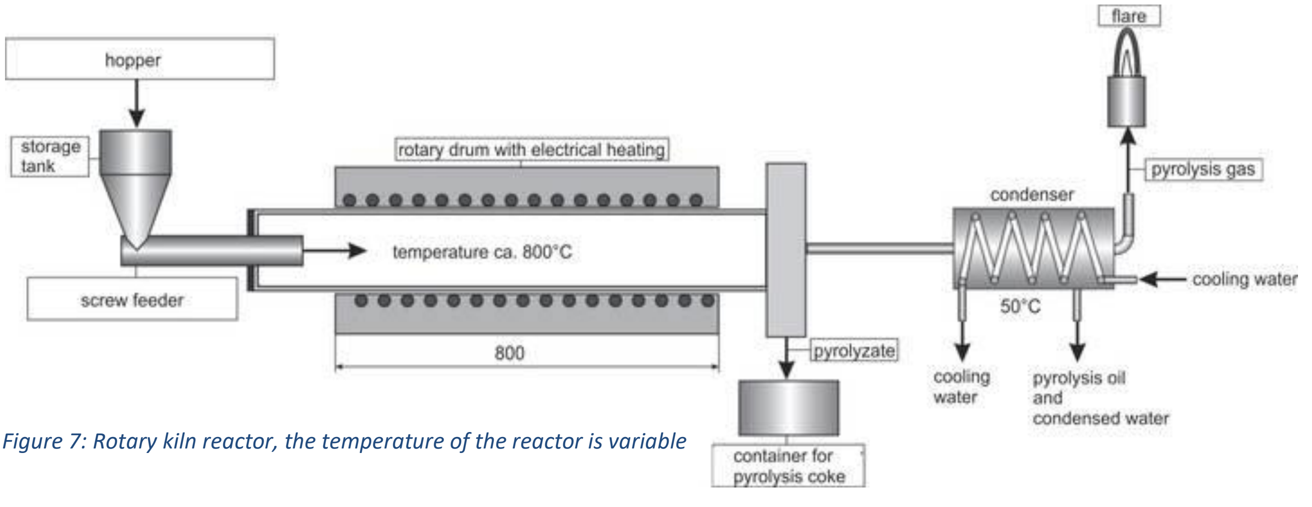


Figure 7: Rotary kiln reactor, the temperature of the reactor is variable

thus pre-treatment of waste is less important[21]. There are worldwide several operational industrial plastic waste pyrolysis processes which use rotary kiln reactors such as the Gibros pec process in Aalen, Germany or the Eddith process in Arras, France, although most of these plants have a diverse input of among other things municipal solid waste, spent tyres, industrial waste and dried sewage sludge and mostly focus on the generation of energy trough power or steam[21].

5.6 Microwave-assisted pyrolysis (MAP)

In microwave-assisted pyrolysis processes microwaves are used to raise the reaction temperature to up to 1000°C in a short period of time. This has several advantages including a fast heating rate and high temperature, this reduces residence time. Due to the high temperature plastic waste contaminated with aluminium, such as toothpaste tubes, can be recycled efficiently and aluminium can be almost fully recovered. MAP processes have a high yield of liquid hydrocarbons (up to 88%), this is most likely partly due to the aluminium oxide in the reactor which serves as a solid acid catalyst. MAP processes are not extensively researched but are promising[9].

5.7 Pyrolysis in supercritical water (SCW)

When pyrolyzing polymers in supercritical water (SCW) the water acts as both solvent and catalyst in the process. Smaller hydrocarbon molecules disperse in SCW therefore condensation and coke formation are reduced. The liquid yield of polyethylene to oils was more than 90 wt.% at 460°C with a H2O/polyethylene ratio of 6:1 and a residence time of 1 minute[22]. This is promising although more research needs to be done when considering mixed or contaminated plastic waste flows.

5.8 Fluid catalytic cracking

A major problem in creating continuous polymer pyrolysis processes is the continuous feeding of solid plastic waste into the reactor. This problem can be solved by dissolving the plastic feed into a solvent (for example vacuum gas oil (VGO)) and subsequently pyrolyze the solution. This has the following advantages; the volume is reduced, containments can be easily removed and the dissolving stage can be used to separate plastic types. Disadvantages include; extra safety measures due to the volatility of the solvent, limited research can create difficulties in reactor design, the solvent influences the product yield and distribution which adds an extra layer of complexity and this process requires an extra step and a solvent which adds to the total cost[9].

5.9 Overview of pyrolysis reactor types

In table 4 and 5 an overview of the different reactor types and their characteristics are presented.

Reactor type	Catalytists	Capacity	Residence time	Relative cost	Energy intensity	Technical maturity
Batch and semi-batch reactor	Optional	Flexible	High	Cheap	Low	High
Fluidized bed reactor	Yes	High	Moderate	Expensive	Moderate	Medium
Conical spouted bed reactor (CSBR)	Optional	Low	Low	Moderate	Low	Low
Fixed bed reactor	Yes	Low	Moderate	Moderate	Moderate	Medium
Rotary kiln reactor	No	High	Moderate	Moderate	Low	High
Microwave-assisted pyrolysis (MAP)	No	Flexible	Low	Moderate	High	Low
Pyrolysis in supercritical water (SCW)	No	Flexible	Low	Moderate	High	Too Low
Fluid catalytic cracking	Yes	Flexible	Moderate	Expensive	Moderate	Low

Table 4: Low residence time is less than 1 minute, high residence time is more than 30 minutes. Energy intensity is based on temperature and pressure of the reactor.

Reactor type	Advantages	Disadvantages	Remarks
Batch and semi-batch reactor	Good for experminting, easy to control parameters	Labour intensive	
Fluidized bed reactor	Good mixing properties, narrow range of products	Risk of bed defluidization, hard to seperate coke from packing	
Conical spouted bed reactor (CSBR)	Low pressure drop, narrow range of products	Not much research	High waxy product yield
Fixed bed reactor	High catalyst surface area	No uniform temperature, catalysts are replaced often	
Rotary kiln reactor	Flexible residence time, good mixing properties, can handle heterogenious materials, easy maintanance	Low maximum heating rate	
Microwave-assisted pyrolysis (MAP)	Suitable for aluminium contaminated flows, fast heating rate	Not much research	High liquid product yield
Pyrolysis in supercritical water (SCW)	Reduced condensation and coke formation.	Too little research	High liquid yield (at 460°C)
Fluid catalytic cracking	Reduced volume, containments can be removed and plastic types can be separated in the dissolving stage	Extra safety measures needed, solvent influences process	

Table 5: Advantages and disadvantages of different pyrolysis reactors

From these tables it can be derived that the rotary kiln reactor is most suitable reactor for creating a mixed plastic waste pyrolysis process. This can be concluded from the high capacity, moderate cost, low energy intensity and high technological maturity. These factors reduce cost and risk. This conclusion is not surprising because most of the current operating plastic waste pyrolysis plants use a rotary kiln/rotating drum reactor. When handling specific purified plastic flows however, the other types of reactors may appear to be preferable because certain variables are more controllable. Coke production might be lower and the amount of impurities might be lower.

6. Influence of temperature on plastic waste pyrolysis

As depicted in table 6, increasing the temperature of thermal pyrolysis process with pure plastics favours the production of gaseous products when pyrolyzing PE in a fluidized-bed reactor, whereas for PP it is the other way around. This highlights the complexity and unpredictability of plastic waste pyrolysis. Although as a rule of thumb gaseous product yield is higher when the temperature rises and liquid and solid yields are higher at lower temperatures. This makes sense because higher temperatures and longer residence times reduce the size of the hydrocarbons trough thermal degradation. The majority of these gaseous products were H_2, methane, ethane, ethylene, propylene, butadiene, benzene and toluene without CO, CO_2, or HCL for PE, PP and PS[21]. Higher pyrolysis temperature also makes the process more energy intensive and can cause a challenge to the safety of reactors[21].

Product yield from the pyrolysis of polyalkene plastics (Williams, 2006).

Feedstock	Reactor type	Temperature (°C)	Gas (wt%)	Oil/wax (wt%)	Char (wt%)
PE	Fluidised-bed	760	55.8	42.4	1.8
PE	Fluidised-bed	530	7.6	92.3	0.1
LDPE	Fluidised-bed	700	71.4	28.6	0.0
LDPE	Fluidised-bed	600	24.2	75.8	0.0
LDPE	Fluidised-bed	500	10.8	89.2	0.0
LDPE	Fixed-bed(batch)	700[a]	15.1	84.3	0.0
HDPE	Fixed-bed(batch)	700[a]	18.0	79.7	0.0
LDPE	Fixed-bed(batch)	500[a]	37.0	67.0	0.0
LDPE	Ultra-fast pyrolysis	825	92.9	5	2
HDPE	Fixed-bed(batch)	450	13.0	84	3
HDPE	Fixed-bed(batch)	430	9.6	69.3	21.1
HDPE	Vacuum	500	0.9	97.7	0.8
LDPE	Vacuum	500	2.7	96.0	1.0
LLDPE	Fluidised-bed	730	58.4	31.2	2.1
LLDPE	Fluidised-bed	515	0.0	89.8	5.9
PP	Fixed-bed(batch)	380	24.7	64.9	10.4
PP	Fixed-bed(batch)	700[a]	15.3	84.4	0.2
PP	Fluidised-bed	740	49.6	48.8	1.6
PP	Vacuum	500	3.5	95	<0.1
PP	Fixed-bed(batch)	500[a]	55.0	45.0	0.0

[a] Final temperature.

Table 6: Increasing the temperature of pyrolysis processes favours the production of gaseous products[20].

7. Overview of plastics

7.1 An overview of the availability of different plastics

Before considering mixed plastic flows, an overview is made of the general availability of pure plastics. Availability is measured in annual European converter demand. Converting companies are companies that create products from plastics among other things. Annual European converter demand is therefore a measure of plastic usage in produced products. This provides a first indication of the composition of mixed plastic waste.

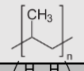
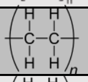
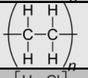
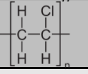
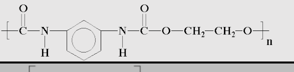
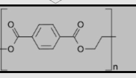
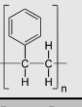
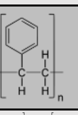
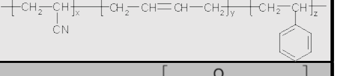
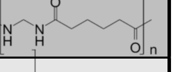
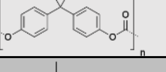
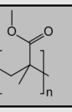
Plastic type	Abbreviation	Plastic type marks	Annual european converter demand (mt)	Percent of total converter demand	Chemical formula
Polypropylene	PP	5 PP	9,7	19%	
Low density polyethylene	PE-LD/ PE-LLD	4 LDPE	8,7	17%	
High/Medium density polyethylene	PE-HD/ PE-MD	2 HDPE	6,1	12%	
Polyvinylchloride	PVC	3 V	5	10%	
Polyurethane	PUR	7 OTHER	3,8	8%	
Polyethylene terephthalate	PET	1 PETE	3,7	7%	
Polystyrene	PS	6 PS	1,9	4%	
Expanded polystyrene	EPS or PS-E	6 PS	1,4	3%	
Acrylonitrile butadiene styrene	ABS	7 OTHER	1	2%	
Polyamide	PA	7 OTHER	0,9	2%	Nylon 1,6: 
Polycarbonate	PC	7 OTHER	0,7	1%	
Poly(methyl methacrylate)	PMMA	7 OTHER	0,4	1%	
Other thermoplastics		7 OTHER	2,8	6%	
Other plastics		7 OTHER	3,8	8%	
total			49,9	100%	

Table 7: Table of different plastic types listed on Annual European converter demand in megaton (mt) (2016)[12]. ABS is a copolymer; the proportions of the monomers can vary. Polyamide has multiple chemical formula's, nylon 1,6 is depicted.

7.2 Suitability for pyrolysis into diesel fuel of mixed plastics

Many possibilities for plastic waste pyrolysis are available. Commonly discussed is thermal plastic waste pyrolysis at (370°C-420°C) into a diesel oil substitute as depicted in figure 8. Due to its relative simplicity, is it a good example to judge general suitability for pyrolysis of different plastics to. The suitability for this pyrolysis process of different pure plastics depends the number of heteroatoms present in the plastics. Heteroatoms are atoms other than carbon and hydrogen, these plastics are called polyolefins.

Although not suitable, a thermal pyrolysis process which creates a diesel oil substitute can, nevertheless,

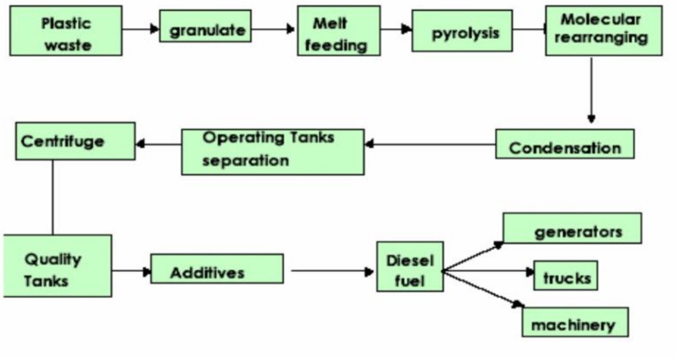


Figure 8: Thermofuel Process[13]

tolerate small quantities (>10%) of plastics containing the heteroatoms; oxygen and nitrogen[13].If the amount of plastic containing heteroatoms in the pyrolysis process does not exceed 10%, the off gas will not exceed 5%[13]. Pyrolysis processes where large quantities of heteroatoms are present tend to create large amounts of off gas[8]. Gaseous products are less desirable for they are harder to handle, and generally less valuable.

Plastics containing chlorine atoms (PVC) are not allowed in small quantities because the chlorine atoms are hazardous for health and the environment. Although dichlorination via low temperature (250°C-320°C) of physical or chemical adsorption is possible in post-processing, chlorine atoms can also affect the catalytic activity of catalysts[10], and HCL will evolve during pyrolysis causing apparatus corrosion[21]. Therefore, no PVC should be in the pyrolysis feed and low concentrations of other plastics containing heteroatoms.

From table 8 it can be derived that 55% of the plastic in produced products in suitable for pyrolysis for diesel substitute, 21% is allowed in small amounts, 10% (PVC) is not allowed, and 14% is unaccounted for because these are uncommon plastics. These plastics are most likely not allowed because most special plastics have heteroatoms.

Fibre reinforced plastics can be used if it is pre-processed and the fibres are removed. The density of the plastic type depends partly on the number of heteroatoms in the plastic. Nitrogen (14,0u), oxygen (16,0u) and chlorine (35,4u) atoms are heavier than carbon (12,0u) and hydrogen (1,0u) atoms. The plastics with a relative high number of heavier atoms are denser. The suitable plastics could be separated with simple plastic density separation processes[16]. Plastic foams are easily separable with sink/float separation.

Plastic type	Percent of total Converter Demand	Contains heteroatoms	Heteroatom type	Suitable for pyrolysis for diesel substitute	Density[14] (g/cm^3)	Relative mass of heteroatoms	Remarks
PP	19%	no	NA	yes	0,9-0,91	0%	
LDPE	17%	no	NA	yes	0,917-0,940	0%	
HDPE	12%	no	NA	yes	0,94-0,97	0%	
PS	4%	no	NA	yes	1,04-1,05	0%	
ESP	3%	no	NA	yes	1,04-1,05	0%	Foam
PU	8%	yes	N and O	small amounts allowed	0.94-1.11[15]	41%	67% Foam[17]
PET	7%	yes	O	small amounts allowed	1,3-1,4	33%	
ABS	2%	yes	N	small amounts allowed	1-1,21	Variable (7% when monomers are evenly distributed)	
PA	2%	yes	N and O	small amounts allowed	1,09-1,19	Variable (38,4% for Nylon 1,6)	
PC	1%	yes	O	small amounts allowed	1,17-1,3	19%	
PMMA	1%	yes	O	small amounts allowed	1.1-1.25	32%	
PVC	10%	yes	CL	no	1,150-1,7	58%	

Table 8: Different plastic types listed by heteroatoms. Heteroatoms are heavier than carbon and hydrogen atoms therefore plastics containing heteroatoms are denser.

The most suitable reactor for pyrolyzing mixed plastics is a rotary kiln reactor as this reactor has a high volume, high technical maturity and can handle impurities well.

7.3 Suitability for pyrolysis of pure plastics

Most plastics form oligomers when pyrolyzed, which creates a mix of products which is hard to separate and can often best be sold as fuel. Current recycling methods of pure plastics such as melting into new products are more cost effective and environmental friendly than creating fuel from these flows. However, pyrolysis of pure plastic can add value if the polymers are broken down into monomers. This is possible trough catalytic pyrolysis, but generally the yields are low and the catalysts are expensive. Only PMMA meets these constraints and can be broken down thermally into monomers.

Pure plastic flows of PMMA can be pyrolyzed into monomers up to 97% using thermal pyrolysis[30]. Due to the high yield, small amounts of coke are created. Because of the absence of melted plastic and small amounts of coke, a fluidized bed reactor is most suitable for PMMA pyrolysis as the reactor bed material can be used for long periods of time. PMMA monomers (MMA) have a price of €3.857 per tonne in Germany[31] on 01-06-2018, which creates a lot of potential for profit and creates a sustainable circular economy.

8. European waste streams and their costs

8.1 Municipal waste

Most mixed plastic waste comes from municipal waste streams. The plastic fraction differs greatly from 92wt% in a film rich sample, 43wt% in a paper rich sample and 60wt% in a glass rich sample[24]. The plastics fraction contains HDPE, PP, PS, PET and PVC. These flows can be directly pyrolyzed using co-pyrolysis, but due to its many impurities it is preferable to separate the plastics first. Advanced municipal waste separation methods are currently implemented throughout Europe. Municipal waste is therefore not a suitable waste flow for plastic waste pyrolysis and should be separated first.

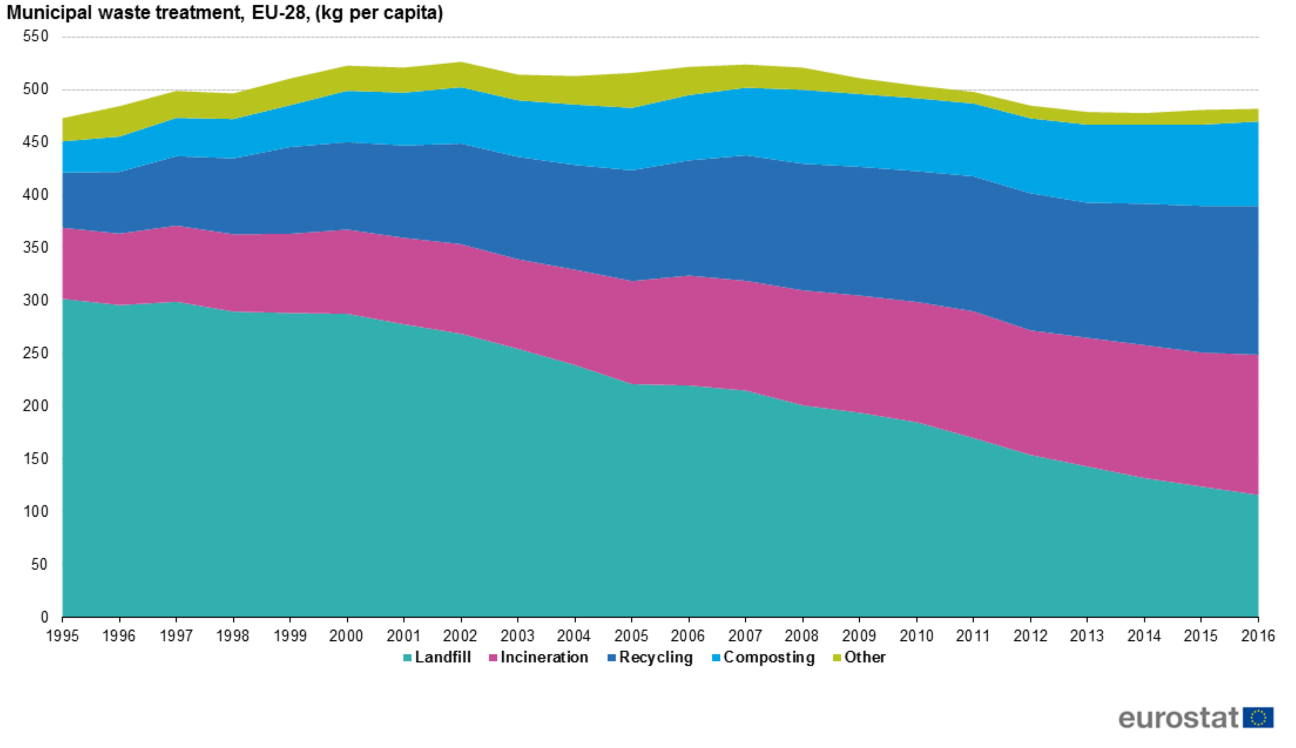


Figure 9: Municipal waste treatment in the EU over time[23]. Municipal waste contains plastics, metal, paper, glass and organics. The fractions may differ.

Cost of manicipal waste treatment	Cost	Revenue	Total cost
Composting	€ 52,92	€ 9,92	€ 43,00
Incineration SNCR	€ 82,57	€ 11,88	€ 70,69
Landfilling	€ 28,78	€ 0,00	€ 28,78

Table 9: The costs associated with the treatment of municipal waste. Prices are per tonne of municipal waste treated. The breakdown of costs and revenues are provided in appendix A.[25] The Gate fees revenue for composting are not included. SNCR incineration is an abbreviation for High-efficiency selective non-catalyst reduction.

Co-pyrolysis of unseparated municipal waste is possible but outside of the scope of this research.

8.2 Separated plastic waste:

Separated plastic waste can directly be bought from companies exploiting plastic waste separation plants. Companies specialized in plastic waste separation like Aterro use advanced techniques to create plastic waste flows with a high purity as they present in a video[26]. The granulates they create are 98% low density polyethylene(LDPE) and 2% Polypropylene(PP)[27]. Attero does not present the prices of their products on their website, but letsrecycle.com provides prices of different separated plastic waste streams, which gives a good indication of the prices of sorted plastic waste.

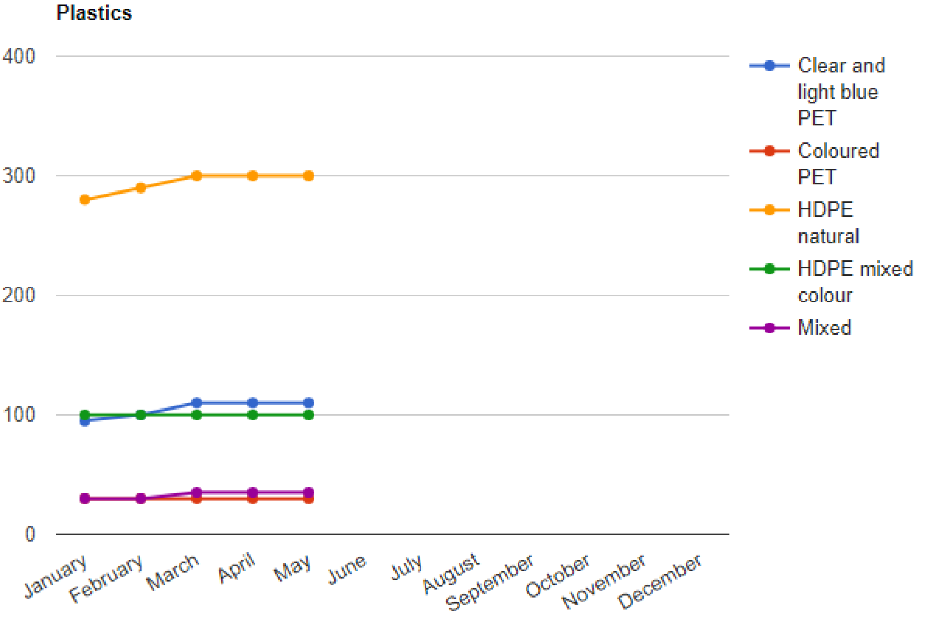


Figure 10: Separated plastic waste prices in the first half of 2018. In £ per tonne[28].

Mixed plastic waste is 10-60£ per tonne, HDPE mixed colour is 90-110£ per tonne, and coloured PET is 25-35£ per tonne. As of 3 June 2018 1 £= €1,413 so it is assumed that mixed plastic waste can be bought for €60 per tonne, HDPE for €130 per tonne and PET €40 per tonne.

8.3 PMMA scrap

PMMA is mostly used in acrylic sheets. Trade names include Plexiglass and Perspex. These sheets are used in a large variety of products. In the shaping process of these sheets PMMA scrap waste is created, which can be bought on Alibaba.com for about $ 250 per ton[32].

9. Overview of plastic waste pyrolysis products

9.1 Price of diesel fuel

The price of diesel is very dependent on the crude oil price. The price of crude oil can fluctuate and hard to predict, and crude oil is bought in dollars while diesel is sold in euro's which makes fuel also dependent on currency value changes, thus selling diesel fuel substitutes can be a risky business.

Diesel fuel is very highly taxed throughout Europe; therefore, the retail price can be deceptive. When calculating possible profits, one should consider the product price as depicted in figure 11. The global diesel price has risen about 20% since 2016 so it is assumed that one litre of diesel substitute can be sold for €0,50.

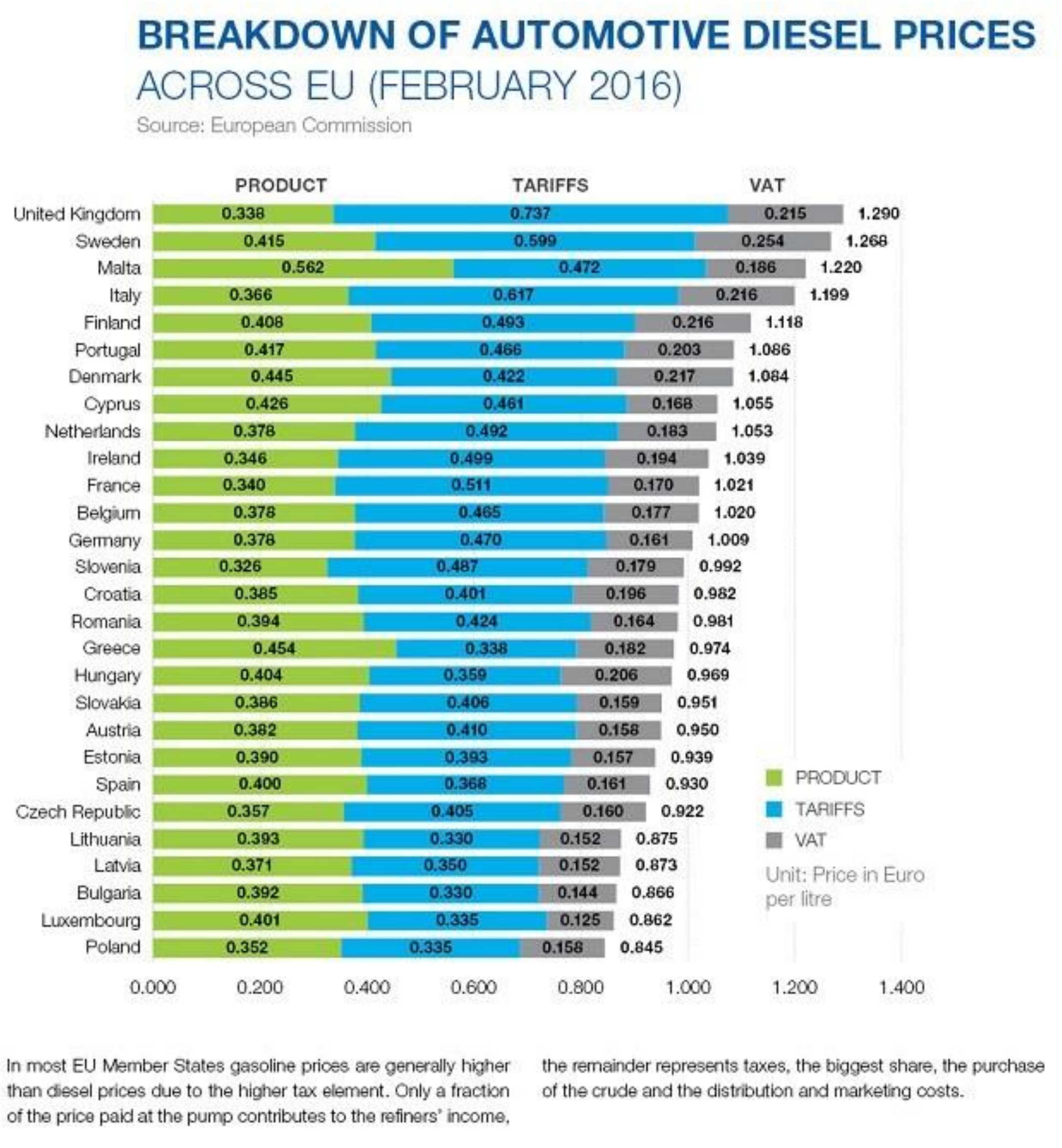


Figure 11: Breakdown of the diesel fuel price in Europe in 2016, the retail price and product price differ highly. Tariffs are fixed duties and are not dependent on crude oil prices, VAT are rates are a percentage of the basic price and are therefore dependent on crude oil prices[29].

9.2 Price of PMMA monomers (MMA)

PMMA monomers (MMA) have a price of €3.857 per tonne in Germany[31] on 01-06-2018**.**

10. Choice and outline of two plastic waste pyrolysis systems

Two promising thermal plastic waste pyrolysis processes will be outlined, both of which are thermal pyrolysis processes. Catalytic pyrolysis processes are generally more complex and harder to control, moreover catalysts are expensive and most catalytic pyrolysis processes require a large amount of catalysts which cannot be reused indefinitely, furthermore is the technical maturity of catalytic plastic waste pyrolysis processes lower which raises the cost even more.

10.1 Polyolefins into diesel fuel

The first outlined process produces diesel fuel from polyolefins. These polyolefins can be extracted from municipal waste or bought directly from municipal waste separation plants.

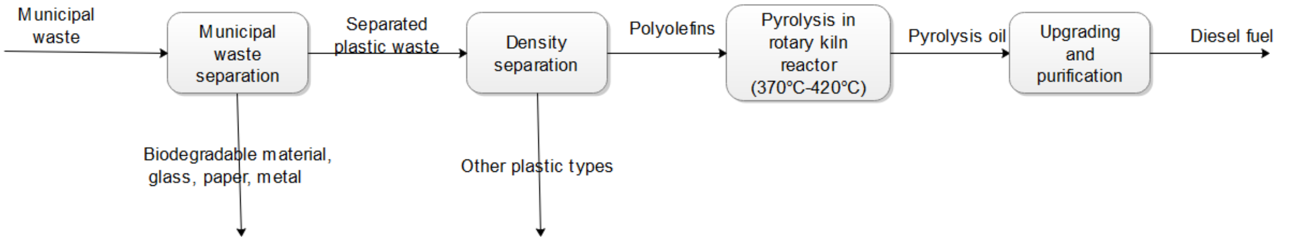


Figure 12: Process outline of Polyolefins to diesel fuel process.

10.2 PMMA scrap into PMMA monomers

The second outlined process produces MMA (PMMA monomers) from PMMA scrap. PMMA scrap can be bought as waste sheets or as pre-crushed pellets. A fluidized bed reactor is a suitable reactor for this process because it ensures high yields of MMA. Other pyrolysis reactors could be considered.

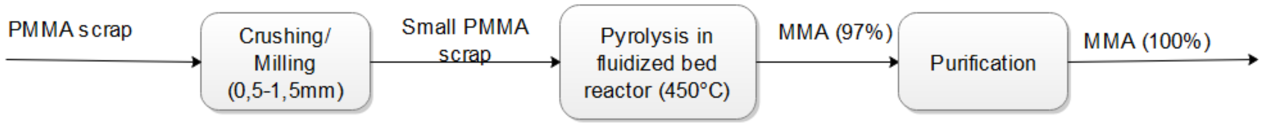


Figure 13: Process outline of PMMA scrap into MMA

10.3 Maximum available earnings of outlined processes

The two outlined processes are pyrolysis of polyolefins into diesel fuel substitute, with a yield of 950ml per kg plastic[13], and Pyrolysis of PMMA scrap into PMMA monomers, with a yield of 97%[30]. The estimated price of the raw materials and products are given in table 10.

Process	Estimated raw material price	Estimated product price	Yield	Maximum profit
Polyolefins into diesel	€60 [28]	€500 [29]	0.95L per KG	€ 418.00
PMMA scrap into PMMA monomers	€250 [32]	€3850 [31]	97%	€ 3,492.00

Table 10: Maximum possible profit per ton of product, diesel price in 1000 litres.

11. Conclusion

The potential of implementing pyrolysis of plastic waste is with current technologies and market forces limited to pyrolysis of PMMA. Thermal pyrolysis of PMMA is environmentally friendly and has a high probability of being cost effective. The technology used is mature and the chemical processes are well understood.

Although the bulk of plastic waste can be pyrolyzed into diesel fuel, other recycling methods are more suitable. Mixed plastic waste is mostly found in municipal waste, which has to be separated either way. The separation processes already implemented are advanced and create plastic monoflows which are easily recycled into new products. Furthermore, due the low potential for profit and risk due to price changes, creating diesel fuel substitutes from mixed plastic waste would create a risky high initial investment business with small margins at best. Moreover, creating a diesel fuel substitute, might not be the right plan of action considering climate change and the effort of creating a circular economy.

With the exception of PMMA plastic, pyrolysis of pure plastic waste is not suitable for most plastic types because these plastic types cannot be pyrolyzed back into monomers without the use of elaborate processes and catalysts. Complicated processes using catalyst do have the potential to create valuable products from pure plastic flows, however these processes are not mature enough to be implemented yet and other recycling methods for pure plastics are available.

Pyrolyzing pure flows of PMMA plastic has a high probability to be profitable and is technically feasible. It is recommended to start a follow-up study for an extensive economic analysis and business case of the proposed process.

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Appendix A:

Costs[6]	Investment €	Payback Period yr	Rate %	Annualised cost €/yr	Specific costs €/t	Maint %	Annual Maintainance €/yr	Specific cost €/t
Cost of land[7]	500.000	20	7%	**47.196,46 €**	**2,36 €**			
Civil Works								
Paving, concrete	595.000	20	7%	56.163,79 €	2,81 €	1%	5.950,00 €	0,30 €
Process Buildings	592.500	20	7%	55.927,81 €	2,80 €	1%	5.925,00 €	0,30 €
Pool(s)	20.000	20	7%	1.887,86 €	0,09 €	1%	200,00 €	0,01 €
Biofilter	117.600	5	7%	28.681,55 €	1,43 €	2%	2.352,00 €	0,12 €
Weighing Bridge	30.000	10	7%	4.271,33 €	0,21 €	2%	600,00 €	0,03 €
Offices	90.000	10	7%	12.813,98 €	0,64 €	2%	1.800,00 €	0,09 €
Utilities	300.000	10	7%	42.713,25 €	2,14 €	5%	15.000,00 €	0,75 €
Wall	60.000	20	7%	5.663,58 €	0,28 €	1%	600,00 €	0,03 €
			TOTAL	**208.123,13 €**	**10,41 €**		**32.427,00 €**	**1,62 €**
Equipment								
Shredder	150.000	7	7%	27.832,98 €	1,39 €	5%	7.500,00 €	0,38 €
Screw mixer	100.000	7	7%	18.555,32 €	0,93 €	5%	5.000,00 €	0,25 €
Turning Machine	250.000	7	7%	46.388,30 €	2,32 €	5%	12.500,00 €	0,63 €
Sieve	100.000	7	7%	18.555,32 €	0,93 €	5%	5.000,00 €	0,25 €
Eddy current separator	100.000	7	7%	18.555,32 €	0,93 €	5%	5.000,00 €	0,25 €
Loader	160.000	7	7%	29.688,52 €	1,48 €	5%	8.000,00 €	0,40 €
Hopper	30.000	7	7%	5.566,60 €	0,28 €	5%	1.500,00 €	0,08 €
Blowers, Fans	250.000	7	7%	46.388,30 €	2,32 €	5%	12.500,00 €	0,63 €
			TOTAL	**211.530,67 €**	**10,58 €**		**57.000,00 €**	**2,85 €**
	Quantity	Unit	Unit cost	Yearly cost €/yr	Specific cost €/t			
Variable Costs								
Manpower	7	w.u.						
Director	1	w.u.	60.000 €	60.000,00 €	3,00 €			
Accounter	1	w.u.	35.000 €	35.000,00 €	1,75 €			
Workers	6	w.u.	30.000 €	180.000,00 €	9,00 €			
TOTAL Manpower				**275.000,00 €**	**13,75 €**			
Fuels	80.506	litres	0,700 €	56.354,12 €	2,82 €			
Energy	944.813	kWh	0,075 €	70.861,00 €	3,54 €			
Maintenance	considered in fixed costs, as (relatively) independent from throughput							
Analysis	-	-	25.000 €	25.000,00 €	1,25 €			
Disposal of rejects	1.000	tonnes	75 €	75.000,00 €	3,75 €			
			TOTAL	**502.215,12 €**	**25,11 €**			
				1.058.492,38 €				
	TOTAL COSTS				**52,92 €**			

Figure 12: Breakdown of Costs and Revenues for Intensive Composting Facility in Italy (20,000tpa)[25]

Revenues	Quantity	Unit	Unit price €	Yearly revenue €/yr	Specific revenue €/t
Gate fees					
food waste	12.000	tonnes	60 €	720.000 €	36,0 €
yard waste	8.000	tonnes	20 €	160.000 €	8,0 €
			TOTAL	**880.000 €**	**44,0 €**
Sale of compost[8]	8.000 tpy	= 16.000 cu.m			
field crops	3.200	cu.m	2	6.400 €	0,32 €
gardening, landscaping	8.000	cu.m	6	48.000 €	2,40 €
pot cultivation, once bagged[9]	4.800	cu.m	30	144.000 €	7,20 €
			TOTAL	**198.400 €**	**9,92 €**
			TOTAL REVENUES	**1.078.400 €**	**53,92 €**

Figure 13: Revenue composting Facility in Italy[25]

	Grate Incinerator SNCR	Grate Incinerator SCR
COSTS		
Capital Cost per Tonne	€ 34.58	€ 37.08
Operational Cost	€ 38.79	€ 40.00
Fixed	€ 30.54	€ 31.76
Variable	€ 8.24	€ 8.24
Overhead	€ 9.23	€ 9.80
Total	€ 82.57	€ 86.88
REVENUES		
Materials	€ 0.00	€ 0.00
Electricity production	-€ 11.88	-€ 11.76
Total	-€ 11.88	-€ 11.76
NET COST	**€ 70.69**	**€ 75.12**

Figure 14: Cost of incineration in Flanders[25]

Site Assessment	€ 320,000.00	10	€ 45,560.80	€ 0.26
Acquisition	€ 1,600,000.00	10	€ 227,804.00	€ 1.30
Capex and Development	€ 14,088,729.60	10	€ 2,005,918.14	€ 11.46
Restoration	€ 960,000.00	10	€ 136,682.40	€ 0.78
Aftercare	€ 4,924,582.40	10	€ 701,149.74	€ 4.01
Total	€ 21,893,312.00		€ 3,117,115.09	**€ 17.81**
Operating costs				
Operation			€ 1,920,000.00	**€ 10.97**
Total Costs		€ 5,037,115.09		**€ 28.78**

Figure 15: Cost of landfilling in the UK[25]