Internship Report

Chemical Recycling with Dutch feedstock

Riya Maria

With Dr ir M.C.M. Bakker (University Supervisor) and
Rolf van Sprang (Company Supervisor of Kennisinstituut
Duurzaam Verpakken (KIDV))
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ABS	Acrylonitrile Butadiene Styrene
EPS	Expanded Polystyrene
EVOH	Ethylene vinyl alcohol
HDPE	High Density Polyethylene
HIPS	High Impact Polystyrene
LDPE	Low Density Polyethylene
PA	Polyamides
PC	Polycarbonate
PE	Polyethylene
PET	Polyethylene Terephthalate
PMMA	Polymethyl Methacrylate
PP	Polypropylene
PS	Polystyrene
PU/PUR	Polyurethane
PVDC	Polyvinylidene Chloride
PVC	Polyvinyl Chloride

A. Company Reflection

Kennisinstituut Duurzaam Verpakken (KIDV) or Netherlands Institute for Sustainable Packaging (in English) is a foundation that helps organizations and businesses design and organize their packaging needs more sustainably. They play an important role in the transition to a more sustainable packaging industry by promoting the reuse and recycling of packaging materials. The organization is funded by the Afvalfonds Verpakkingen (AFV; the Dutch Packaging Waste Fund). AFV is a private organization that is responsible for the collection and recycling of packaging waste in the Netherlands. To guide KIDV's present and future activities and ensure that these activities are in line with their vision and goals, a Supervisory Board is established. This board typically comprises 5 members, and each of these members is an expert in specific aspects of the packaging industry. Additionally, KIDV has a Committee of Independent Experts providing technical and logistic advice and keeping them updated on the trends and noteworthy developments in the packaging industry. This committee generally includes academics as members.

KIDV is associated with various companies and organizations in the packaging industry. KIDV is linked with Nedvang, a Dutch private organization that monitors the collection, sorting, and recycling of packaging waste. KIDV also collaborates with other organizations like Nederland Schoon and Statiegeld Nederland which also aims to promote the recyclability of packaging and reduce waste. The KIDV is also in partnership with universities including Wageningen University & Research, Leiden University, and the Delft University of Technology to share knowledge and expertise and collaborate in research projects on typical topics such as packaging materials, recycling technologies, and consumer behavior. Currently, KIDV, AFV, Nedvang, Nederlands Schoon, and Statiegeld Nederland are in the process of forming a unified organization called the Afvalbeheerstructuur (ABS). The above-mentioned four organizations, producers, users, and importers of packaging are the direct stakeholders of ABS. Consumers, the Dutch government, municipalities, consultancies, and academic institutes are indirect stakeholders.

The vision of KIDV is:

'Towards intrinsically sustainable packaging'

They pursue their vision by advising producers and organizations involved in the packaging industry to opt for the latest packaging designs that have a lower environmental impact. They also offer professional training and workshop sessions on packaging design and development. These trainings are focused on employees (of companies who work with packaging daily) to help design and develop sustainable packaging strategies in their businesses. The KIDV also researches innovative and sustainable packaging solutions. This helped them develop several free access tools, such as:

- Recycle Checks – easy way to check whether the packaging is recyclable. The tool accommodates rigid plastic, flexible plastic, paper, and cardboard, glass, and metal packaging into their analysis.
- Sustainable Packaging Compass – assesses the overall sustainability of the packaging product through recyclability, circularity, and environmental impact.
- Packaging Barometer – sales and packaging data of a product is mapped out to provide companies with insight into where the most profit can be by making packaging more sustainable.

The organization has a specialized team of Sustainable Packaging Experts with a background in the industry and a lot of knowledge concerning packaging materials (such as glass, metal, paper, and plastics). They also focus on the collection, sorting, and recycling of Dutch household waste. The size of the organization makes it easy to team up for projects and share information regarding their field of expertise. It was interesting to watch how everyone collaborated and easily cooperated to work on projects that were specifically assigned to them based on their expertise. Regular meetings were organized in the company, to ensure everyone was informed about the ongoing projects across the organization. These weekly meetings provided more transparency to the employees by sharing personal and overall updates. I also observed that the work environment appeared to be relaxed and calm because the KIDV is not driven by profits. A common positive drive is that everyone shares the idea of creating a positive impact on the environment and searching for the best possible solution to the problem at hand.

Being an international student in an all-Dutch environment can be challenging due to language and cultural differences. However, I found this internship an interesting way to learn a bit about the Dutch language and culture. The company did try its best to create an environment that included me, for example by switching their conversations to English and having more conversations about topics to which I can relate. I had kennismaking sessions with everyone at the office to understand the workings of the organization and to learn more about each other. Using the Hofstede method, I was able to compare my experiences in a Dutch and Indian work environment. This method also highlights the cultural differences and how they can impact professional dynamics. The Hofstede method focused on the following aspects:

- Power distance: at KIDV it was easy to tell that the organization followed an egalitarian method of working, giving their employees more freedom in their work. However, in India, hierarchical systems are practiced at workplaces to bring about an organized structure and meet the goals and aspirations of the company.
- Individualism and Collectivism: this is relatively similar in Dutch and Indian workspaces. I have observed that everyone exhibited a level of individualism in their working style but still nurtured a sense of common ground. Although flexibility at work is less in India, people actively work together and form interpersonal relations to make their workplace more comfortable.
- Masculinity and Femininity: at KIDV, I observed that there is a significantly higher proportion of female employees. In India, this is the opposite scenario.
- Long and Short-Term Orientation: I believe that KIDV has designed its projects to meet their long term goals and not create short-term benefits in the packaging industry. Their projects like Recycle Checks still undergo regular updates to make sure that it is up-to-date. This would be a difficult aspect to access in India since it varies from company to company.

KIDV and AFV observed the potential and rising number of chemical recycling companies within the Netherlands. This is why they took an interest in better understanding the potential and specific recycling routes that chemical recycling may offer. This prompted them to further investigate chemical recycling technology in the context of the Dutch plastic packaging waste landscape. My function in the organization as an intern was to help provide a better understanding of chemical recycling possibilities in connection with Dutch feedstock. Here, the feedstock is considered to be a fine household waste since KIDV focuses on consumer packaging. Earlier this year, the KIDV had published a vision document for Chemical Recycling. This was just the beginning for KIDV. After this, I worked individually on documenting chemical recycling techniques under the guidance of my professor and company supervisor. Apart from chemical recycling, I was also able to learn about various societal aspects of plastic packaging from the employees of the company, such as legislation.

I did not face any ethical issues with the other members of the organization due to my individual work assignment. However, I did face certain moral difficulties in my research. Chemical recycling is a new technology or recycling route for plastics. Oftentimes it is advertised as an alternative way to recycle the residues leaving the system, but in practice, this is not the case. Producing high-quality products would require cleaner and purer input streams. This is essentially greenwashing, but this cannot be proven since companies are not willing to provide information regarding the specifications of their feedstock and process. Furthermore, this could confirm the fact that chemical recyclers at present are competing with mechanical recyclers over feedstock. Many sorted input streams currently entering the mechanical recycling facilities would be diverted while the environmental impacts may turn out less favorable. When working in a knowledge institute it is important to protect the interests of its partners as well as provide accurate facts. This creates an ethical dilemma, but sticking to facts while making claims along with transparency of information and good communication will help with such problems.

Another ethical dilemma that I faced was trying to provide a solution to balance mechanical and chemical recyclers. Mechanical as well as chemical recycling technologies have their advantages and disadvantages, such as product quality and the environmental impact of the process. Unlike mechanical recycling, many petrochemical industries are interested in chemical recycling due to the potential chemical applications of the output produced. These companies are willing to provide chemical recyclers with feedstock and resources to grow in the industry. This gives chemical recycling companies more incentive to grow and control the feedstock flow. I believe that it was important to analyze the market and provide a solution that prevents the 2 techniques from competing with each other. In the end, I was able to conclude that to coexist with each other, fair partnerships should be considered between mechanical recyclers, chemical recyclers, and incinerators.

As a third person in the organization, I believe that the company has the potential to expand into fields that are beyond packaging, for example, plastic used in products. Packaging waste is one of the environmental problems in today's world due to the excessive material consumption lifestyle. But KIDV should not be limited to plastic packaging alone. However, the company is funded by AFV and it is of great interest to brand owners since they are knowledge providers. This means, KIDV is not in control of its direction and cannot change its focus on its own. Additionally, the very same goal of sustainable packaging places them in a political situation. The organization deals with people in influential positions and organizations that work to safeguard their interests, in particular lobbyists. Though this causes delays in decisions that need to be taken, it is interesting to watch the organization navigate through these challenges with diplomacy and efficient communication. In my opinion, after the amendments to the Packaging and Packaging Waste Regulation (PPWR) in the EU, the company's position in the market will be of higher importance for the Netherlands. They will be a vital source of information and guidance for producers or other interested organizations. This will demand an increase in cultural and academic diversity in their workspace. From an academic point of view, diversity would include expertise in end-of-life alternatives besides manufacturing and designing packaging. I believe their interest and my planned research in chemical recycling could be a part of the starting point for this expansion.

Overall, I had the chance to learn and expand my knowledge regarding the plastic packaging industry. With this experience, I was able to identify my strengths and areas of improvement such as organizing my work in a professional setting. This increased self-awareness will help me perform better in my future assignments. The company offered me plenty of opportunities to connect with experts in the various aspects of chemical recycling, this helped me expand my professional network and broaden my understanding regarding the topic. Moreover, I was able to experience KIDV's work culture and learn how to operate more effectively in a professional environment. I found the project challenging and personally rewarding. I was able to understand the project from academic and professional points of view and conditions. Through this internship, I was also able to apply my academic knowledge to more practical applications.

B. Personal Reflection

My internship at Kennisinstituut Duurzaam Verpakken (KIDV) was an invaluable experience, offering me a chance to understanding how plastics can be chemically recycled in the Dutch landscape. This covered the technological, commercial, and environmental aspects of four different types of chemical recycling routes.
As an environmental engineering student coming from a physics background, I found this topic to be rather challenging yet rewarding. While I had a good grasp on mechanical recycling through my masters program, chemical recycling added a new layer of complexity.

Plastic recycling and closing the loop for plastic to decrease pollution and increase resource efficiency is not a new concept for a Resource and Waste Engineering student. However, I viewed it as an opportunity to address this seemingly familiar subject from a different discipline. Chemical recycling techniques were originally designed for other purposes, but today they have the potential to be a part of the solution for plastic recycling. Nevertheless, this came with its own challenges. Prior to starting the internship, my knowledge in chemistry was very basic, so, the most time consuming part of the internship was the understanding of the reactions in these technologies. But, the most intriguing part of this internship was comprehending the market for chemical recycling. This was very fascinating to me since I was able to interview several industry experts, chemical recyclers and consultants who focused on understanding and evaluating chemical recycling for plastic waste.

Before starting my internship, I had set 4 main personal goals that I needed to achieve through this internship, they are:

1. Identify my strengths and weaknesses in a professional setting.
2. Trying to learn Dutch.
3. Asking the right questions in an interview
4. Understanding plastic recycling in a Dutch landscape from a corporate perspective.

The first objective would appear very repetitive, but it is a very significant objective to me. This internship is my first real work experience and I have often heard from my peers that work life is different from university. I believe that the difference between the 2 would influence my strengths and weaknesses, making it a crucial objective for my professional development.
In my internship, I learned from a few mistakes. I did not always organize my work or logistics well. I did not do simple tasks like recording a meeting or taking minutes of the meetings. This resulted in me missing out on several important points or key points of improvement. I also did not provide my university supervisor with weekly updates and sometimes informed certain details or information a bit late. Since I did not provide my supervisor updates regarding my work, I interpreted one of the internship objectives incorrectly. Although this was later on resolved with his help, I realized that consistent communication was a very important aspect for mu future assignments. Once these slip-ups were pointed out to me, I made sure to take the necessary steps and pay more attention to small details. Furthermore, frequent conversations and efficient communication are very important elements in a professional setting. I understand that this provides others with timely updates on my progress and helps me solve my mistakes in the early stages of my work. These were some of the mistakes that did not make when I was working in student groups at the university. I also recognized the need to improve my report-writing skills. I try to achieve this with the help of Grammarly and by reading additional reports to understand their writing style.

Despite these weaknesses, I believe that I made a conscious effort to adapt and progress in those areas of improvement. I believe that I actively tried to find a possible solution to address the problems that I encountered. If finding a solution was not possible independently, I would try to get help in finding one. In my opinion, keeping an open mind towards other's opinions and acknowledging my mistakes help me continuously learn and make sure that I don't repeat these errors. Seeking guidance from my mentors, I was able to efficiently navigate through many of the problems I faced with finding information and writing this report.

After receiving the opportunity at KIDV, I realized that learning Dutch is an important aspect of working in a Dutch work environment. The language helps in effective participation and engagement in a workspace. It is a common fact that when people who speak the same native language get together, they tend to speak in their own language. So, when I was placed in a Dutch work environment, having a certain proficiency in the language would help me in engaging casual conversation or expand my network. So, I took the Dutch language course at the university and passed my A1 level. The other employees at KIDV helped me during this course by having short and easy conversations in Dutch and explaining certain Dutch grammar and words. Although I took time to respond and understand the sentences or statements they said in the conversation, they were very patient and helped me with the conversation. During the lunch hours, conversation in Dutch among other colleagues in the office also helped me with my listening skills.

In order to gain more insights on the commercial facets of chemical recycling, I reached out to various experts with the help of my company supervisor. Due to confidentiality reasons, I couldn't get detailed information but our conversations were helpful. From the interviews conducted, I realized that asking the right questions would provide me with the needed information, even when specific details were not provided. This was a vital learning experience for me in my professional development. This improved my ability to carry out an interview while respecting the limits set by the other person. It was also a valuable lesson on how to handle sensitive information professionally.

During my internship, I was able to learn from my professor that plastic recycling is not as simple as it appears to be. One of the reasons for this is the complexity of various types and forms of plastic that are available in the market. This can be a rather simple process of collection, sorting and separation, but these waste plastics can yield significant profits for certain companies when handled properly. This is something that I underestimated in my study and something I did not grasp fully during my masters. I did not realize that the quantification of these large amounts of plastic into various categories and types is a tedious process. Additionally, I learned that careful evaluation is required when considering these numbers so that incorrect information is not used in the report. With the help of my professor, I realized why the allocation of plastics to certain routes might not be a possible solution to achieve balance in reality. I was particularly motivated to achieve this objective because I believe that what we learn in the university may not be always applicable in real-world situations. I also understood that several powerful companies have a great impact on these systems and that is something beyond our control.

During my time at KIDV, I was able to get a peek at the business world. Yet, I believe that for someone new to the profession should gain more hands-on experience in the field before transitioning into a consultancy world. I am aware that KIDV is not a consultancy firm but such firms require individuals who are experts in the industry. In my opinion, for a fresher like me, operational tasks and challenges would help improve my fundamental knowledge of the industry. I believe that I will be able to receive more insights on this during my thesis when I work with another company to help optimize their systems. Additionally, I also believe that working in a more diverse group would align better with my professional preference. Although I felt very much welcomed and included by the company, I did feel like I stood out from the group. In my opinion, working in a group with people of different backgrounds would fit me better. My experience at KIDV highlighted that people do not need to come from different cultural backgrounds to have different ideas and opinions on the same problem. Having a diverse workspace would enhance the working atmosphere by increasing a sense of inclusion and different perspectives.

To conclude, I believe that my experience at KIDV over the past 3 months has been a valuable contribution to my professional and personal development. Despite of all the challenges, I believe I was able to address my personal learning objectives and receive crucial insights into this new route of plastic recycling. This experience expanded my understanding of the industry including the existing systems. I hope to learn more in the coming months and ensure that I do not make the same mistakes made in my internship. I also hope to improve my professional communication and organizational skills while expanding my knowledge. Finally, I aim to create a meaningful impact on the environment through my career by sincerely making sustainable choices and making decisions that positively affect others.

1. Abstract

This report explores the technological and commercial development of four main chemical recycling technologies with the Dutch feedstock. The 4 technologies are: Pyrolysis, Gasification, Solvolysis and Dissolution. This report presents a clear understanding of the potential Dutch feedstock that would be considered for these techniques. The selected category is fine household waste. This is explained and written with the help of my university supervisor, Dr ir M.C.M. Bakker.

The report also lists the various existing chemical recycling companies in the Netherlands. Although pyrolysis is the most researched and commercially established technology, the findings suggest that dissolution is a promising technique for the feedstock stream considered here. Dissolution has the potential to recycle a wide stream of polymers by creating a lesser environmental impact. This report is written based on the information available in scientific papers and with the help of expert opinions.

2. Introduction

Plastic is a wide range of lightweight, durable, and affordable polymer materials with tunable properties [3]. The efficiency of this polymer resulted in economic growth, making it an important part of society. After the introduction of plastic globally as we know it today, in 1950, on an average 1.5 million tonnes of plastic per year was produced. In 2018, this number has risen to 359 million tonnes per year. In the same year, the EU recycled 32.5%, incinerated 42.6% and the rest was landfilled. **Error! Reference source not found.** presents the recycling rates in the EU countries (including UK). The Netherlands is presented as one of the top recycling countries along with Slovenia, Belgium, Germany and Latvia [5].

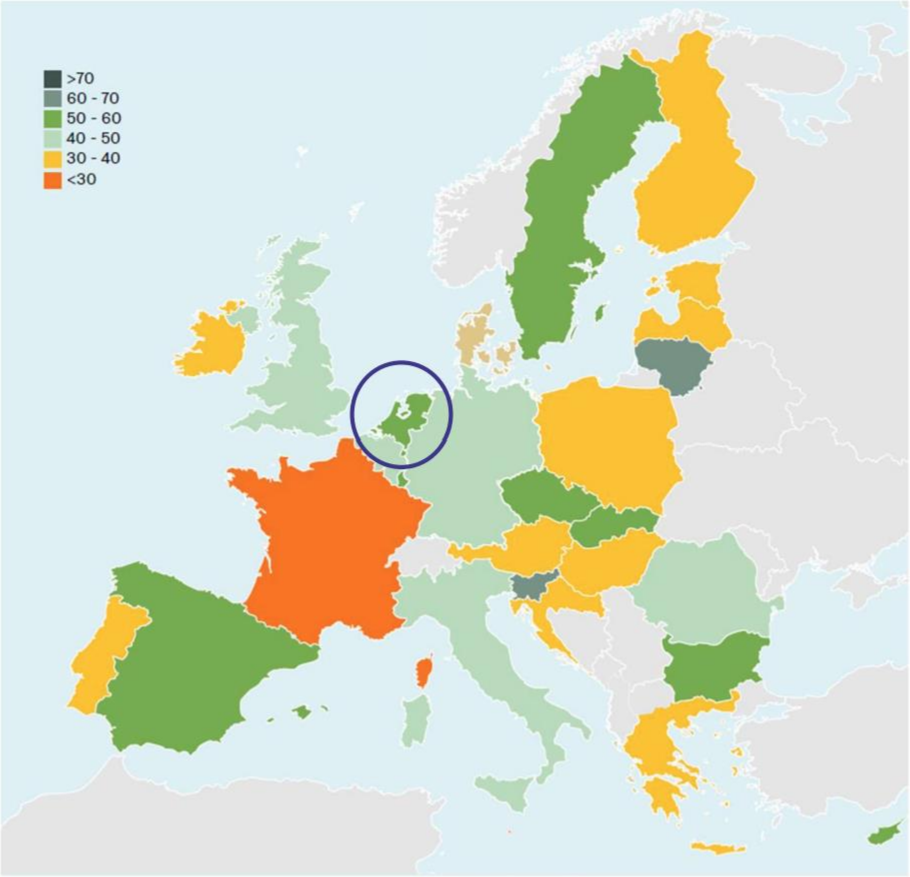
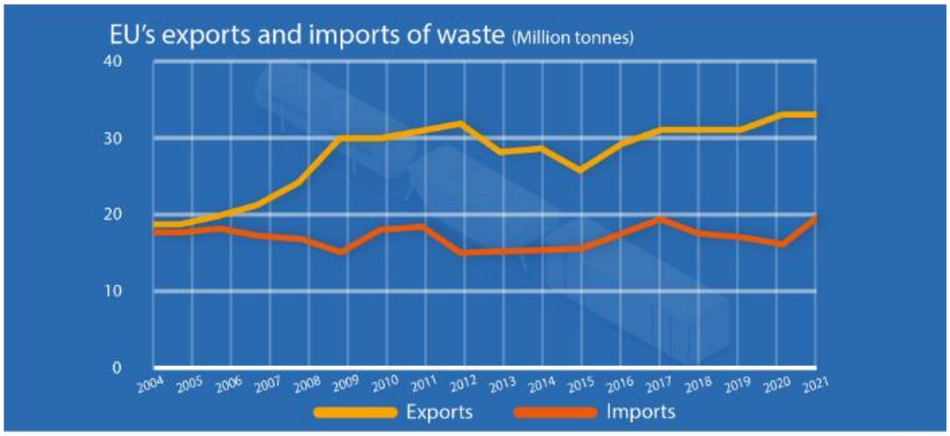


Figure 1: Europe's recycling rate of plastic packing waste in 2018 [5]

Furthermore, the EU exports waste to non-EU Countries such as Türkiye, India, Egypt, and Switzerland. From Figure 2, it can be observed that EU exports have grown significantly while the imports have slightly increased 11% in 2021. Figure 3 shows the amounts of waste exported to the non-EU countries [2].



ec.europa.eu/eurostat

Figure 2: EU imports and Exports [2]

ec.europa.eu/eurostat

Figure 3: Main destinations of waste exported from the EU [2]

With this growth in plastic production, plastic waste is also increasing and raising environmental concerns. In 2019, it was recorded that 29.1Mt of plastic was generated in the EU, and as mentioned before approximately 9.4Mt (67%) was landfilled or incinerated. These numbers are not accurately verified because the flows are complex and a part is missing due to illegal exports and dumping and litter. Nearly 7-15Mt is estimated to be unidentified/undocumented flows [3] [6]. With these numbers, the recycling rate of 32.5% is low and will not help Europe reach its sustainability goals in 2030 and perhaps also not in 2050.

39.9% of all the plastic in the EU is used for packaging. The introduction of the draft Packaging & Packaging Waste Regulation (PPWR), will be an important step forward to reducing waste in this sector. In fact, it should help improve packaging recycling in the EU to become more efficient than ever before.

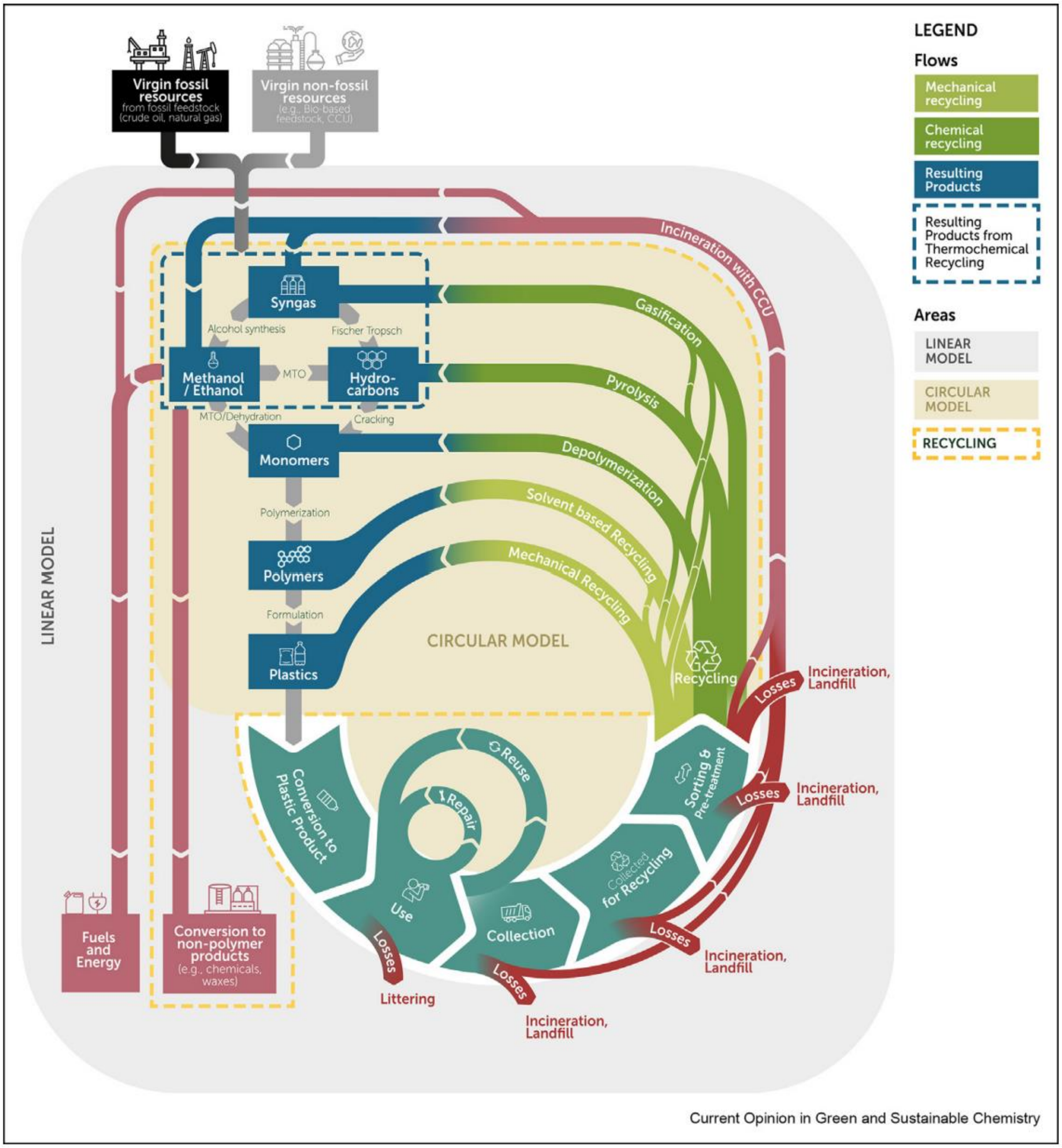
The PPWR aims to promote the use of recycled content in plastic packaging entering the market by 2030. The draft regulations specify the need to include by 5% by 2030, increasing to 10% by 2035, and 15% by 2040 compared with 2018. And by 2029 countries must create deposit return schemes for metal and single-use plastic beverage containers. By the end of 2025, 65% (by weight) of all packaging waste should be recycled including 50% of plastic, 50% of aluminum, 70% of glass, and 75% of paper and board [1][4]. The proposal also outlines these minimum food packaging reuse and refill targets to achieve by 2030:

- 10% of non-alcoholic beverages, 25% by 2040
- 20% of hot and cold take-away beverage containers, 80% by 2040
- 10% from consumer-facing businesses such as restaurants and cafes, 25% by 2040
- 5% of wine bottles, excepting sparkling wine, 15% by 2040 [4][1]

However, these goals cannot be met by mechanical recycling sector without significant investments to grow the required processing capacity of the sector and to innovate their technologies in order to cope with the high quality demands of the market. Mechanical recycling also has problem dealing with highly contaminated and complex plastics, multilayered plastic packaging. Also mechanical recyclate is not allowed for food contact purpose. Therefore, chemical recycling can play a vital role [3]. Figure 4 provides a future view of the possible recycling technologies in the EU landscape.

This report focuses on the most promising chemical recycling techniques to help solve the plastic problem in the Netherlands and the EU. The report answers to the following research questions:

1. What part of Dutch waste feedstock could be diverted to chemical recycling?
2. What are the promising chemical recycling techniques for this Dutch feedstock?



Current Opinion in Green and Sustainable Chemistry

Figure 4: Overview of different circular pathways for plastics [7]

2.1 Reference

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3. Potentially available Dutch Feedstock

A substantial part of the Dutch annually produced plastic packaging waste (PPW) is incinerated for energy recovery. Reasons are that it was not collected properly, or that it could not be recycled due to technical limitations of the used sorting and cleaning technologies, or that recycling could not add sufficient value to make it worthwhile. These causes result in different PPW containing residual waste flows that may instead be of interest for future chemical recycling. Here, the main idea is that chemical recycling could be developed complementary to mechanical recycling (separators, sensor sorters and washing facilities), rather than competing over already successfully recycled PPW streams. With successful is meant that the environmental and resource-benefits outweigh those of chemical recycling.

But also the achieved quality of the recycled material plays an important role in the contest for plastic feedstock. If chemical recycling can prove to consistently produce a higher quality product than mechanical recycling, the corresponding plastic feedstock may be reconsidered as chemical feedstock. However, it should also be noted that there is a substantial market for low-grade plastic products as well as for high-grade. So, displacement of all less successful mechanical recycling solely based on potential quality must also be considered with care.

But not all waste flows contain interesting volumes of PPW and, unfortunately, a fact is that much data on waste tends to be inaccurate and sometimes even unreliable. This necessitates that this study focuses on flows for which reliable data is available, which is the fine household waste that is collected from Dutch municipalities. Even so, to quantify these flows they still have to be reconstructed by consulting various information sources.

3.1 Plastics brought onto the Dutch market and discarded

In 2017, 1900 kiloton of plastics was brought onto the Dutch market with this breakdown to sector: 40% large and small utensils, 30% packaging, 15% building materials, 11% textiles, 3% automobile and 3% electronics & electric appliances [4]. This number has certainly grown, for example, the packaging by 10% from 2013 to 2017 [4]. More recent data was not found. The total PPW produced in 2017 in the Netherlands was 512 kiloton [4], which amounted to 27% of the new plastics. The correspondence in these annual fractions (27% PPW vs. 30% new) confirms the general notion that the lifespan of the majority of packaging plastics is much shorter than a year.

Though the focus is here on PPW, it is noted that chemical recycling may also be an attractive option for other plastic wastes than packaging and perhaps especially for complex products for which it is not possible to liberate the plastics. For example, in high-end and high-tech products such as medical appliances, medical disposables, electronic devices and glass-fiber cables.

The Dutch import and export of plastics, new or waste, is outside the direct scope of this report. But it is of interest to mention that the Netherlands up to recent exported significant volumes of plastic waste including PPW. In this context it is also of interest to mention that such exports often ended up in countries with questionable motives or technical capabilities as to its proper disposal. It was even claimed that in 2021 the Netherlands were the EU's largest exporter of plastic waste to non-OECD countries [5][9]. In any case, the CBS reports the export of 412 kiloton plastic waste in 2020 [1], an unknown part of which was PPW.

In 2018 China banned the import of low-quality plastics. This was the main reason for diverting those waste flows to the aforementioned alternative countries. It also stimulated that more plastic company waste is incinerated inside the Netherlands. More recently, the EU is working on new Waste Shipment Regulations [6] that will make plastic waste exports illegal to non-OESO countries and much more restrictive in general if the proper disposal of the waste cannot be confirmed by the sender and the receiving country. This all means that more plastic waste will remain inside the Netherlands. This puts more pressure on its proper recycling and probably leads to more potential feedstock for chemical recycling.

3.2 Municipal waste flows

Fine household wastes: Either separately collected PMD or separately collected PPW (a rare collection system) and residual waste. In 2021, 228 municipalities out of 352 (also) made use of automated mixed waste separation (AMWS) [1]to recover PPW from the residual waste. The total volume of fine household waste in 2021 was 6186.8 kiloton (78.6% of total household waste) of which 2567.8 kiloton was residual waste (147 kg/capita) [2].

Coarse household wastes: Typically consists of building and renovation waste, WEEE, furniture and other large objects that are delivered to a local recycling street. It contains relatively small amounts of PPW. The total volume of coarse household waste in 2021 was 1688.7 kiloton (21.4% of total household waste), of which 536.2 kiloton was residual waste (30.7 kg/capita) [2].

City waste: From governmental offices, city hall, street and park waste, waterways cleaning, etc. Makes up less than 10% of the total municipal waste with relatively small amounts of PPW.

Small companies: Similar waste as households and often collected by the municipality as part of the household waste. Data on annual amounts of PPW from such companies seem unavailable.

Large companies and industry: Have private contracts with waste collectors and recyclers. Data on annual volumes of produced PPW seem unavailable.

Hospitals, nursing homes: Have private contracts with waste collectors and recyclers. Data on annual volumes of produced PPW seem unavailable.

3.3 PPW volumes in waste flows from fine household waste

The focus is on fine household waste and the three associated waste flows. For the calculations the CBS [2] provides data on the wastes collected per municipality and per resident. On another site the CBS [3] provides the number of residents per municipality in 2021. It is noted that the number of municipalities has since decreased as several have merged. Combining these data allows the calculation of the Dutch annual volume per waste flow.

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[1] In the Netherlands, AMWS is commonly known as ‘nascheiding’. However, also separately collected PMD is separated and cleaned into three product flows in an AMWS installation at a recycling facility. The difference is that the processing is more involved for the more complex and potentially more contaminated residual waste.

Information on the average PPW content is obtained from references [11][12]: PPW in PMD makes up 62% and in residual waste 13%. The sorting rate is defined as: kg-sorted-plastic per kg-collected-PPW and is shown in Table 1 where the low-high estimates are adapted from [10].

	Low rate estimate	**High rate estimate**
from separate PPW collection	70%	80%
from separate PMD collection	71%	77%
from AMWS	40%	60%

Table 1: Sorting rates for PPW [10]

PMD sorting of course also recovers metals (M) and drinking cardboards (also called as beverage cartons) (D). Reference [12] gives an estimate for the MD content of 6% M and 11% D. As for the potential sorting efficiency, reference [8] gives the estimates 95% for M and 54% for D in case of separately collected PMD. Since reliable estimates for AMWS are not found in literature we use the same numbers. Reasoning here is that also from residual waste the metals are easy to recover while the drinking cardboards, perhaps more contaminated, are quite distinct and recognizable for the average NIR sensor sorter. Overall, this means an additional 0.06x0.95+0.11x0.54= 11.6% of the feed mass is sorted in the form of M and D.

A correction concerns the limited Dutch capacity for AMWS, which was 1900 kiloton in 2022 for the five active companies HVC, AEB, AVR, Attero and Omrin [7]. But the total volume reported by the CBS as being sent to an AMWS facility in 2021 is much larger, which means the excess could not be sorted and is assumed to be incinerated directly.

Combining all these data, the volumes of PPW can be traced from collection to the recovered volumes as well as to the incinerated volumes, where the latter are here considered as potential feedstock for chemical recycling. The flows and PPW volumes are depicted in Figure 5 for the low (left panel) and high (right panel) sorting rate estimates.

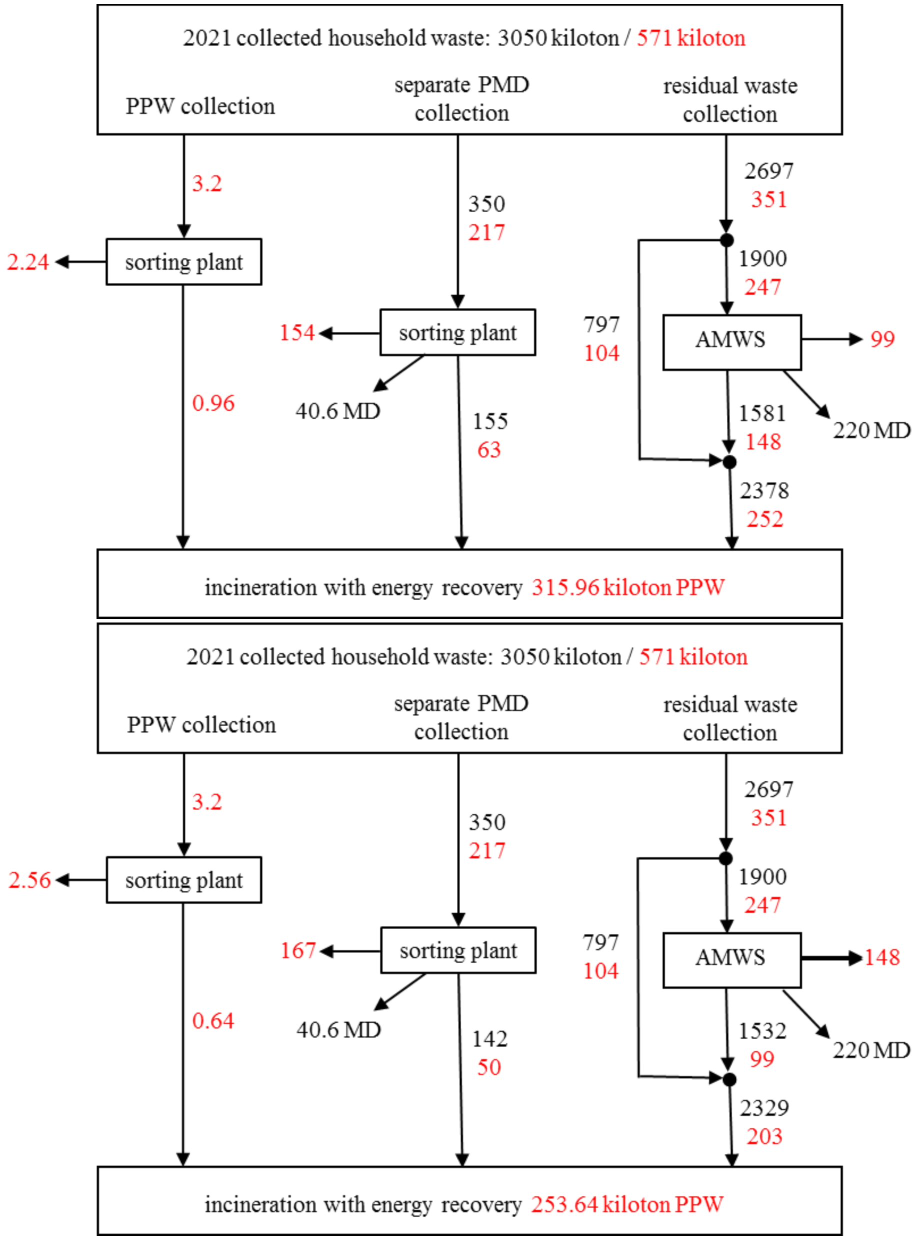

Figure 5: Volumes of PPW in different flows. The PPW mass (red numbers) are part of the total waste mass (black numbers). Combined mass of metals and drinking cardboards is indicated as MD.

Top: Low sorting rate estimates. Bottom: High sorting rate estimates.

If it is assumed that the in 2021 sorted PPW volumes are fully recycled (reused in products), the recycling rate for Dutch packaging plastics from PMD plus separately collected PPW lies between 8.9 and 9.7 kg/capita and for AMWS it lies between 5.7 and 8.5 kg/capita. Using the same assumption, the percentage total recycled PPW in 2021 lies between 44.7% and 55.6% (reminder; this does not include large company waste and the wastes from other sectors).

An important difference between the reject flows from PMD mechanical sorting and AMWS is that the concentration of PPW from AMWS reject flow is 8.7-11% and from PMD 22-41%. Seeing also that PMD is mostly cleaner makes the PMD reject flow even more attractive as potential chemical feedstock. This flow mainly consists of rejected flexibles and mixed plastics (hard plastics of different types) plus a mix of contaminating materials that probably did not belong in separately collected PMD in the first place.

3.4 Composition of Plastics in PMD and residual waste

The composition of plastic objects in residual household waste is shown in Table 2 and the composition to plastic type in separately collected PMD in Table 3. Unfortunately, neither one can be used to quantify the reject flows because the best pieces are taken out and a reject flow is relatively more contaminated than the feed flow. Recycling companies do perform sample testing of their products and reject flows for processing efficiency and quality control, but this is confidential information. And the fact that there is no clear market for reject flows also explains why there is no reliable composition data to be found in the literature or on the Internet.

Component	**Content %**
Other plastics (not PPW)	34.3
Rigid	21.5
Non-beverage bottles	18.3
Drinking bottles	10.4
Foils plastic-Al laminates	5.8
Carrier bags	4.5
EPS foam	3.7

Table 2:Breakdown of moist contaminated plastic objects in the residual waste flow [11]

Type	**Content %**
Flexibles (LDPE-PP)	37
PET	14
PET Trays	18
PP	16
PE	11
PS	3
Other	3
PVC	0

Table 3: Breakdown of plastic types in separately collected PMD [12]

3.5 References

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4. Pyrolysis

The most used and commercially mature chemical recycling process is pyrolysis. This particular process is also known as ‘Thermolysis’ [23][29][28].

Pyrolysis is a type of thermochemical recycling process that is defined as the process in which hydrocarbon bonds in plastic waste are broken down using heat in an oxygen-free atmosphere to produce a range of solid, liquid, and gaseous products [29][10].

4.1 Processes

The basic principle of pyrolysis is converting solid plastic to pyrolytic gases that can be condensed into liquid. Generally, this requires temperatures in the range of 350-800°C [26]. The main factors affecting a pyrolytic process are temperature, pressure, residence time, presence of catalyst, and rate of heating [35]. Depending on these factors there are different types of pyrolysis processes. In the following processes, laboratory scale experiments are explained to get a better understanding of the process. It should be noted that not a lot of information available online regarding the specifications of these process on a commercial scale.

4.1.1 Thermal Pyrolysis

This process is rather economical when compared to other types of pyrolysis. The heating temperature and the reactor type are the main factors affecting the process. A typical temperature range would be 300-900°C [19].

The process can be best explained through an example. Consider PE as the input and a fluidized bed reactor system is selected for the reaction. Figure 6 is the schematic diagram for Thermal pyrolysis of PE [44].

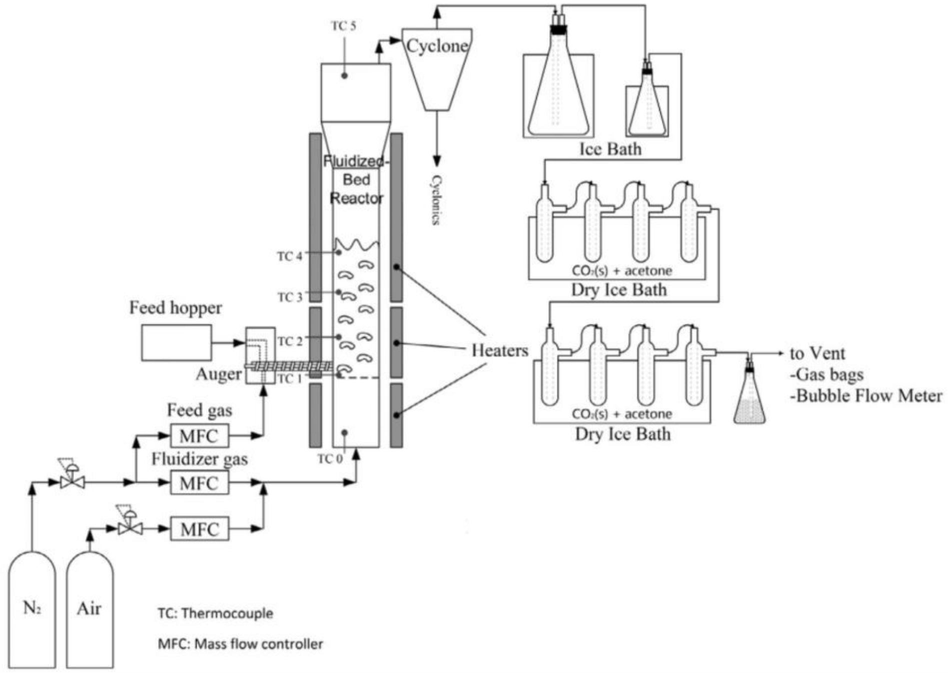


Figure 6: Schematic diagram of a Thermal pyrolysis process [44]

The fluidized bed reactor is filled with acid-washed silica sand. The reactor and the space beneath the sand bed are heated to a targeted temperature that is within the range of 500-600°C. The temperature is monitored by thermocouples placed at various points in the reactor as shown in the diagram. The process time is 1 hour with nitrogen gas being the fluidizing agent pumped at a rate of 300 cm^3/sec. This creates a residence time of 12.4-20.4 secs. After the reaction, the vapor product enters a cyclone to remove solids. The vapors enter the condenser, which is at a temperature of 0 °C, and then the dry ice bath of -78 °C to remove residual organics. From the process, the product yield varied from 87% to 98%. It was also observed that at the lowest temperature (500°C) the reaction could produce the highest liquid product [44]. At 500°C, the output from the process is presented in Table 4 [44].

Residence Time	13.4 secs
Gaseous Product (wt %)	8.2
Liquid Product (wt %)	81.2
Char Product (wt %)	<0.1
Total (wt)%	89.4

Table 4: Output composition for Thermal Pyrolysis [44]

For this experiment, after the reaction cleaning the reactor is required to prepare it for the next reaction. The sand is tested for total organic content. The reactor is heated to 600°C, with air replacing nitrogen to oxidize the residual organic (char) for 2 hrs [44].

4.1.2 Catalytic Pyrolysis

This process occurs at a lower temperature (450-550°C) and at a shorter duration compared to thermal pyrolysis. This reduces the production cost and energy consumption. There are several catalysts used for the pyrolysis of different types of plastic. Table 5 provides a brief overview of the general catalysts [19].

Feedstock	Reactor	Catalyst	Operating Temp (°C)	Reaction time (h)	Product	Yield (%)
PE	Microwave	Nitric acid	180	2	Water-soluble dicarboxylic acids	71
PET	Tube Furnace	Pd/C	400-700	-	Polycyclic hydrocarbon	44
LDPE, PP and HDPE	High-pressure autoclave	Cu doped TiO_2	300	0.5	Hydrocarbon oil	80
PET	Cylindrical reactor	C/MoO_2	220	19	Terephthalic acid, ethylene	84

Table 5: Different catalytic pyrolysis processes [19]

Consider the catalytic pyrolysis of HDPE in a conical spouted bed reactor, this is an experimental setup, not an industrial-scale plant. Figure 7 is a schematic diagram of the process. The properties of the input HDPE are analyzed before entering the reactor. In this process, a HY zeolite catalyst is used at 500°C for different reaction times ranging from 20-150 secs. Nitrogen gas is the pure gas used and the bed consists of 100g of catalyst with batches of 3g of plastic of particle size 2mm Thermo

Couples (TC) detectors are placed on the reactors to monitor the temperature and the final non-condensable gases are analyzed in the Micro- Gas chromatograph (GC) before being [12].

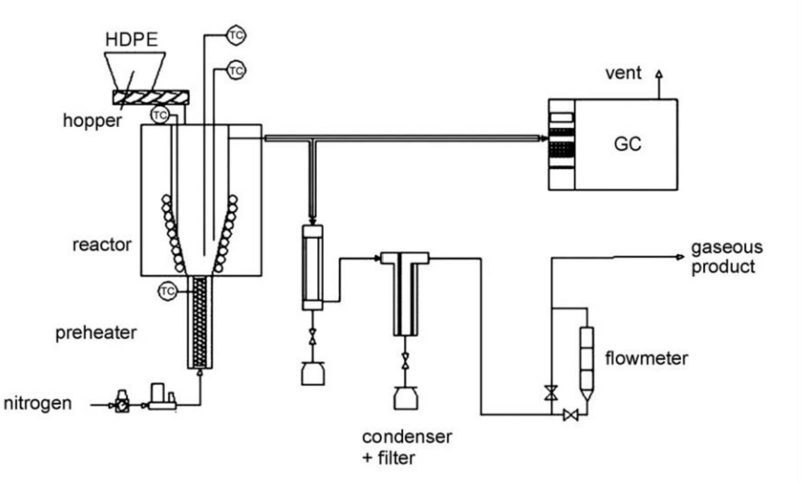


Figure 7: Schematic Diagram of catalytic pyrolysis [12]

In Table 6, presents all the products this process produced [12].

Product	Wt %	Remark
Gas (C_1-C_4)	24.44	High proportions of propene, isobutene, isobutene and 2-butene
Non-aromatic (C_5-C_{10})	44.55	High proportions of isopentane, 2-Methyl pentane and 2-Methyl 2-butene
Aromatic (C_5-C_{10})	24.10	Mostly (m,p)-Xylene
C_{10+}	3.14	
Coke	3	

Table 6: Yields from the process [12]

Gasoline, which is all the C_5-C_{10} fraction (69 w%) was the major product from the process, the composition of gasoline is presented in Table 7 [12].

Property	wt %
Olefins	15.66
Aromatics	35.83
Benzene	<0.04
Sulphur	~0 ppm

Table 7: Properties of the gasoline produced [12]

An important fact of this produced gasoline is the absence of benzene formation, which is carcinogenic and therefore it meets the EU requirements for commercial gasoline [12].

This process is an important topic for research because further optimization of the process is possible. However, the technology is already implemented on an industrial scale, some of which are listed in Table 8 [8][35].

Process	Country	Temp (°C)	Feedstock	Catalyst	Yield
Zadgaonkar	India	350	PE, PP,PS, PVC, PET	Unkown	75%oil, 20% ga,,s, 5% coke, 95% oil
Fuji	Japan	390	PE, PP, PS	Highly Siliceous Zeolite Socony Mobile-5 (HZSM-5)	75% oil
Smuda	Poland	350	PE, PP, PS, PVC, PET	Ni-silicate, Fe-silicate	95% oil
NanoFuel	Germany	270-370	PP, PE, Biomass	HY	94% oil
T-Technology	Poland	390-420	PE, PP, PS	Unknown	78% oil

Table 8: Industrial facilities for plastic catalysis [8][35]

The major drawback of this process is that it is highly sensitive to the feedstock. Therefore, pre-treatment of feedstock is an important aspect of process efficiency and product quality. Feedstock composition can also affect the activation capability of the catalyst. Compounds like chloride and nitrogen can deactivate the catalyst reducing the number of cycles it can be used and making it more expensive [3][35].

4.1.3 Plasma Pyrolysis

This process integrates the thermochemical process of plasma into the pyrolysis process producing syngas from plastic waste. This process is extremely fast as it only takes 0.01-1 secs, but requires temperatures as high as 1730-9730°C. The polymer undergoes a comprehensive breakdown producing syngas which is mostly composed of CO and H_2 [35].

This technology is only present at a laboratory scale, but thermal plasma technology is a commercial technology in metallurgy processing [35]. Figure 8 is a schematic diagram of a laboratory setup. From the diagram, it can be observed that two hoppers are provided for the feedstock to enter the reactor. The first hopper is the temporary storage unit while the second ensures continuous inflow. The reactor is fed at a rate of 20 kg/hr and is preheated to a temperature of 1200°C. The graphite rods connected to the reactor act as cathodes and maintain high voltage to generate high temperatures. Below the gasifier carbon electrodes are placed acting as the anode to complete the flow of current [27]. In other words, a direct current (DC) transferred arc plasma system is used [39]. The distance between the electrode are adjustable. Similar to the other pyrolysis processes, thermocouples monitor the temperature within the reactor. Tar formed is removed through the slag outlet and the syngas produced is passed through the water scrubber to reduce the heat and remove further impurities [27].

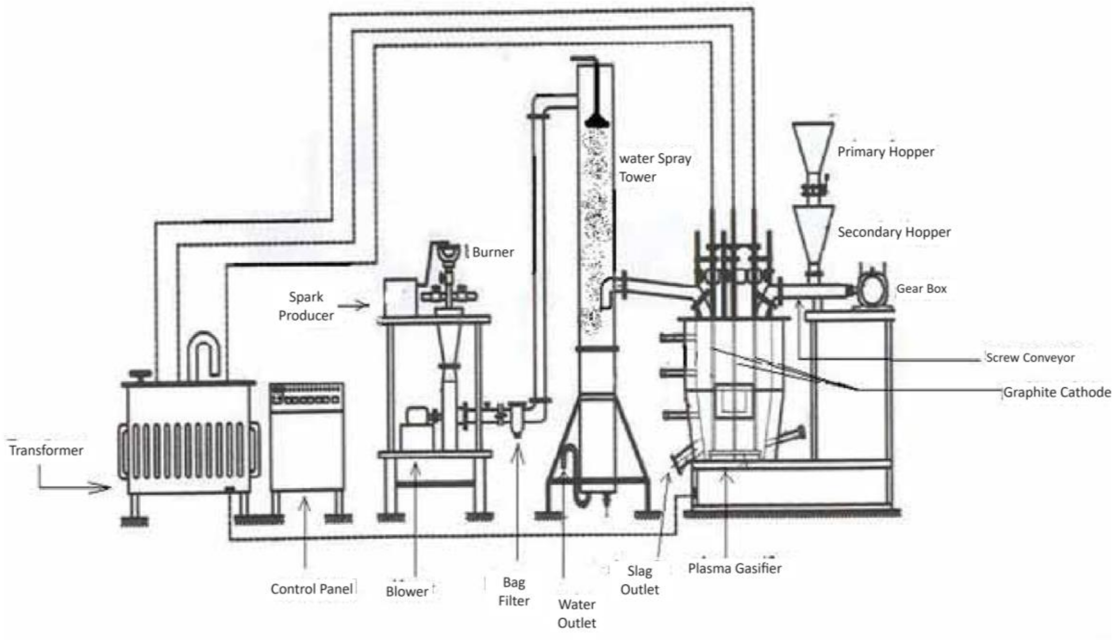


Figure 8: Schematic Diagram of plasma pyrolysis [27]

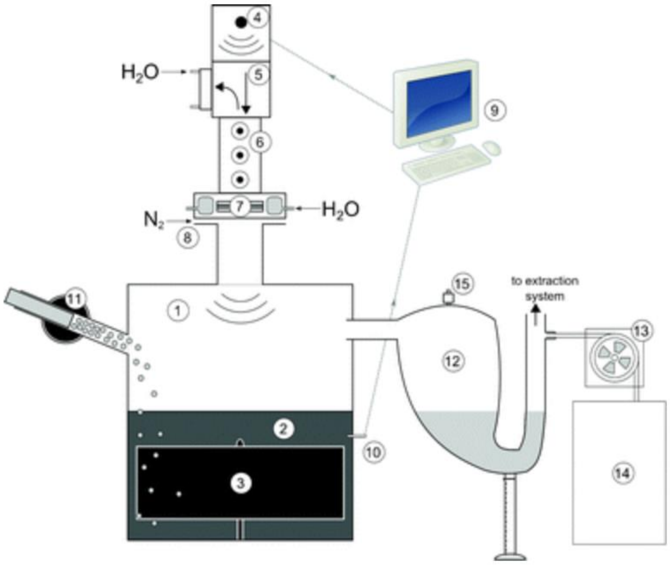
From the laboratory setup, it was observed that no tar formation had formed. Furthermore, the graphite rods continuously erode and require regular adjustment and replacement [27]. Replacing DC transferred arc plasma system with a radio frequency (RF) plasma system can solve electrode erosion, but this would result in reduced efficiency of energy use [39].

Despite the extensive energy consumption, it has low tar content and can be used to generate electricity or be used in hydrogen production due to its high heating value. Moreover, it limits the production of free chlorine for HCL and other toxic compounds [35].

4.1.4 Microwave Assisted Pyrolysis

This process is similar to conventional pyrolysis, except the heating mechanism is different. The feedstock is mixed with microwave-absorbent dielectric material, which can efficiently absorb the heat from microwaves and transfer it to the plastic in contact [35][5].

Consider the input feedstock comprising of HDPE and Aluminum/polymer laminates (eg: toothpaste packaging, beverage packaging). This experiment is conducted at a laboratory scale.



1. Reactor
2. Reactor bed comprising of activated carbon
3. Bed stirrer
4. Microwave radiator
5. Isolator diverting reflecting energy
6. Three stub tuner
7. Silicone window
8. Nitrogen gas input valve
9. Digitalized temperature control
10. Thermocouples
11. Feedstock valve
12. Pyrex condenser
13. Pump
14. Aluminum-lined gas bag
15. Pressure release valve

Figure 9: Schematic diagram of microwave-assisted pyrolysis apparatus [32]

The experiment presented in Figure 9 is conducted at a temperature range of 400 to 600ºC. The reactor bed comprises of activated carbon, an excellent microwave absorbent. It has 2 main functions in this process, heat transfer and act as a catalyst. A 3Kw 2.45GHz magnetron to generate microwaves for the process, while the tuner was used to help maximize the energy transfer and minimize energy reflection. After the process, the pyrolysis gases enter the condenser which is set at -78 ºC using dry ice. Non-condensable liquids are pumped out to the aluminum-lined bag. From the process, it was observed that 450 ºC is the optimal temperature for the highest oil production. Below 400 ºC the process is extremely slow, making the process not practical or efficient. At 450 ºC, 9% of the input was left behind in the reactor and 50% of the pyrolytic gases were condensable to oil/wax [32].

4.1.5 Vacuum Pyrolysis

This technology is used in combination with the other types of pyrolysis. Conventional pyrolysis uses N_2 to create an oxygen-free environment for the reaction to take place. Pumping out the air from a sealed reactor using a vacuum pump also creates an oxygen-absent environment. This technology is not widely studied for plastic recycling except with microwave pyrolysis. However, various parameters like heating temperature or pressure, possible dielectric material used, and the residence time of the feedstock are unknown [21].

This technology is interesting as it substitutes N_2, possibly reducing operational costs [21]. It could also be more environmentally friendly alternative but this is debatable since no knowledge of the residual stream is not known.

Table 9 provides an overview of all the different types of pyrolysis.

	Thermal Pyrolysis	**Catalytic Pyrolysis**	**Plasma Pyrolysis**	**Microwave Assisted Pyrolysis**
Operational temperatures (°C)	300-700	450-550	1200-10000	Up to 1000
TRL	9	9	4	4
Advantages	Simple Technology	Final product has similar properties of fossil fuels	Decomposition of toxic compounds	More control over the process
Disadvantages	Products require further upgrading for further use	Chloride and Nitrogen components can deactivate the catalyst	High energy consumption	Requires large feedstock volumes to be feasible
Feedstock Sensitivity	High	High	Low	Medium

Table 9: Comparison of different types of pyrolysis [35]

Technological Readiness Level (TRL) is a method used to estimate the maturity of technologies during the initial period of learning. Here, the comparison is based on the type and size of the developing technology. The values are set on a scale of 1-10, with the lowest being 1. Technologies that are still academically researched will stand on a scale of 1-5. Developing small companies are 4-7 TRL scale. While developed companies will have a TRL value between 8-9 [35].

Apart from the different types of pyrolysis, the choice of reactors also plays an important role. It enables the maximum utilization of the feedstock. The type of reactor that needs to be used for the process depends on the heat and mass transfer efficiency [28]. It also plays an important role in deciding the flow of the feedstock into the process, whether the process is continuous or not [9]. Some of the commonly used reactors are:

1. Fixed Bed
2. Fluidized Bed
3. Rotary Kiln
4. Screw kiln
5. Batch Reactor

6. Melting vessels or stirred tank reactors – used in companies like Plastic Energy Limited and Smuda Process [28][9].

The functioning of these reactors is further explained in

Appendix.

4.2 Pyrolysis Feedstock and Products

The feedstock considered here is household waste which is post-consumer plastic waste. Due to the high levels of contamination, a large portion of these plastics are incinerated. Despite pyrolysis being widely advertised as a solution to this problem, it also has its limits. However, it can tolerate higher levels of contamination in its feedstock when compared to mechanical recycling. This would in turn reduce the waste that is diverted to incineration and reduce the cost of pretreatment [28].

4.2.1 Input

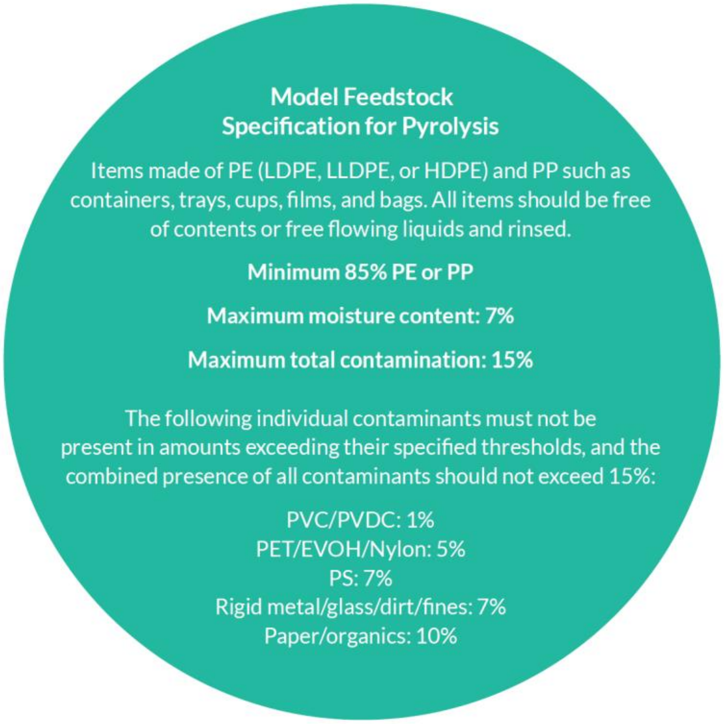
Polyolefins are the dominant type of plastic in the targeted waste stream, but there is a significant presence of PVC and PET. Both these plastics are problematic for pyrolysis. It is preferred to have feedstock with PET presence of <5% and PVC to be between 1-2%. When PVC undergoes degradation it produces chlorinated hydrocarbons and hydrochloric acid (HCl). This results in corrosion of the equipment and oil halogenation. While with PET, phthalic acids are formed on decomposition. This results in the deterioration of the oil quality and also clogs the pipes [28].

Recycling PET is an established process within mechanical recycling and it can be chemically recycled through depolymerization. However, for PVC, these quantities are small in post-consumer waste streams and usually have a 20 to 30-year shelf life. But PVC can be used in pyrolysis after a pretreatment step, i.e., the dehalogenation process. The effect of chlorine can be reduced through catalytic dechlorination, hydrothermal treatment in supercritical water, or by adding PVC with small concentrations of biomass [43].

As mentioned before, pyrolysis is an established technology. Still, proper legislation is not in place, this affects the technology on a commercial scale in the following ways:

1. No clear standards on the quality of input waste accepted for chemical recycling, will result in contamination, compromised quality of recyclate and lack of transparency for assessment of environmental impact.
2. Chemical recyclers have a restricted access to the market causing consumers to question on the quality and credibility of its products.
3. Delay in project implementation due to complex regulatory framework.
4. Difficult to evaluate and compare the performance of the plant due to lack of certification and testing procedures.

Eunomia Research and Consulting firm has created a model feedstock specification. Figure 10 provides an overview of the feedstock requirements for an individual process.



Model Feedstock
Specification for Pyrolysis

Items made of PE (LDPE, LLDPE, or HDPE) and PP such as containers, trays, cups, films, and bags. All items should be free of contents or free flowing liquids and rinsed.

Minimum 85% PE or PP

Maximum moisture content: 7%

Maximum total contamination: 15%

The following individual contaminants must not be present in amounts exceeding their specified thresholds, and the combined presence of all contaminants should not exceed 15%:

PVC/PVDC: 1%
PET/EVOH/Nylon: 5%
PS: 7%
Rigid metal/glass/dirt/fines: 7%
Paper/organics: 10%

Figure 10: Model Feedstock Requirements [15]

After talking to several experts in the field, it is observed that for pyrolysis there is no distinction between PP and PE. Further presence of metal or glass must be removed from the system since they cause significant damage to the equipment during the reaction.

4.2.2 Output

Pyrolysis oil is the output of the pyrolysis process. However, the quality of the output depends on the level of contamination in the input feedstock. Hence, refining the oil or wax is an important step to ensure good quality output [26][28].

One of the popular refining options opted by companies like Clariter is hydrocracking or hydro treatment for high-quality plastics [41]. The technique is important to reduce the concentrations of heteroatoms and aromatic compounds. Since the technology they use is confidential information, consider a laboratory setup of a batch reactor for the distillation of pyrolysis oil. A schematic diagram is presented in Figure 11 [16].

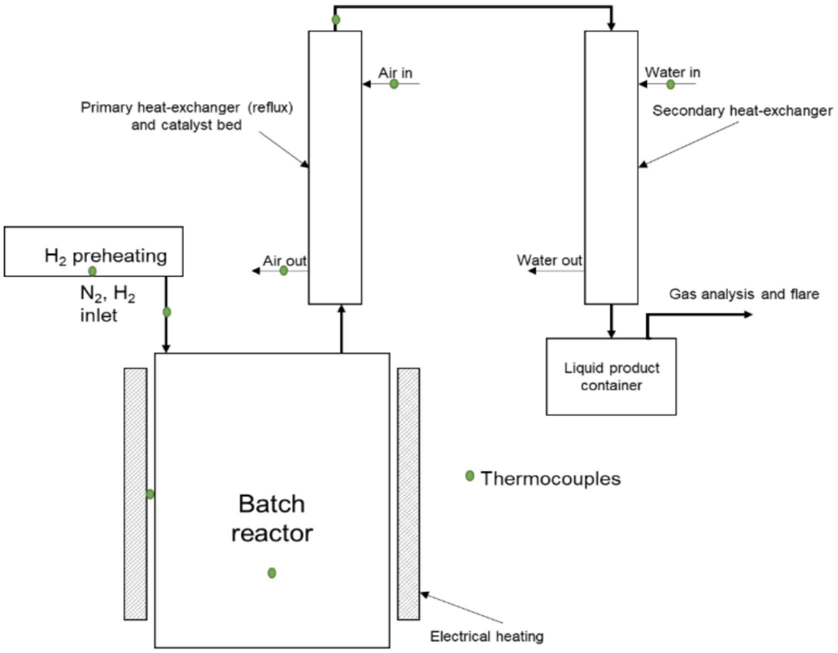


Figure 11: Schematic diagram for hydrogenation[16]

This particular experiment was conducted with a hydrogen temperature of 300ºC and a flow rate of 15 l/hr. An air-cooled reflux is connected to the reactor and the secondary heat exchanger is water-cooled. There is a certain amount of loss in this process, which would be light hydrocarbon with low boiling points. The pyrolysis oil is heated to a maximum of 530ºC. The gases pass through the first exchanger to change molecular weight distribution and the second heat exchanger to condense the gases [16].

After hydrogenation, distillation is conducted to extract various components from the pyrolysis oil depending on the boiling points. The graph shown in Figure 12 provides the boiling point distributions, while the Table 10 provides the general proper ties of plastic pyrolysis liquids [20]. There would be slight variations from these values depending on the input feedstock.

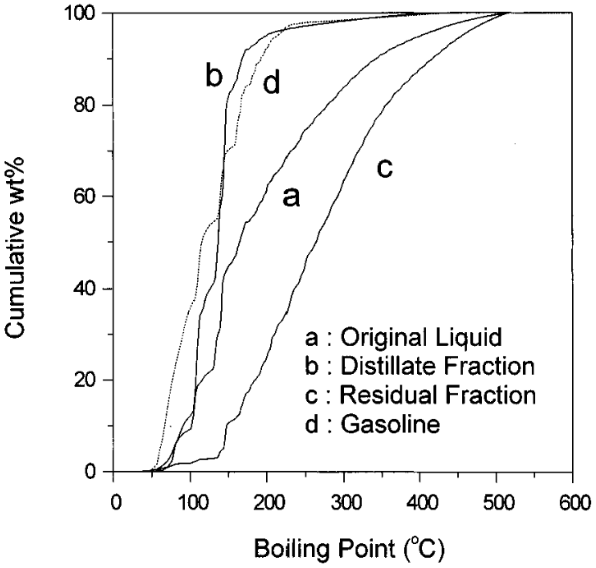


Figure 12: Boiling Point distributions of plastic pyrolysis liquids and commercial gasoline [20]

	wt %		
Boiling point range (°C)	**Original Liquid**	**Distillate fraction**	**Residual fraction**
Naphtha (<205)	62.3	98.9	28.7
Gas oil (>205)	37.7	1.1	71.3
Average boiling point (°C)	199.6	131.6	272.3

Table 10: Properties of Plastic Pyrolysis Liquids [20]

However, in general, Table 11 presents the temperature at which the products can be extracted through distillation are [9]:

Product	**Temperature (°C)**
Naphtha	<170
Kerosene	170-280
Diesel	280-400
Wax	>400

Table 11: Distillation Temperatures for product extraction [9]

4.2.3 Mass Balance

The main goal of chemical recycling is closing the loop for plastic and reducing plastic waste, it is important to keep track of the mass of material entering and leaving the process, as well as record the form in which they are leaving the process. This tracking is based on mass balance and it is important to set a systemic boundary to ensure double-counting [7]. Along with mass balance, allocation rules and credit transfer are also of great relevance for chemical recycling. Allocation of rules is the allocation of recycled content in the output products created is necessary to ensure consumers are not exposed to greenwashing. While, the credit transfer system ensures traceability and transparency of the recycled content in the product [42].

There are 3 main allocation rules, and one of them will be accepted by the European Union:

1. Proportional allocation: recycled content claims cannot be transferred from one output product to another.
2. Polymer only: recycled inputs can be freely allocated among plastics linked to the production of polymer from secondary raw materials.
3. Fuel-use exempt: recycled content used as fuel is excluded, while the remaining amount can be freely allocated to output products [42].

The 3 main variations of credit transfers concerning these allocation rules are:

1. Rolling average within a chemical production line: product is sold based on the input ratio of recyclate and virgin plastics.
2. Credit method within a specific organization: the credit tokens created by the input ratio (recyclate: virgin) can be freely allocated to the plastic output products within a specific organization.
3. Nationally restricted credit transfer: credit tokens are transferrable within an organization in a country [42].

A pictorial representation of these allocation rules and credit transfer methods is present in Figure 13 [42].

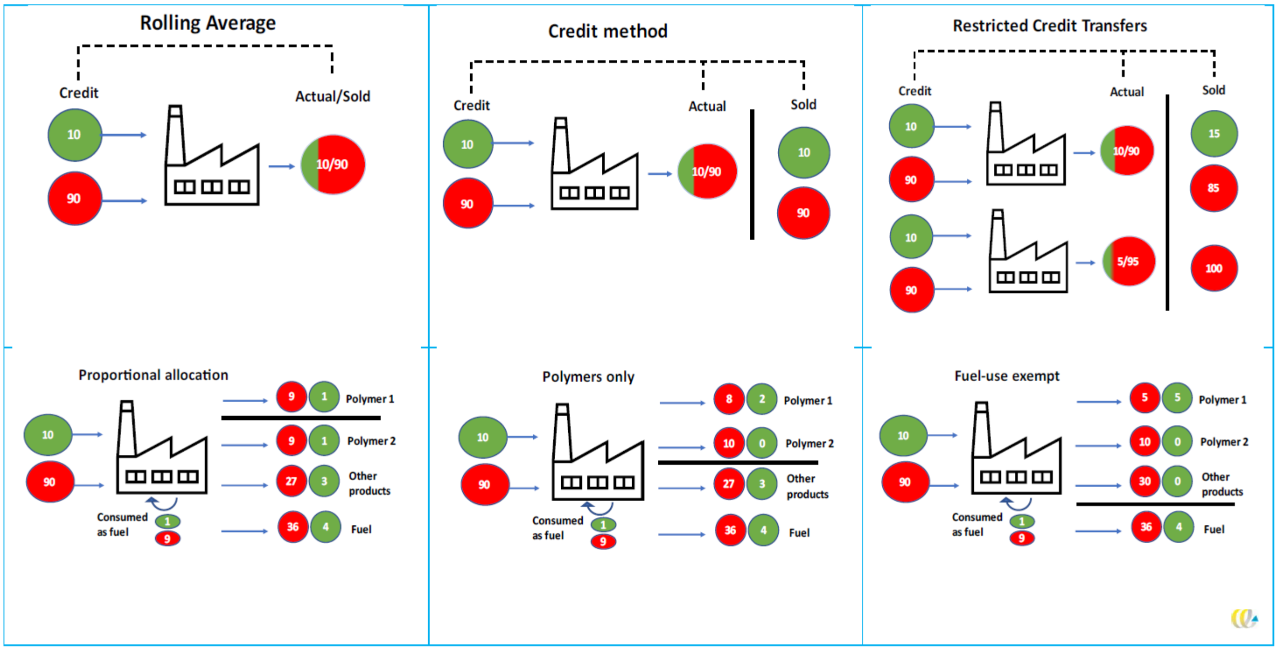


Figure 13: Visualization of Allocation and credit transfer methods [42]

With the help of allocation rules and credit transfers, there is a possibility to provide an equal level playing field for mechanical and chemical recycling. For example, when proportional allocation and rolling average is used, chemical recyclers can only sell products based on actual content just like mechanical recyclers [42].

This topic is very much lobbied in the EU to ensure mechanical recyclers are not at a disadvantage. Currently, fuel use exempt method is highly preferred, which automatically encourages polymer to polymer production enabling relatively less complicated mass balancing of the output [42].

4.3 Applied Technologies

There are various pyrolysis plants present in the EU, some of these companies are:

Pryme is an innovative cleantech company converting plastic waste into valuable feedstock for the petrochemical industry through pyrolysis. Their pyrolysis plant is situated at Rotterdam harbor [36]. A company representative confirmed that the company has a strong partnership with Shell, to whom they sell their product. He further explained that their pyrolysis process is rather simple (thermal pyrolysis) and they do not distill their output. The company uses electricity to reduce the carbon footprint of its process. Due to confidential reasons, he was not able to explain the specifications of the feedstock required. However, the Netherlands does not currently provide any feedstock to this company and the company uses the feedstock from other countries like India and Indonesia.

Clariter global cleantech company converting plastic waste to green sustainable petrochemical products. They claim to be an alternative to fossil-based products in various industrial and consumer applications. Their products are solvents (used in cleaning products, cosmetics, paints, and inks), oils (used in wood polish, baby oil, lubricants, hair products etc.), and waxes (floor wax, shoe polish, candles, crayons, etc.) transforming 60,000 tons of plastic waste into 50,000 tons of products, performing at an efficiency of approximately 85%. They use a patented pyrolysis technology. The schematic diagram is presented in Figure 14 [41].

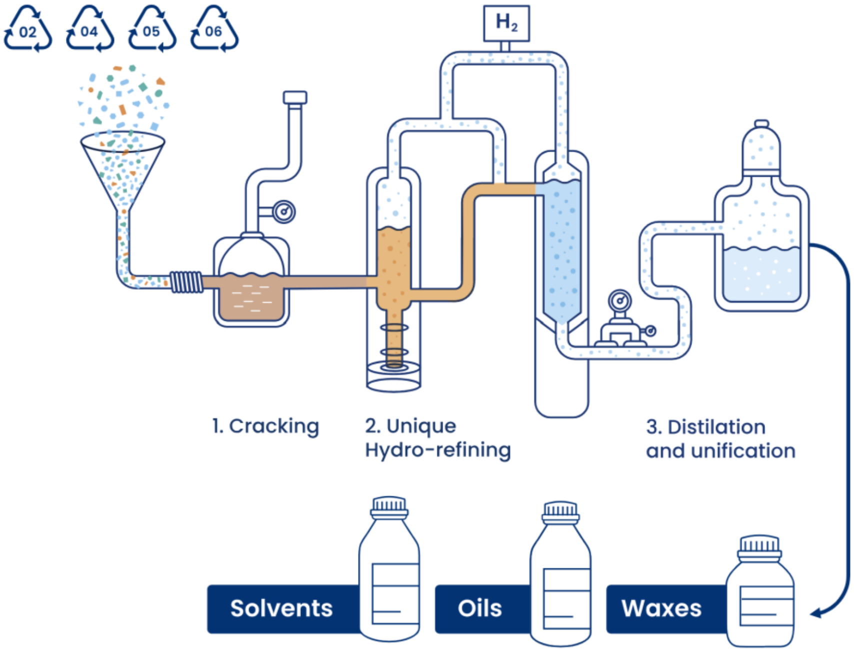


Figure 14: Pyrolysis process used by Clariter [41]

The 3 steps in the process:

1. Thermal cracking: converting HDPE, LDPE, PP, and PS into liquid hydrocarbons. They claim that the gas produced in this process is used in the process as energy.
2. Hydro-refining: removal of impurities.
3. Distillation and unification: creating their final products which are waxes, oils, and solvents.

Their company representative mentioned that sorting and pretreatment of the input feedstock to their specifications is an important step. This is done mainly to ensure high-quality products are produced and the equipment is not damaged. The pretreatment process mainly comprises NIR sensors after which they are shredded, washed, and dried. They accept multi-layered plastics which have a high percentage of polyolefin. They do have the facility to do the presorting by themselves. They have various collaborations with Ocean Clean Up, Total Energy Fluids, HP Printers and CE Delft.

They have an operational Pilot Plant in Gliwice, Poland, and an industrial-scale plant in East London, South Africa [41]. The company plans on further expanding in the Netherlands at Delfzijl in the Groningen Seaports area along with BioBTX, Bollegraaf, and N+P. This new plant is expected to be the state-of-the-art raw material preparation center and is expected to be operational in 2025. The plant would have an annual capacity of 350,000 tonnes. Clariter and BioBTX handle the offtake of raw material, N+P handles the supply of feedstock, and Bollegraaf handles the delivery of the technology[37].

BioBTX is a Dutch pyrolysis company based in Groningen which uses biomass (non-food) and plastic as its feedstock. The final products of this process is benzene, toluene and xylene (as the name suggests BTX). They claim that these products have the properties of virgin counterparts. Currently, they only have pilot plant of 10kg/hour capacity of continuous flow in Groningen [40].

Obbotec is a chemical recycling company that uses hydro-pyrolysis and dissolution (which will be explained in the dissolution chapter) to divert plastic waste streams from incineration and landfilling. The hydro-pyrolysis technology is called OBBOTEC-HydroCat and it is situated at Rotterdam Harbour [24]. This project is currently in its construction phase and expected to be operational in 2025. Just like Clariter, they have integrated a hydrogenation process to attain high-quality marketable fuel. However, their input is a blend of biomass and mixed plastic. This particular technology can process 10 kilotons of feedstock per year. They have partnerships with CE Delft, Suez, AVR, Gemeente Rotterdam and renewi [24].

Blue Cycle a chemical recycling company situated in Heerenveen, the Netherlands with a plant capacity of 20,000 tonnes per year. The company claims to process plastic of low-tier quality to produce oil (Pyroil), that can be used as a substitute for diesel fuel or creating new plastic. With 50 tons of plastic processed per day, the plant produces a total of 14.7 million liters of oil per year, 30 kilotons of CO_2 reduction. The company claims to use the flammable gas produced in the process as energy for the reaction. They have partnerships with Bollegraaf, Count, Ingenia and Waste Connections [22].

Fuenix ecogy is another Dutch pyrolysis plant started in 2013 situated in Weert, Limburg. They use the Ecogy® process to create their high-quality products (naphtha, paraffin, and LPG). Figure 15 is a schematic diagram explaining their cycle [14].

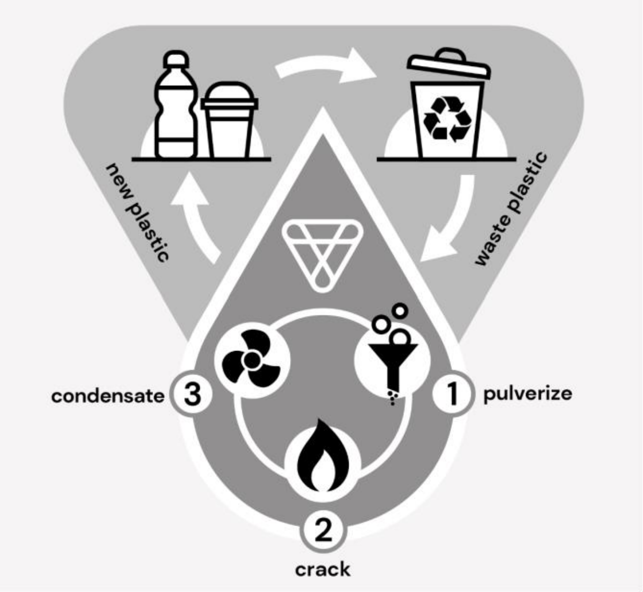


Figure 15: Ecogy® process[14]

The company is in partnership with DOW in 2019 and Sulzer in 2023. The agreement with DOW ensures that a second plant is constructed with a capacity of 20,000 tonnes converting mixed plastic to pyrolysis oil feedstock to create circular plastics in the Terneuzen (Netherlands) production facilities of DOW [14][11]. While Sulzer has acquired strategic stake in the company, enabling Fuenix Ecogy technology to experience advanced purification and separation techniques [38][14].

Mura Technology is a UK-based chemical recycling company. Their exclusive technology Hydrothermal Plastic Recycling System (HYDROPRS™) uses supercritical steam to convert flexible and multi-layered waste plastics into industry-ready products, i.e. Naphhta, Distillate Gas Oil, Heavy Gas Oil, and Wax Residue. The company claims that the process does not require the separation of waste; in other words, it accepts contaminated waste. Their targeted polymers are POs, PET, PS, ABS, and Polyamides [17]. Figure 16 provides an overview of the Mura technology[25].

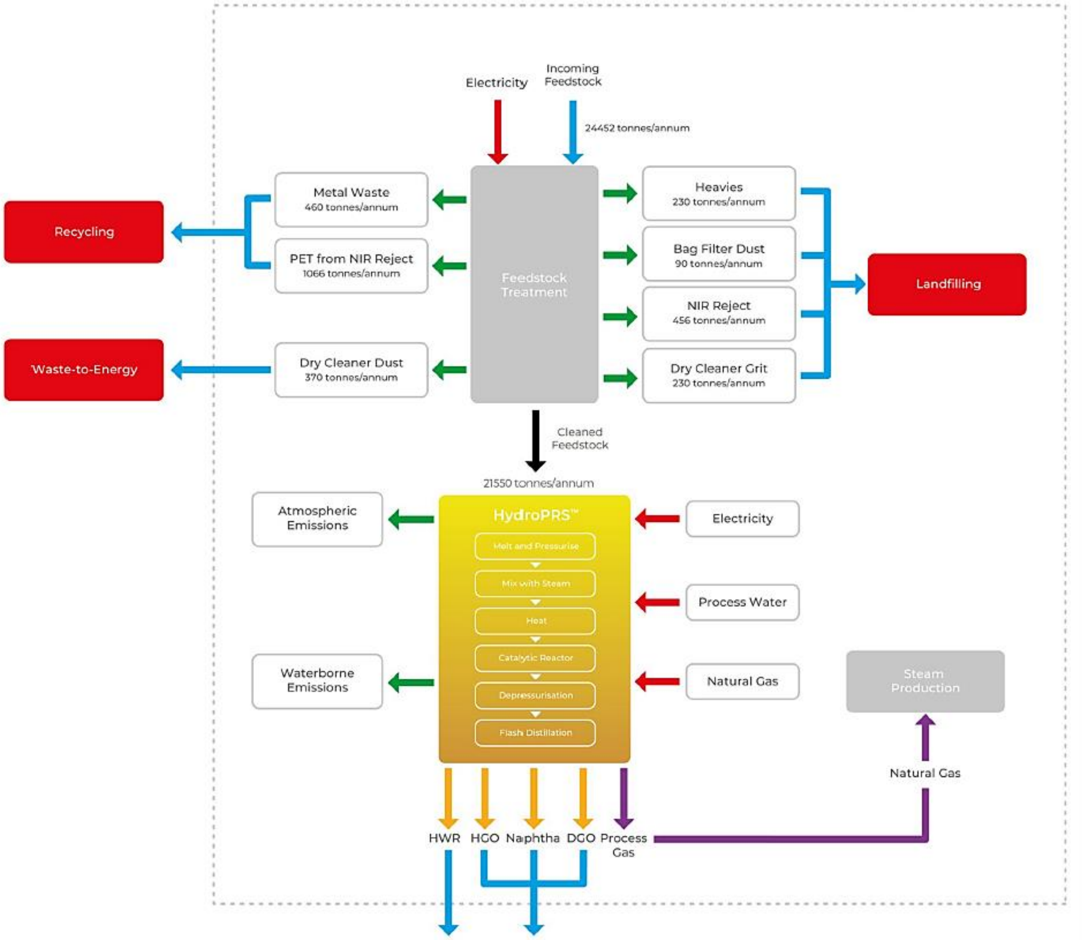


Figure 16: Process flow of Mura Technology [25]

They further claim to not be a competition to mechanical recyclers. They are constructing their first plant in Teesside, North East England, and is expected to operate at a capacity of 20 kilotonnes per year by 2024. It also has 4 plants each under construction in the US and Germany, each with a capacity of 100 kilotonnes per year. In 2021, the company partnered with KBR (science and technology solutions company) and Mitsubishi Chemical Corporation to deploy HYDROPRS™ in Japan. This project was expected to complete in 2023 and process 20 kilotonnes of plastic waste per year in Japan [30]. Furthermore, LG Chem has bought a license to build this technology in South Korea with a capacity of 23 kilotonnes per year [31].

BlueAlp is another Dutch pyrolysis company that uses its patented pyrolysis-based 'slow-cracking' technology which processes plastic waste to pyrolysis oil in low energy consumption. Its first successful demonstration was in 2014 with a pilot plant of capacity 3,000 tonnes/year in Switzerland. In 2020, it launched its first commercial plant with a capacity of 17,000 tonnes of plastic feedstock per year at Ostend, Belgium. In 2021, they signed an agreement with Shell to build 2 plants with of capacity of more than 30,000 tones/year. The plant is expected to be operational in 2023 [6][34]. Figure 17 provides an overview of their patented technology [6]. Furthermore, the company would have some type of pretreatment since unsorted waste cannot be directly used in the extruder, as it would damage the equipment and also provide poor quality output.

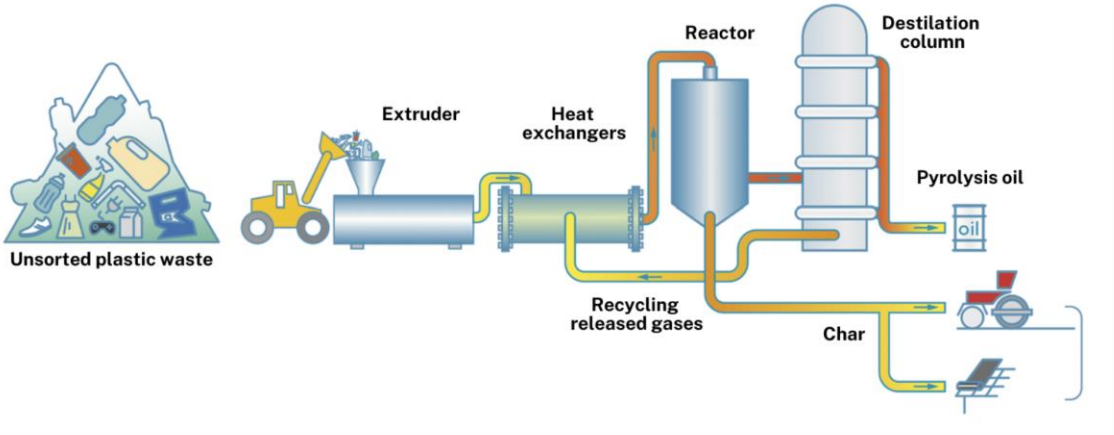


Figure 17: Process overview of BlueAlp [6]

Sabic is a Saudi-based petrochemical industry. in 2021, it partnered with **PLASTIC ENERGY** to construct an advanced recycling unit in Geleen, The Netherlands. This 50-50 joint venture is called **SPEAR** (SABIC Plastic Energy Advanced Recycling BV). This is a contribution with 2 other strategic partners Siemer and Landbell groups. Siemer is a German collection and sorting facility and Landbell Group is a German waste management service provider. Nedvang is offering 10kilotons of flexibles from AMWS for the project. The project was expected to be operational in the second half of 2022. The project is in its construction phase and aims to be the world's first commercial unit for upscale production of certified circular polyolefin. It focuses on 4 types of plastics: HDPE, LDPE, LLDPE, and PP. However, due to certain issues, the plant will be operational at the beginning of 2024 [33] [2].

4.4 Environmental Impact

When considering the environmental impact of pyrolysis, setting the boundary conditions is an important aspect. From the previous section, we are aware that pyrolysis has multiple outputs, and deciding which output could lead the path in a circular economy is crucial. Figure 18 given below is an apt representation of closing the loop for plastic [1].

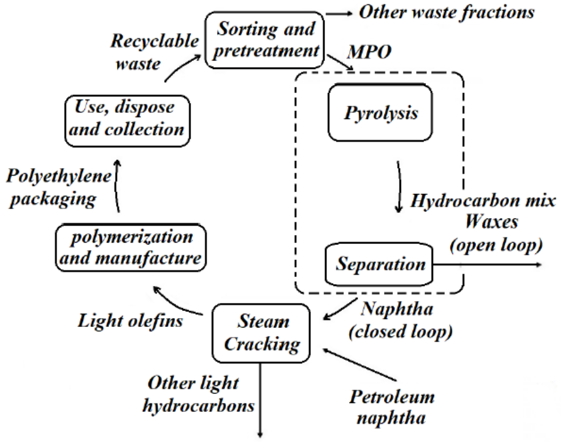
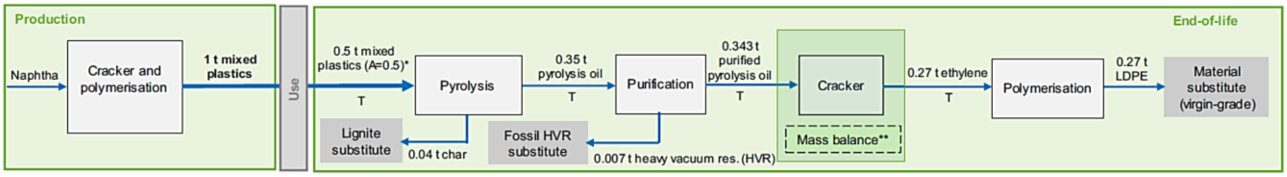
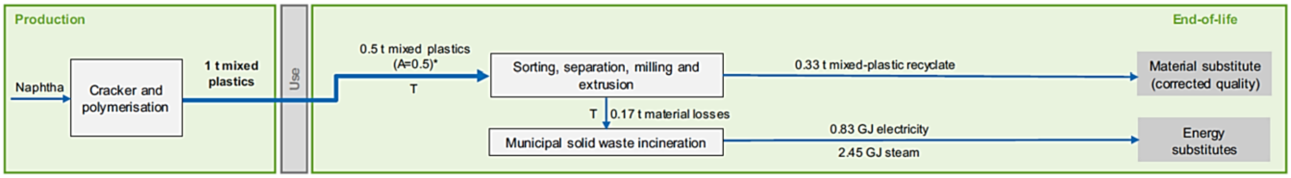


Figure 18: Possible plastic value chain [1]

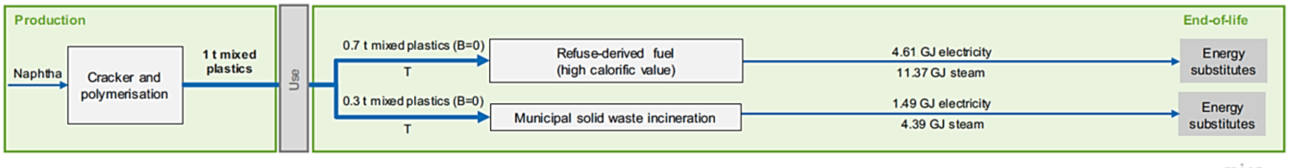
Since the goal of chemical recycling is closing the loop, naphtha production is the most important output. Therefore, Figure 19 is a comparison of pyrolysis with existing systems. Figure 19 provides a flow chart for mechanical recycling too, the figure does not take into account the monostreams it forms at the end and does not provide mixed plastic recyclate. The feedstock that is processed here mainly comprises PE, PP, and PS [18].



Pyrolysis of mixed plastic waste



Mechanical recycling of mixed plastic waste



Energy Recovery of mixed plastic waste

T: Transport, A: Substitution factor considering recyclability and recycling content, B: Substitution factor considering energy recovery

Figure 19: Pyrolysis, Mechanical Recycling, and Incineration routes for EoL Plastic [18]

To understand the environmental impact values, Table 12 has provided more understanding of the processes. For this evaluation, mechanical recycling is split as 2 steps: pre-treatment and production of granulate. The pretreatment step involves, sorting, grinding, washing and drying. While the production of recycled granulates involves separation, removal of contamination, further sorting, extrusion and palletization.

Process	Energy use (MJ/ton of input)
Sorting	250
Pyrolysis	3260
Mechanical Recycling	1890

Table 12: Energy Use for each process [18]

For this analysis, the waste-product perspective is considered and the functional unit would be 1 tonne of mixed virgin plastics and their end-of-life treatment. Other key aspects of this analysis are:

- The system efficiency for mechanical is 66.5%.
- The system efficiency for pyrolysis is 71%.
- 3 circularity parameters are considered, which are:
    1. A factor = recyclability and recycling content is captured by allocating environmental burdens and credits between the 'virgin' and 'recycled' life cycles as per market realities.
    2. B factor = share burdens and credits for energy recovery between the end-of-life energy recovery process and recovered energy.
    3. Q_{Sout} = ratio to capture the quality of the recycled materials [18].

Circularity Parameters	Pyrolysis	Mechanical Recycling	Incineration
A factor	0.5	0.5	0.5
B factor	0	0	0
Q_{Sout}	1	0.5	-

Table 13: Circular Parameters for the technologies [18]

Figure 20 presents the environmental impact of the 3 different recycling technologies[18]

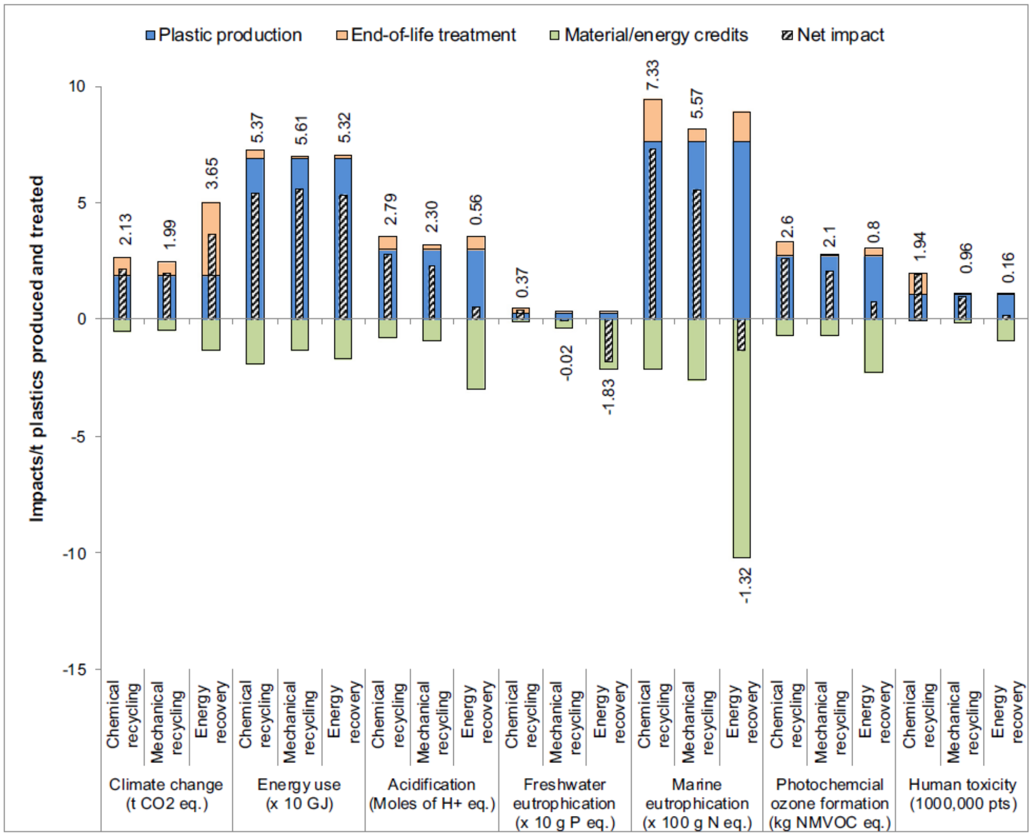


Figure 20: Environmental impact of different recycling techniques of mixed plastic waste[18]

It can be observed that mechanical recycling and chemical recycling have only small differences in all the categories when compared to incineration. Pyrolysis has higher impacts due to the purification process. Chemical recycling appears to be a better alternative than incineration. However, when the results are compared to the production of virgin plastic, pyrolysis is a better option. This is presented in Figure 21 [18].

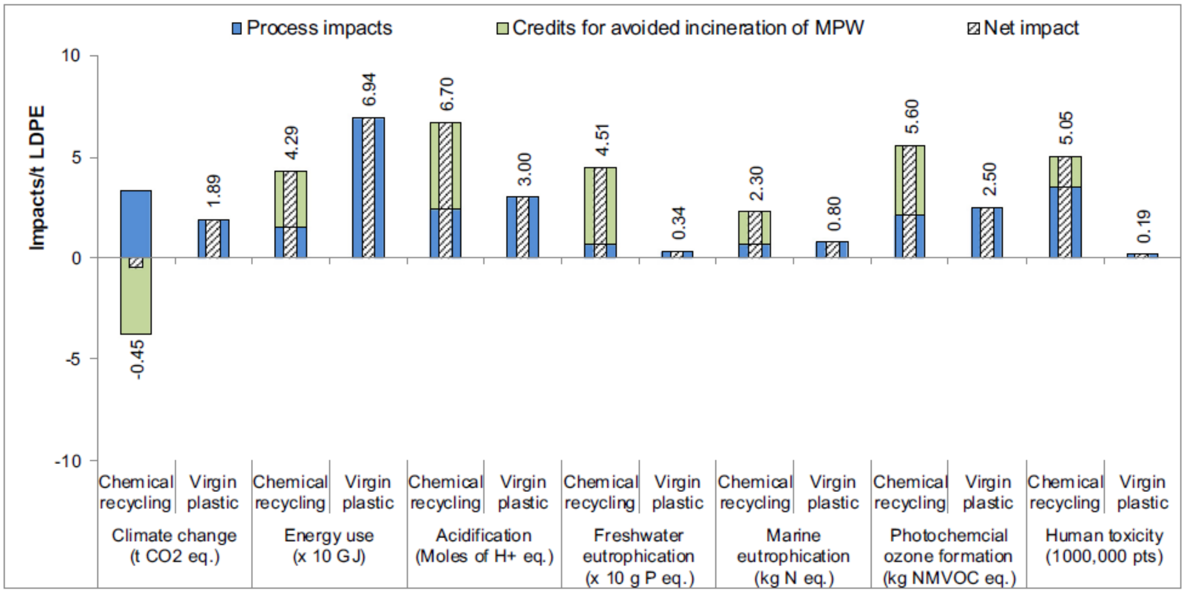


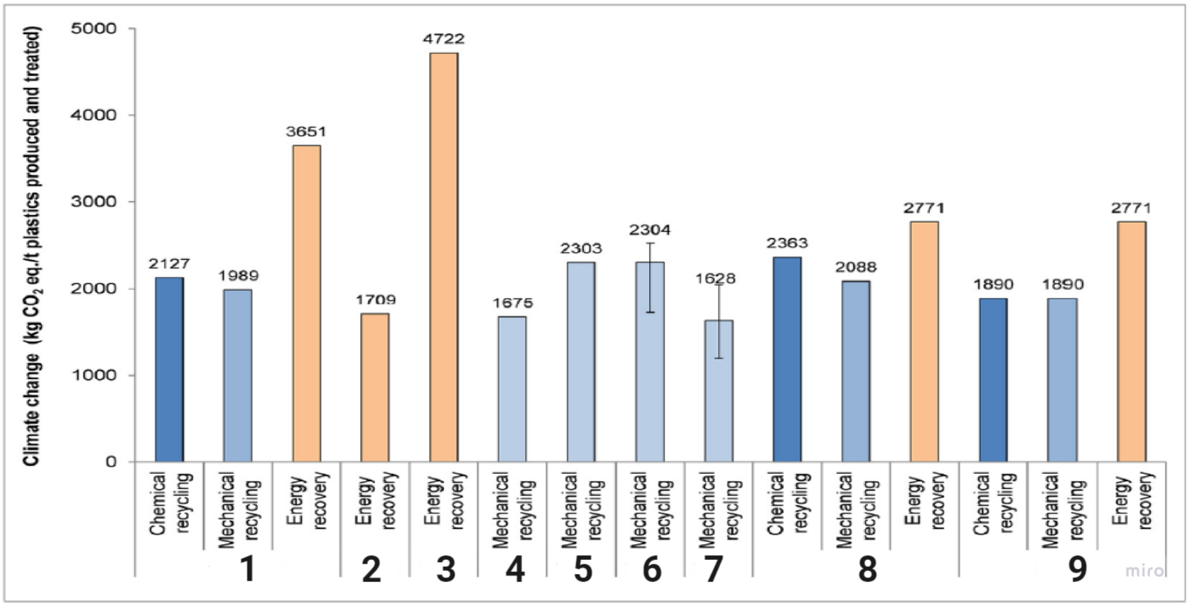
Figure 21: Environmental impact between Chemical Recycling and Production of virgin plastics [18]

A sensitivity analysis is necessary to achieve more accurate numbers. The analysis can be done on:

- Quality of mechanical recycling recyclate,
- Source of energy,
- The system efficiency
- Circularity parameters.

It is important to note that the analysis is considered only for climate change [18].

Figure 22 provides the results of the sensitivity analysis. It can be observed that there are significant differences (>10%) in the values. The values in cases 2 and 3 vary extensively since the use of renewable sources (like biogas, and hydropower) are more sustainable and long-term solution when compared to incineration. For cases 8 and 9, it is interesting to observe the mechanical and chemical recycling. This result exhibits how dependent the system is on energy. The variation is observed to be higher in chemical recycling since it is a more energy-intensive process than mechanical [18].



1: Original case, 2: Energy was provided by fossil fuels, 3: Energy is provided by Renewables, 4: Recyclate has the same quality as a virgin, 5: Poor recyclate quality, 6: Lower system efficiency 7: Higher system efficiency, 8: full burdens and credits for material recovery and halved burdens and credits for energy recovery, 9: no burdens and credits for material recovery and halved burdens and credits for energy recovery

Figure 22: Result of Sensitivity Analysis [18]

The results from the previous graphs can be consolidated in Figure 23. This figure only focuses on the carbon footprint of each of the processes using different feedstock [13].

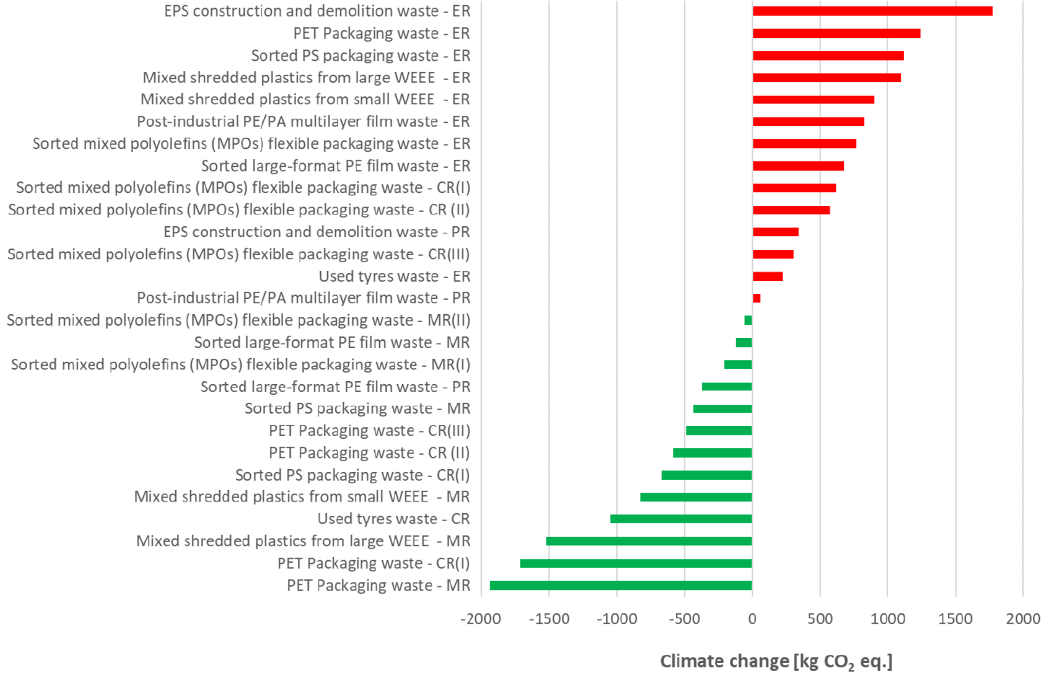


Figure 23: Climate change Analysis concerning carbon footprint[13]

Despite these developments in pyrolysis technology, legislations are the most significant obstacle. Absence of testing procedures and certification standards, restricts the market access. With relevant legislation, consistent of feedstock and operational cost can be mediated. This also results in significant environmental and social benefits, increasing resource efficiency and reducing the carbon footprint [4].

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5. Gasification

Similar to pyrolysis, gasification is a type of thermochemical recycling [16][13]. The main difference between these 2 technologies is the presence of limited oxygen in gasification for decomposition of the feedstock [17].

Gasification is defined as the process that transforms a carbon-based solid material of energy value into a gaseous fuel of low molecular weights [13][20][25]. The final gaseous product is called synthetic gas or syngas which main contains carbon monoxide (CO) and hydrogen (H_2) [25]. This process requires the highest temperature (700-1200ºC) among all the technologies discussed in this report, to attain its desired product [16].

5.1 Processes

Gasification is an age-old technology that is widely practiced in many parts of Europe. It is also an important technology in the petrochemical industry, enabling power generation in turbines, fuel cells, and chemical synthesis. Recently this technology has been of great interest in chemical recycling to help with the plastic waste problem.

A general layout of a gasification plant would be:

1. Mechanical feeder at ambient temperature
2. Gasification reactor
3. Bottom ash discharge system
4. Cooling of syngas
5. Cleaning/upgrading
6. Syngas energy recovery
7. Auxiliaries

Figure 24 presented is a general outline of the process [22].

Figure 24: General outline of gasification [22]

The main steps of the technology are:

1. Drying: plastics have low moisture content (when compared to biomass), so this step is very rapid and takes place at 100-150°C.
2. Pyrolysis: This endothermic process results in volatile substances and residues. This is a delicate step since plastics melt and agglomerate.
3. Oxidation: At elevated temperatures and the presence of partial oxygen, results in the formation of CO and steam. The amount of oxygen entering the system depends on the equivalence ratio (explained in 5.1.2 Operating conditions). This is an exothermic process and the thermal energy provides the necessary heat. The reactions involved in this step are presented in Figure 25.
4. Reduction: An endothermic process at high temperatures occurring in the absence of oxygen. The reactions involved in this step are presented in Figure 25 [4].

Oxidation Reaction		Reduction Reaction	
$C + O_2 \leftrightarrows CO_2$	$\Delta H = -393.5$ kJ/mol	$C + CO_2 \leftrightarrows 2CO$	$\Delta H_{R1} = 172.5$ kJ/mol (Boudouard reaction)
$H_2 + \frac{1}{2} O_2 \leftrightarrows H_2O$	$\Delta H = -285.9$ kJ/mol	$C + H_2O \rightarrow H_2 + CO$	$\Delta H_{R2} = 131.3$ kJ/mol (Char steam reforming)
		$CO + H_2O \leftrightarrows H_2 + CO_2$	$\Delta H_{R3} = -41.2$ kJ/mol (Water-gas shift reaction)
		$C + 2\,H_2 \rightarrow CH_4$	$\Delta H_{R4} = -74.5$ kJ/mol (Carbon hydrogenation reaction)
		$CH_4 + H_2O \leftrightarrows 3\,H_2 + CO$	$\Delta H_{R5} = 205.8$ kJ/mol (Methane reforming)

Figure 25: Reactions that occur in gasification process [4]

To understand the process more clearly, the next sections will elaborate on the commonly used different types of gasifiers, operating conditions, and cleaning techniques.

5.1.1 Types of gasifiers

There are many types of gasifiers available in the market. This section will explain 2 types of gasifiers that are frequently used.

a. Fixed/Moving Bed Gasifier

This is the simplest gasifier and has several advantages like:

i. High char burnout,
ii. Excellent heat exchange
iii. Efficient use of available thermal energy

Some of the disadvantages would be:

iv. Cannot handle moisture content
v. Feed size limits
vi. Output gas has high concentrations of methane

This type of gasifier is present in 2 types depending on where the output is collected.

1. Downdraft
2. Updraft

Figure 26 clearly illustrates the functioning of the gasifier. It is important to note that the tar formation in downdraft is lesser than updraft. This is because the tar produced is cracked while passing through the combustion zone [20][24].

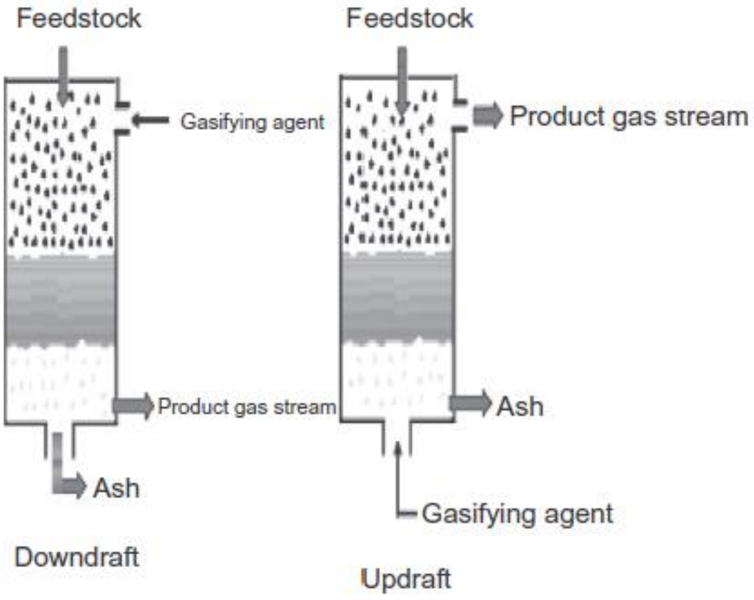


Figure 26: Fixed/Moving Bed Gasifier [20]

b. Fluidized Bed Gasifier

The main feature of this gasifier is the constant mixing process using small particles usually sand with the help of a gasifying agent (explained in the next section). In almost all the literature regarding gasification, it can be observed that this gasifier is used. The following are the advantages:

i. Shorter residence time with increased particle contact
ii. Increased production efficiency
iii. Better char conversion
iv. High calorific value gas production [20][24]

There are 2 types of fluidized bed gasifiers and the change in fluidization velocity is the main difference:

1. Bubbling fluidized bed gasifier (velocity = 0.5-2m/s)
2. Circulating fluidized bed gasifier (velocity = 2-5m/s)

Figure 27 illustrates this gasifier [20][24].

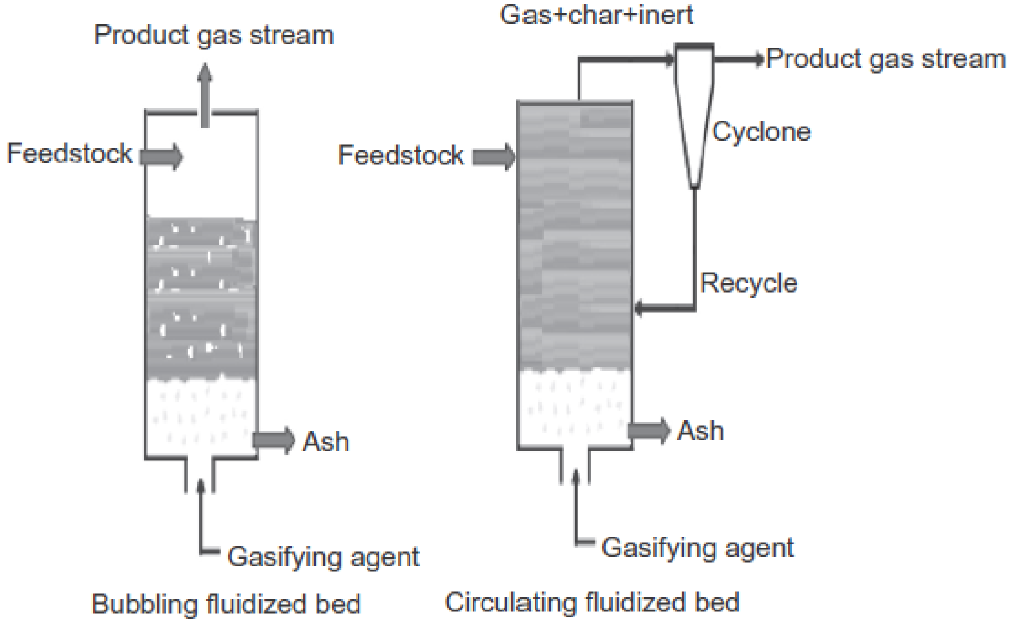


Figure 27: Fluidized Bed Gasifier [20]

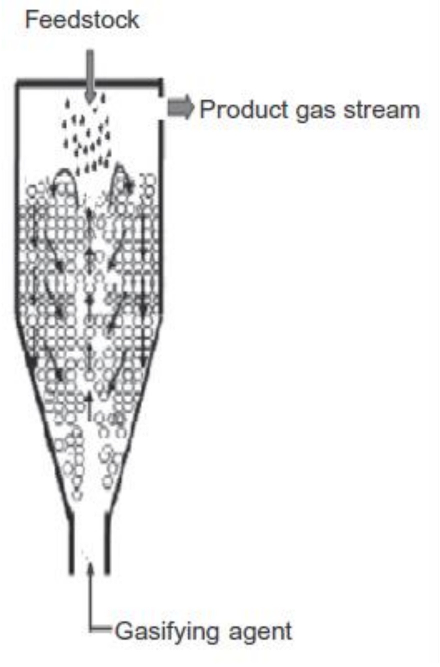


Figure 28: Spouted Bed Gasifier [20]

Figure 28 represents a spouted bed gasifier which is a variation of a fluidized bed gasifier. This is not a type of fluidized bed gasifier because of the difference in solid particle behavior. The gasifying agent creates a particle upward movement as observed in Figure 28 [20].

5.1.2 Operating conditions

The following are the main parameters that play a significant role in the process:

1. Equivalence Ratio (ER): the ratio between the actual air-fuel ratio to the stoichiometric air-fuel ratio for combustion. This ratio helps improve the quality of gas yield in air gasification. Increasing this ratio would increase the air in the gasifier, improving oxidation reactions and improving the formation of CO_2, H_2O, and N_2. For plastic gasification, increasing ER and maintaining high temperatures would result in more H_2 production [17]. It was observed that increasing ER results in reduced tar formation with reduced gas heating value [27]. Therefore, optimal ER value is an important parameter. Table 14 provides the significance of the value [17][20][4].

ER > 1	Fuel rich mixtures
ER < 1	Lean fuel
ER = 1	Stoichiometric mixture

Table 14: Significance of the ER Value [17]

2. Operating temperature: it is an important variable that determines the yield and composition of syngas. Higher temperatures result in increased gas formation and reduced tar, CH_4 and char yield. Temperatures higher than 800°C do have reduced tar formation. Optimal syngas formation occurs at 900°C [20][14].
3. Gasifying agents: they create the gasifying medium and actively participate in chemical reactions for the desired output. O_2, CO_2, air and steam are the most commonly used gasifying mediums. This is the distinguishing feature between air gasification, steam gasification carbon dioxide gasification, etc. Air is the most popular medium since it is an inexpensive agent and lower tar contents are formed when compared to steam. However, one of the drawbacks of using air is the production of lower calorific value gas due to the dilution of N_2. This can be avoided by removing nitrogen before use, creating a cleaner gas with a higher calorific value. Combinations of agents can improve the output, for example, steam and air/O_2 do not require external heat and can increase the quality of the syngas produced [20][4].
4. Operating pressure: this parameter is not as significant when compared to the previous parameters. At the lab-scale most of the gasification processes are operated in atmospheric pressure but at an industrial level the technology operates at an elevated pressure with increasing pressure, it is observed that there is an increase in the CH_4 concentration and tar formation [20][24].

5.1.3 Cleaning techniques

Tar/char removal and gas cleaning are important steps to ensure high standard output [20]. Currently, there is no universally accepted definition for tar, but 'it is a complex mixture of condensable hydrocarbons, including oxygen containing 1- to 5-ring aromatic and complex polyaromatic hydrocarbons, among others.' [2]. Char is also produced in the reduction process and is less volatile and has a greater percentage of carbon than tar. Char has a higher percentage of ash content [27].

One of the methods to reduce tar formation is the choice of bed material. Bed materials with catalytic properties (examples provided in Table 15) are the most economical, simplest, and widely used method [20][25].

Catalyst	Feedstock	Gasifying Agent
Dolomite ($MgCO_3.CaCO_3$)	PP	Air
Olivine ((($(Mg,Fe)_2SiO_4$))	PE, PP, HDPE, Mixture of PE, PP, PS, PVC, PMMA, and PET	Air Steam Combination of Air and Steam
Activated Carbon	Mixture of PE, PP, PS, PET, PVC and PMMA	Air
Ni-based catalysts like Ni/Al_2O_3, Ni-Mg-Al, Ni/MgO	Mixture of PE, PET, PS, and PP	CO_2

Table 15: Tar cracking catalyst for various feedstocks [20]

Water scrubbers, fabric filters, and other mechanical techniques can also be used to remove tar from the output. Despite being efficient, they are expensive and sometimes too complex [20].

Another method to crack tar would be altering a specific operational parameter. Increasing the temperature would increase the cracking of tars and other light hydrocarbons. However, this is only possible at temperatures as high as 1100°C [4][20].

Tar formation depends on operating conditions, reactor design, and feedstock composition (further explained in 5.2 Gasification Feedstock and Products).

The composition of syngas produced is a mixture of H_2, CO, CO_2, and CH_4 [19]. However, traces of sulfur and nitrogen compounds are observed, depending on feedstock composition.

For example, the production of HCN in syngas is due to the presence of polyamide. The removal of HCN is a vital step before selling the product since it is a dangerous gas and extremely fatal for humans. The removal of this gas is possible using oxy- and red- Ni/Mg/Al catalyst during the gasification process [11]. The same catalyst is useful for removing nitrogen-based compounds from the syngas [15].

For the removal of sulfur from syngas, calcium-based absorbents like limestone slurry are used. This system can remove 95% SO_x compounds at low temperatures [15].

Char will be produced in the process and only the production can be reduced. It is collected separately through fly ash and bottom ash collectors. The reduction in its production is possible through the optimization of operational conditions [1].

5.2 Gasification Feedstock and Products

Due to the high temperatures in a gasification reactor, it has a greater flexibility when compared to pyrolysis. However, since the stream entering incineration is the targeted feedstock there is a large variety of plastic entering the facility in different forms [12].

Just like pyrolysis, polyolefins are preferred, but, the feedstock would contain PVC, PMMA, PS and PET, which would impact the output if not limited into the system [4]. PET is rich in oxygen, this would change the ER resulting in increased evolution of CO and enhancement of hydrogen by water-gas shift reaction. For PVC, once again, the presence of chlorine affects the process. Production of HCl in the process should be avoided, otherwise, it results in halogenated hydrocarbons and corrosion of the equipment [20]. PMMA has a similar effect on the process as PET due to the presence of oxygen in the polymer [10]. On the other hand, the presence of PS in the system does not have any serious effects on the system [26].

According to many researchers, a two-stage gasifier with a catalyst (preferably Ni-Mg-Al catalyst) is preferred for the gasification of multiple polymers [4]. Consider a plastic mix of PE, PP, PS, PVC, PMMA, and PET with a low heating value of 41.5 MJ/kg. The composition of the feedstock is presented, not the amount of each polymer in Table 16 [3].

Elements	**Wt%**
Carbon	80.8
Hydrogen	12.8
Oxygen	5.2
Chlorine	1.13

Table 16: Elemental analysis of the feedstock [3]

A schematic diagram of the experiment is provided in Figure 29. The experiment occurs at 750ºC with air as the gasifying agent. The bed materials in the Bubbling fluidized reactors are dolomite (lower reactor) and activated carbon (upper reactor). The feed rate was 3.5- 6.8 g/min and the operation time was 44 - 85 mins. The experiment was conducted multiple times with varying operational conditions [3].

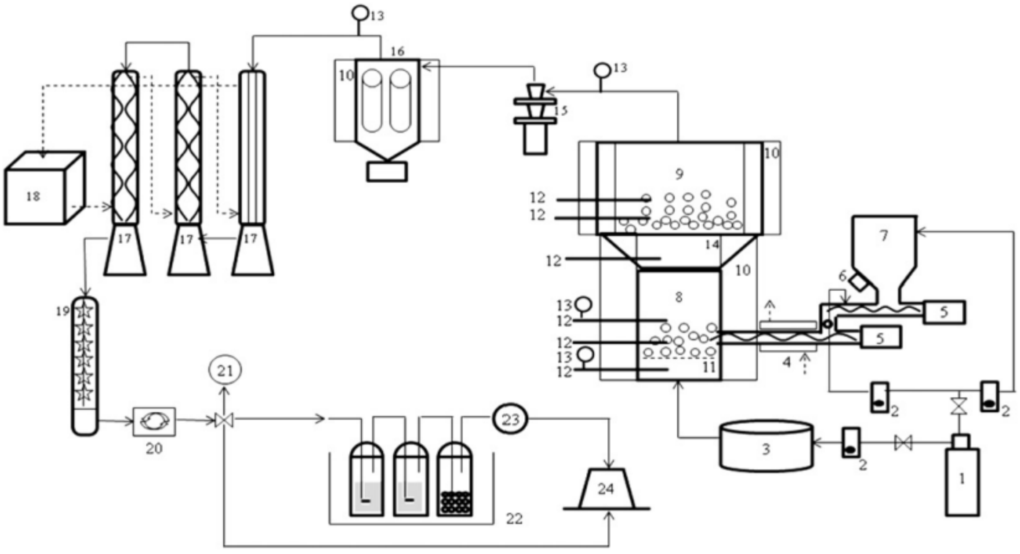


Figure 29: Overview of a two-stage gasifier plant [3]

1.Air, 2. Flow meter, 3. Pre-heater, 4. Water-jacket, 5. Screw feeder, 6. Vibrator, 7. Silo, 8. Bubbling fluidized bed (Lower reactor), 9. Activated carbon zone (Upper reactor), 10. Electric furnace, 11. Porous plate type distributor, 12. Thermocouple, 13. Pressure gauge, 14. Perforated distributor, 15. Cyclone, 16. Hot-filter system, 17. Condensers, 18. Chiller, 19. Electrostatic precipitator, 20. Gas meter, 21 Gas sampler, 22 Impingers for HCl gas absorption, 23. Isokinetic sampling pump, 24. Burner

Table 17 provides the case where the output gas had the maximum lower heating [3]. The experiment also provided other results with varying operational parameters, such as a reduction in tar formation with the increase in ER (from 0.21 to 0.32), an increase in temperature (750 to 900ºC) Several companies used carbon (300 to 900g). These changes also resulted in increased hydrogen and a decrease in methane presence in the output gas, which in turn reduces the LHV [3].

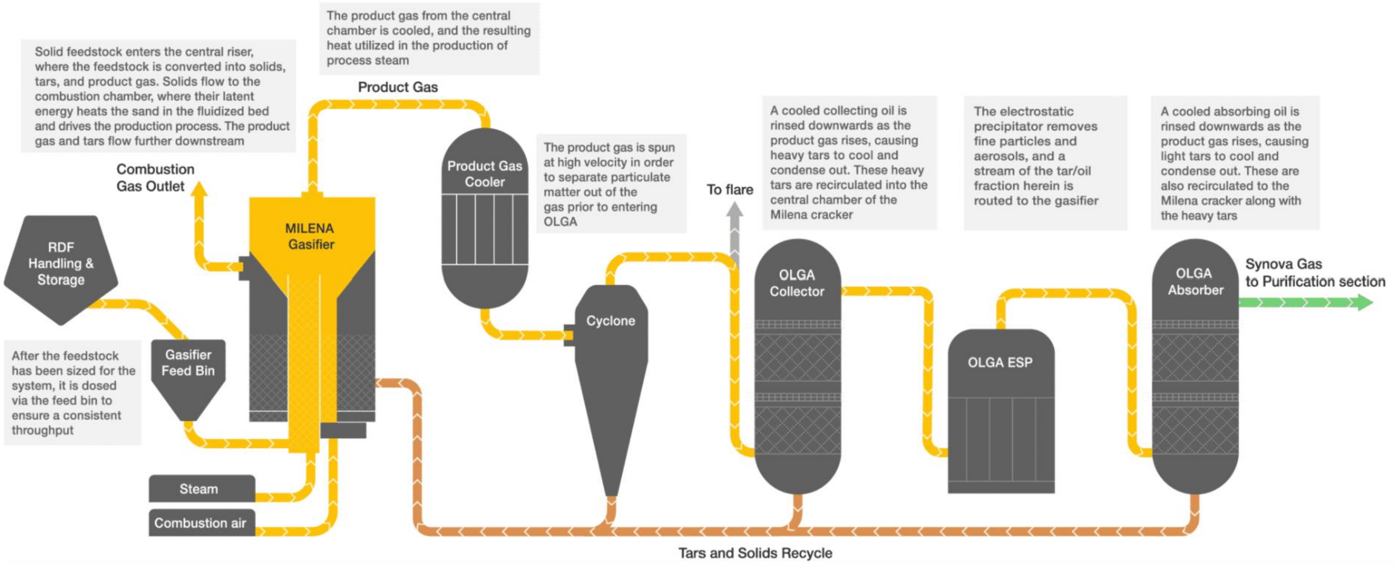
Composition	Vol%
N_2	45.34
CO_2	3.06
H_2	17.73
CO	13.65
CH_4	12.68
C_2H_6	0.53
C_2H_4	5.50
C_2H_2	0.17
$C_3+C_4+C_5$	0.21
Benzene	1.01
Toluene	0.07
Tar (mg/Nm_3)	3490
Lower Heating Value (MJ/Nm_3) (LHV)	13.42

Table 17: Syngas composition [3]

5.3 Applied Technologies

There are several companies that use gasification, however, this is widely used for biomass feedstock. This section only takes into account the companies that opt for plastic as their feedstock.

Synova is an independent Dutch research organization that has developed MILENA-OLGA technology, the process is presented in Figure 30. This technology claims to produce sustainable energy and electricity by gasifying mixed plastic that cannot be mechanically recycled. the company initially installed a 30kWth lab scale project in 2004 and later started its 80kWth pilot in 2008. The OLGA (gas cleanup technology) was added to the pilot in 2009. The plant is situated in Maasslui, Netherlands [23].



Solid feedstock enters the central riser, where the feedstock is converted into solids, tars, and product gas. Solids flow to the combustion chamber, where their latent energy heats the sand in the fluidized bed and drives the production process. The product gas and tars flow further downstream

The product gas from the central chamber is cooled, and the resulting heat utilized in the production of process steam

The product gas is spun at high velocity in order to separate particulate matter out of the gas prior to entering OLGA

A cooled collecting oil is rinsed downwards as the product gas rises, causing heavy tars to cool and condense out. These heavy tars are recirculated into the central chamber of the Milena cracker

The electrostatic precipitator removes fine particles and aerosols, and a stream of the tar/oil fraction herein is routed to the gasifier

A cooled absorbing oil is rinsed downwards as the product gas rises, causing light tars to cool and condense out. These are also recirculated to the Milena cracker along with the heavy tars

After the feedstock has been sized for the system, it is dosed via the feed bin to ensure a consistent throughput

Figure 30: Process of MILENA-OLGA technology [23]

The company currently has entered a partnership with Sabic and Technip Energies. Technip Energies is engineering and technology company focusing on energy transition. The partnership would combine Synova and Technip Energies technologies to produce olefins and aromatics from plastic waste, all the while Sabic is an investor in Synova. Technip Energies will provide their gas treatment technology (Pure.rGas™) for purifying the final product before entering the cracker furnace [5].

RWE is a German energy company, that focuses on wind and solar energy in the Netherlands. They have started their hydrogen project in Limburg called the **FUSE REUSE RECYCLE (FUREC**). This project obtains hydrogen through the gasification of municipal waste. The waste is first collected and transported to a plant in Buggenum which removes metals, stones, ceramics, and glass. Then they are compressed into pellets through torrefaction which is transported to Chemelot by waterways. At Chemelot, the pellets undergo gasification where syngas is made. From the syngas, hydrogen and carbon dioxide are extracted. The company claims that it substitutes 280 million m3 of natural gas per year by producing 54,000 tonnes of hydrogen per year [18]. This project is co-funded by the EU Sustainable Fund and has not started yet [18].

Enerkem is a Canadian biofuel company, that gasify municipal waste to ethanol or methanol. The company claims to use bubbling fluidized bed gasification vessel and their proprietary syngas cleaning and conditioning process to attain their purified synags. After which, through catalytic synthesis, liquid methanol and then fuel grade ethanol is obtained. Their technology is presented in Figure 31. The company claims that their process take less than 5 mins to produce low-carbon transportation biofuel for 400,000 cars [6].

They that will open its gasification plant in the port of Rotterdam with Shell. The project is expected to be operational in 2025 or 2026 with the aim to convert waste-to-jet. The waste gasification technology of Enerkem is combined with Shell's Fischer-Tropsch technology to produce sustainable aviation fuel. The company claims that the aim of this partnership is to reduce the carbon emissions upto 80% when compared to conventional fuel [7].

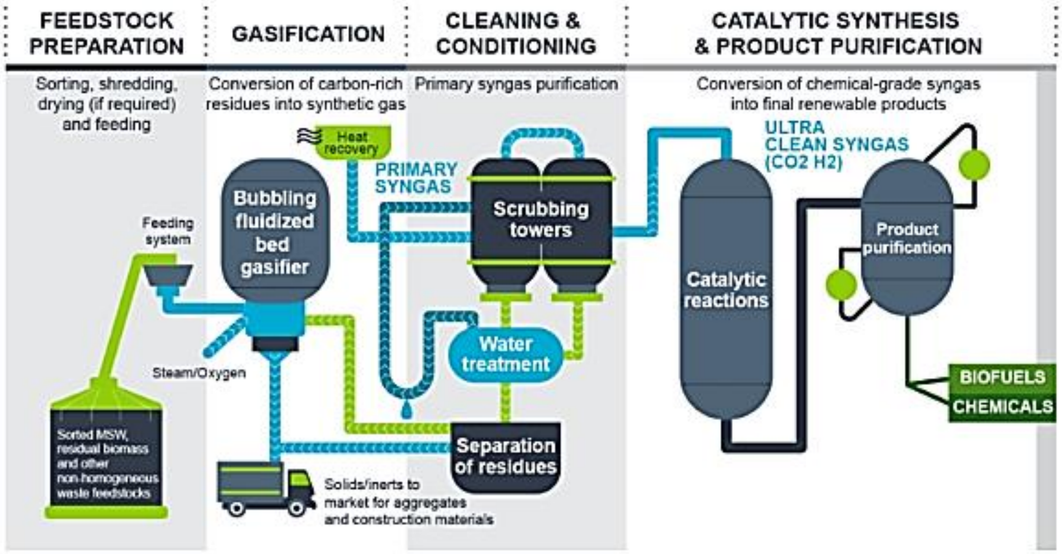


Figure 31: Gasification technology of Enerkem [6]

Gidara Energy is a German company that focuses on green technologies. The company has a patented gasification technology called High-Temperature Winkler (HTW®) technology that is used to convert non-recyclable waste to biofuels that can be used in road transport, marine and aviation sector. This technology uses a bubbling fluidized bed (operating on air or oxygen blown modes). They claim that their syngas does not contain any tars, phenol or other heavy aromatic compounds due to high outlet temperatures. Figure 32 provides an overview of the technology [9].

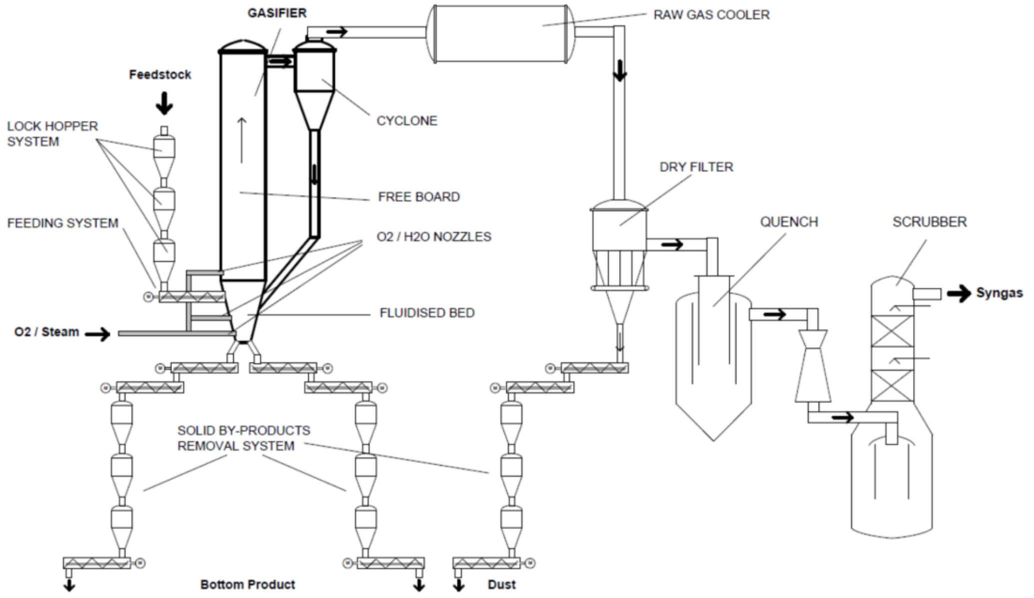


Figure 32: Gasification technology of Gidara Energy [9]

The company has received a permit to start a project at BioPark, Amsterdam port converting waste to bio-methanol that can be used in the marine sector. The project is in collaboration with px Group, which would participate in the construction phase. Ara Partners will finance this project. The plant is known as Advanced Methanol Amsterdam (AMA) and is expected to be operational in 2024 [8].

5.4 Environmental Impacts

The output produced from gasification can be converted to polymers or chemicals, as well as used as a fuel. Therefore, just like pyrolysis, mass balance is an important aspect of the commercialization of gasification and the same rules are applied here.

However, the TRL for each of these outputs would vary since converting syngas to polymer has more steps and would have higher impacts on the environment when compared to using it as a fuel. Table 18 provides an overview of the efficiency and TRL of pyrolysis and gasification [21].

Technology	**Product**	**TRL**	**Efficiency**
Gasification	Syngas	8-9	Polymer Dependent
Gasification	Monomers/ Hydrocarbons	5-7	Polymer Dependent
Pyrolysis	Diesel	8-9	Polymer Dependent
Pyrolysis	Paraffin/ Wax	8-9	50% paraffin, 10% lubricating oil
Pyrolysis	Monomers/ Hydrocarbons	5-7	Polymer Dependent

Table 18: Gasification and Pyrolysis Assessment [21]

Gasification can handle a wide variety of polymers, but not necessarily create a lower impact on the environment. For example, recycling of PET. Unlike pyrolysis, on controlling ER value PET can be incorporated in the input feedstock for gasification. Figure 33 provides an overview of the environmental impact of various technologies for recycling PET [21].

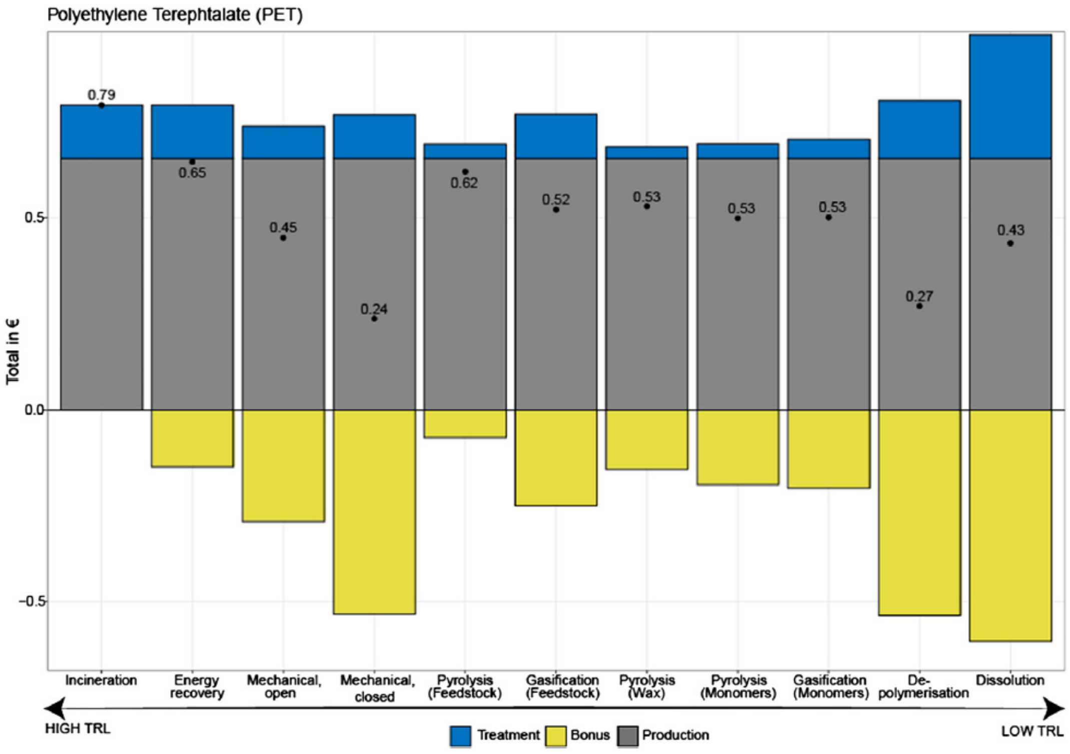


Figure 33: Environmental Impact of recycling PET for different technologies [21]

From Figure 33, closed mechanical recycling is the best option for PET Recycling and not Gasification. Dissolution and Depolymerization also has high hopes, but require optimization [21].

Consider a different type of polymer, for example ABS plastic with flame retardants. The presence of flame retardants affects the other recycling technologies and not gasification, making it the best option. Figure 34 provides and overview of the CO_2 emission of each technology [21].

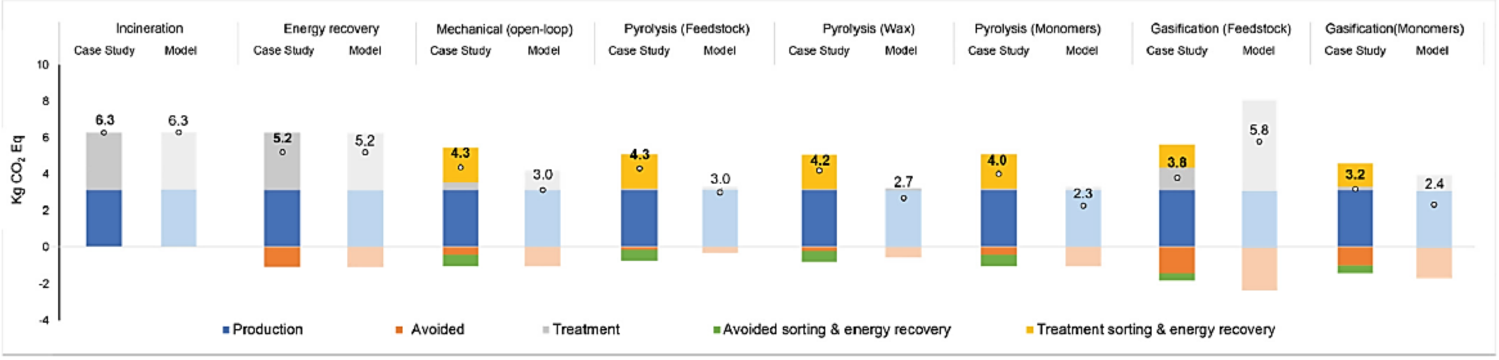


Figure 34: Comparison of CO2 emissions for per kg of ABS [21]

Figure 35 provides the life cycle impact of gasification of PO waste to produce high-value chemicals (HVC). Gasification mainly produces ethanol and small quantities of benzene, liquefied petroleum gas (LPG) and butadiene from syngas [1].

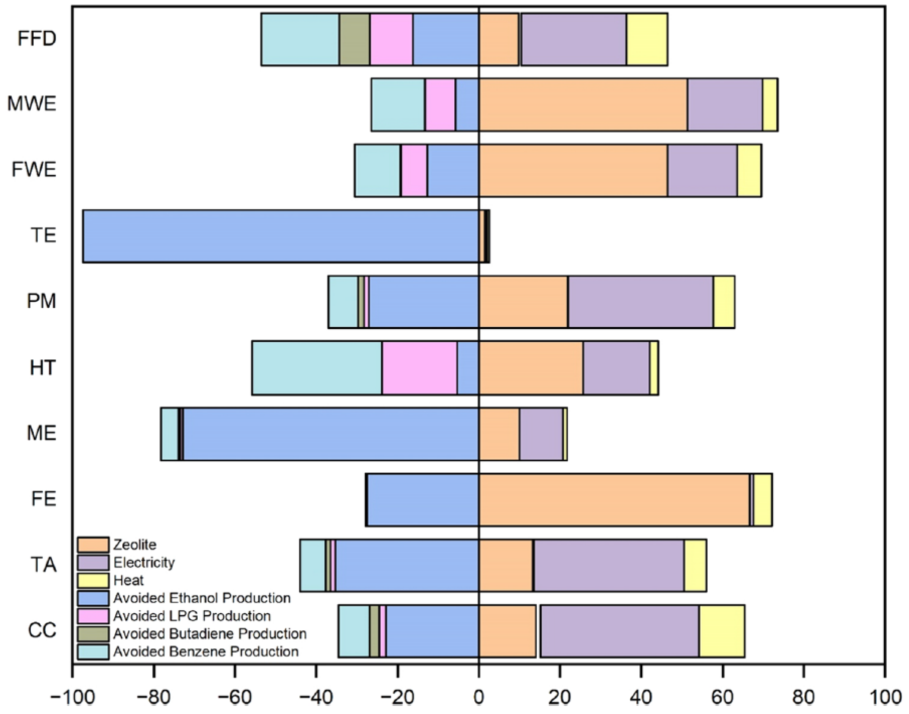


Figure 35: Life cycle impact of Gasification for HVC production [1]

The Figure 35 considers the following impact categories:

- FFD – Fossil Fuel Depletion (kg oil eq)
- MWE – Marine Water Eutrophication (kg N eq)
- FEW – Fresh Water Eutrophication (kg P eq)
- TE – Terrestrial Ecotoxicity (kg 1.4-DB eq)
- PM – Particulate Matter Formation (kg PM10-eq)
- HT – Human Toxicity (kg 1.4-DB eq)
- ME – Marine Ecotoxicity (kg 1.4-DB eq)
- FE – Freshwater Ecotoxicity (kg 1.4-DB eq)
- TA – Terrestrial Acidification (kg SO_2 eq)
- CC – Climate Change (kg CO_2 eq)

Figure 35 presents the significant impact of ethanol production for FEW, PM, TA and CC. The major impact contributors for the technology is from the consumption of electricity, heat and zeolite. However, the pyrolysis of PO waste for monomer recovery provides more environmental benefits than gasification [1].

5.3.1 Difference between combustion, gasification and pyrolysis

Oftentimes, gasification and pyrolysis are viewed as glorified combustion. However, there are significant differences between the 3 types of thermal waste treatment routes, they are presented in Table 19 [1].

	Combustion	Gasification	Pyrolysis
Process	Waste converted to CO_2 and H_2O	Waste converted to CO, CH_4, and H_2	Waste decomposed to condensable gases
Reaction environment	Oxidizing	Reducing	No oxidant
Reactant gas	Air	Air, oxygen, steam, or a combination of gases	None
Temperature (°C)	850-1200	700-1200	500-800
Pressure	Atmospheric	Atmospheric	Higher than Atmospheric
Pollutants	SO_2, NO_x, HCl, PCDD/F, particulate	Tar, char, sulfur, nitrogen, and chloride compounds	Tar, sulfur, nitrogen, and chloride compounds
Gas cleaning	Treated in air pollution control units	Clean syngas to required standard limits	Clean syngas to required standard limits

Table 19: Comparison between Combustion, Gasification and Pyrolysis [1]

5.5 References

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6. Depolymerization - Solvolysis

Apart from thermochemical recycling, depolymerization is a type of chemical recycling that follows the reverse process of polymerization. It is defined as the process that reduces polymers to their constituent monomers or oligomers (short segments of the polymer chain) [15][19].

It is also known as monomer recycling, monomer recovery, or chemolysis [15].

This report only focuses on the Solvolysis process, a type of depolymerization. Solvolysis is a process that applies to polymers with heteroatoms in their backbone and cannot break C-C bonds [2][19].

6.1 Processes

Solvolysis is a very selective process when compared to pyrolysis and gasification and must be adapted for the polymer entering the system [14]. It involves several steps and these steps are named based on the types of cleavage agents (agents used to break a chemical bond) used, such as hydrolysis, alcoholysis, aminolysis, and many more. This selective breaking of bonds makes it easy to recycle polymers formed by polycondensation (eg: polyesters, PET, and polyurethanes) and polymers with heteroatoms (eg: PC) [19].

To observe the process closely, a laboratory experiment is considered. Figure 36 provides an understanding of all the chemical reactions that occur to attain the final product bis-2-hydroxypropyl terephthalate (BHET), terephthalic acid (TPA), bis(2-hydroxyethyl) terephthalamide (BHETA) or dimethyl terephthalate (DMT) [11]. PET undergoes glycolysis first at an operating temperature of 208°C for 150 mins. In this reaction, ethylene glycol (EG) is used as a solvent at a ratio of 6 w/w (EG/PET) and Zinc Acetate ($ZnAc_2$) is used as a catalyst to improve the efficiency of the process. After the glycolysis, BHET can be further broken down to TPA at a temperature of 150°C for 240 min. The solvent used here is sodium hydroxide (NaOH). This results in the production of 85% of BHET and 90% TPA. This experiment uses highly colored and complex multilayered post-consumer PET. The quality of BHET and TPA produced are similar to their virgin counterparts [1].

Similar to the previous experiment, PET after undergoing ammonolysis (ammonia is the solvent) at 70-180°C produces terephthaldiamide and EG [11].

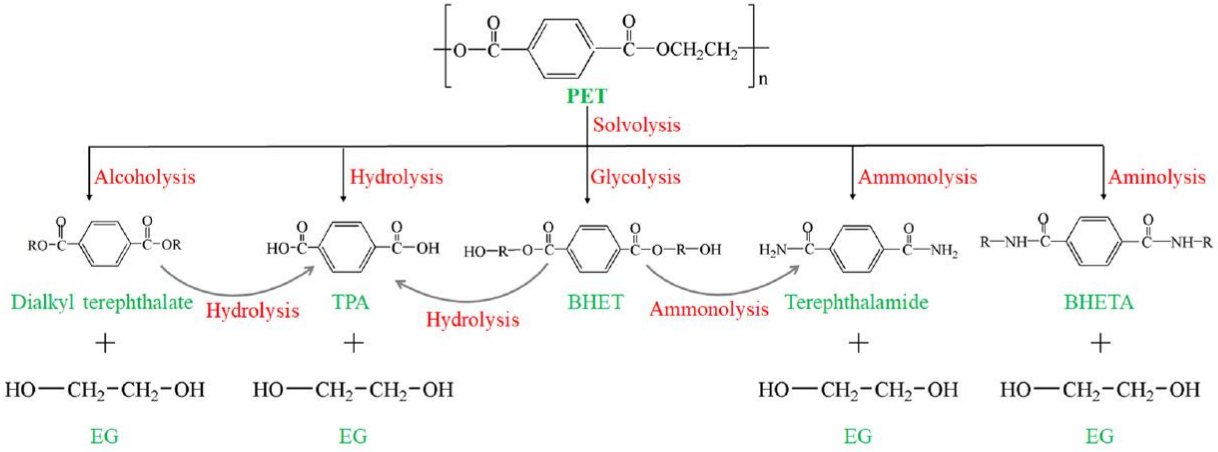


Figure 36: Solvolysis of PET [11]

Another example is the solvolysis of PC. When PC undergoes alcoholysis, bisphenol A (BPA) and dialkyl carbonate (DAC) is formed [11]. Initially 0.77g of PC is dissolved into 8ml of dry dioxane (solvent) with a catalyst (KOH/NaOH). This solution is warmed up to a 100°C for 25-120 mins. The reaction is monitored and once the PC is consumed, the solution is cooled to room temperature. The solution is neutralized with acetic acid. Then the solution is washed with ethyl acetate (30ml) and then with 50ml of water to remove the residue and concentrate the solution [8]. During the warming up, BPA is evaporated and condensed, while DAC formed is collected from the solvent.

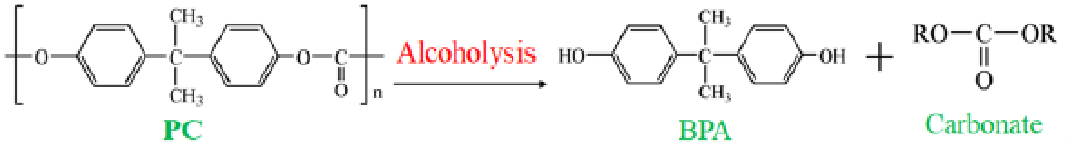


Figure 37: Solvolysis of PC [11]

The processes explained in Figure 37 are basic and commonly used techniques to depolymerize polymers.

There is increasing research around incorporating microwave radiation technology. Microwave heating is observed to be a more efficient source of heating. It can help provide a more even heating in the reactor, thereby accelerating the reaction [11][19]. For example, PA is normally depolymerized using superheated steam at 305oC and 12MPa FOR 55-60 mins. This produces a yield of 96% of ε–caprolactam (CL), which is the monomer of PA [13].

Another example for solvolysis of PA through hydrolysis was conducted with phosphoric acid as the catalyst in the presence of water. The sample was subjected to heat using 200W of pulsed microwave irradiation for 20 mins. The experiment considers the use of phosphoric acid since it is a good absorbent of microwave power. The samples are then cooled to room temperature and neutralized using KOH and water. The solution is filtered to remove any precipitates. Due to the presence of a strong phosphoric acid, 90% of ε-aminocaproic acid (ACA) is formed along with other linear oligomers [13].

Furthermore, academics are also interested in using alternative solvents or 'green solvents' like ionic liquids (ILs) and deep eutectic solvents (DES). DES is a better alternative than ILs since they are cheaper, less toxic, and biodegradable. DES acts as a catalyst and helps in optimizing the process [21].

6.2 Solvolysis Feedstock and Products

The feedstock entering a solvolysis plant is very specific when compared to pyrolysis and gasification plants. Polymers with heteroatoms and polymers formed by polycondensation can be easily recycled using this technology. So, unlike other recycling technologies, PO plastics are not preferred here. PET, PC, PU, and PLA are the most commonly recycled plastics through this technology.

Since the report focuses on household plastic waste, a variety of polymers will be found present. The waste entering the plant is mechanically sorted and then fed into the reactor. Sensors like optoelectronic separators are used to understand the composition of the input [6].

Since the input from this technology is polymer-specific, Table 20 and Table 21 provides an overview of the common reagents and catalysts used to obtain the monomers of the input polymer [22].

Glycolysis	Hydrolysis
Reagents	**Reagents**
Ethylene Glycol, Propylene Glycol, Dipropylene Glycol Glycerol, Aromatic Polycarboxylic Acids, Bis (2-hydroxy-ethoxy-ethyl) glutarate	Water/Ethylene Glycol/ NaOH Water/NaOH
Catalysts	**Catalysts**
Zn, Pb, Mn, Co-acetate Amines Benzenesulfonate	Sodium acetate, Sulphuric acid

Table 20: Reagents and Catalyst for Solvolysis of PET [22]

Glycolysis/Alcoholysis	Hydrolysis/Hydroglycolysis
Reagents	**Reagents**
Ethylene Glycol, Propylene Glycol, Dipropylene Glycol Polyether glycol I ,6-hexane diol	Superheated Steam Steam/NaOH Glycerol/Steam
Catalysts	**Catalysts**
Group I-IV Metal Alkoxides Potassium Acetate Chlorides of Ti, Cr, Zr	-

Table 21: Reagents and Catalyst for Solvolysis of PUR [22]

And as presented in Figure 36, depending the type of bond broken in the polymer several different types of outputs can be formed. Figure 38 provides an overview of the various outputs for each input polymer.

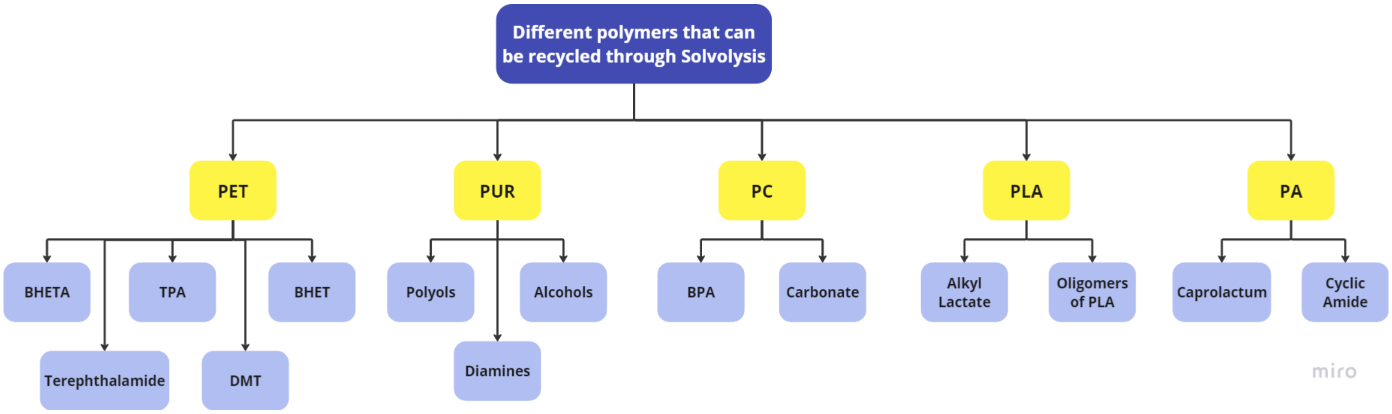


Figure 38: Outputs from Solvolysis

Quality is a subjective property to analyze, depending on the combination of reagents and catalysts used, different proportions of outputs are produced. When 5g of PC pellets undergo hydrolysis by placing it in Tetrahydrofuran and water solvent for 8 hours with NaOH catalyst, 70% of BPA. But when 1,4-Dioxane replaced Tetrahydrofuran, then 94% of the output was BPA [12].

Since the output of this process is only the monomers of the input polymer, mass balance is not required.

6.3 Applied Technologies

Ioniqa is a Dutch clean-tech company that was founded at Eindhoven University of Technology in 2009. The company claims to process colored PET waste into high quality PET alternatives for virgin counterparts. This output would be suitable for the application of food-grade plastics. In 2019, the company scaled up its technology and opened a depolymerization plant producing an output of 10 kilotonnes at Brightlands Chemelot Campus in Geleen [3]. The company is also focusing on licensing its technology for other PET producers [8]. The company has partnered with Koch Technology Solutions to scale up and commercialize its technology. they have partnerships with Unilever, Indorama, and Coca-Cola. In 2019, they helped Coca-Cola to launch its first bottle created from recycled marine plastic [9].

CuRe Technology is a Dutch depolymerization company that converts Polyester and PET to high-quality products. They mostly focus on polyester rejuvenation. They first sort (by color) and clean the input plastic. After the CuRe technology, transparent and virgin-grade granulates are produced [5]. In 2021, they opened their pilot plant (this is lab-scale) at Emmen, The Netherlands. This pilot plant can process 20kg of polyester input per hour. They plan to scale up to 25 kilotonnes in the coming years [20].

Gr3n is a Swiss chemical recycling company focusing on the depolymerization of PET. Their exclusive technology is Microwave Assisted Depolymerization (MADE) [17]. Figure 39 provides an overview of the technology.

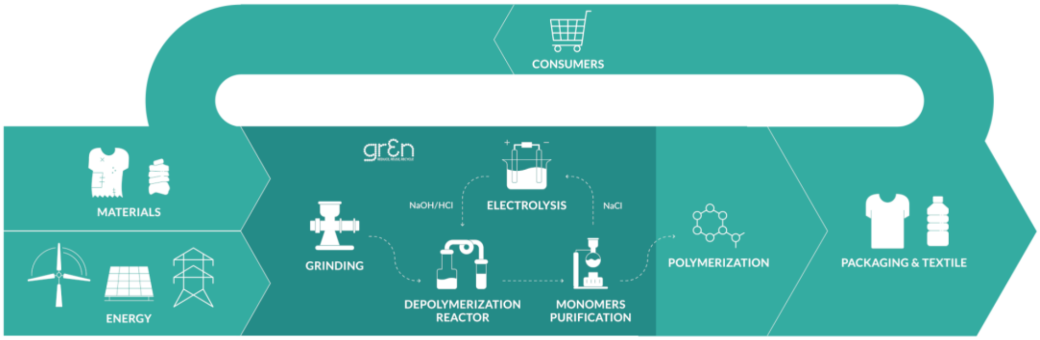


Figure 39: Overview of MADE [17]

The MADE is a hydrolysis process that takes less than 10 mins and at temperatures less than 200ºC. They claim to not degrade the plastic and the process can be repeated multiple times. The NaCl generated from the hydrolysis is converted to NaOH and HCl through the electrolysis process. The output obtained from this process is TPA and Monoethylene Glycol (MEG) which are polymerized again and used in textiles and bottles [17]. In 2021, the company set up its first demo plant in Chieti, Italy with a capacity of 30 kilotonnes of plastic waste per year. Currently, the company is constructing another plant in Spain that will produce 40 kilotonnes of virgin-like PET by the end of 2024 [4].

6.4 Environmental Impact

Figure 40 provides an overview of the position of solvolysis in the recycling landscape. Solvolysis is widely present for PET recycling and PET is collected largely in monostreams. Therefore, it has lower contamination levels and can be readily recycled. But Figure 40 states that solvolysis is a better alternative than mechanical recycling for PET by reducing the number of pet that needs to be produced at the end [19].

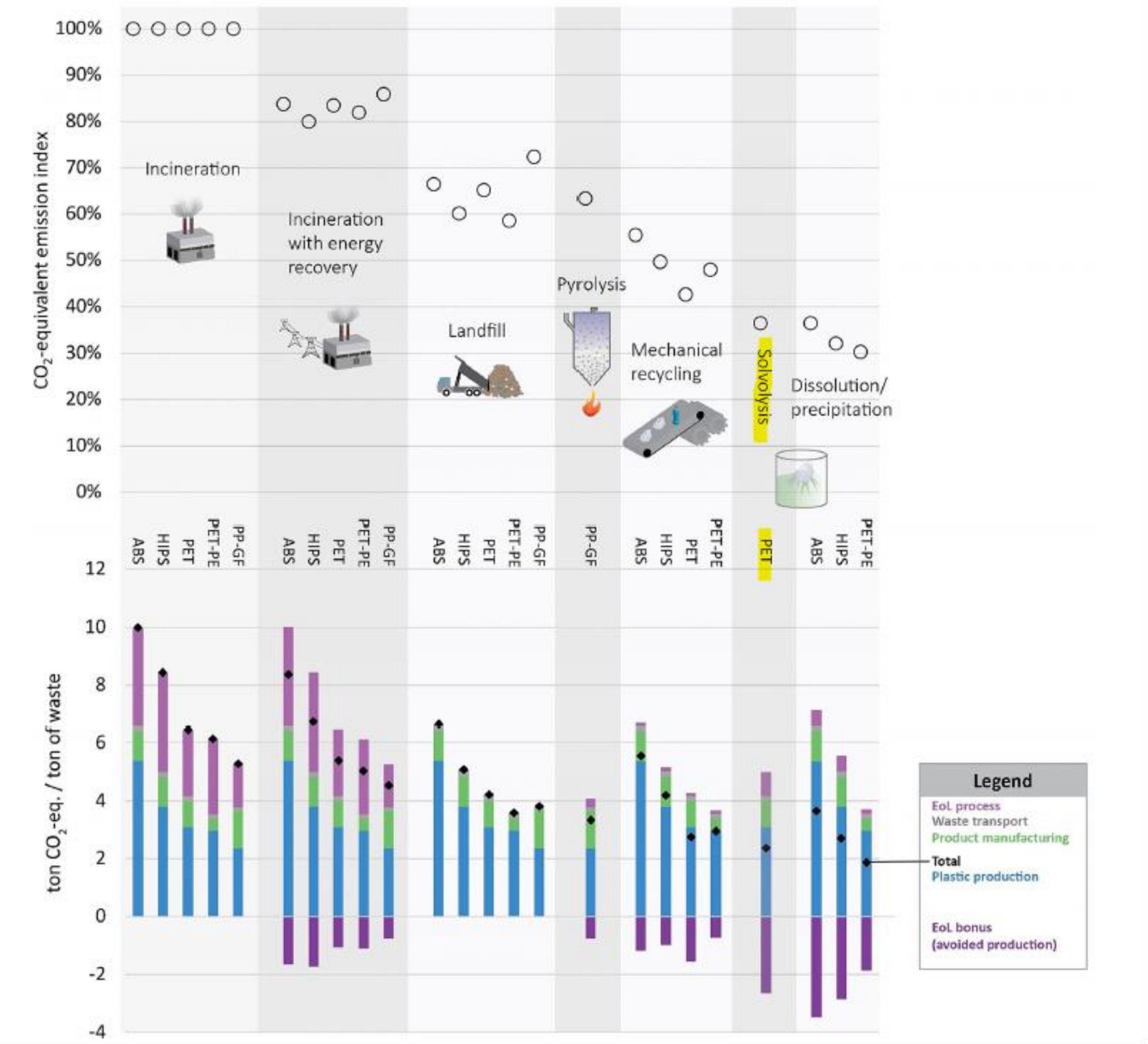
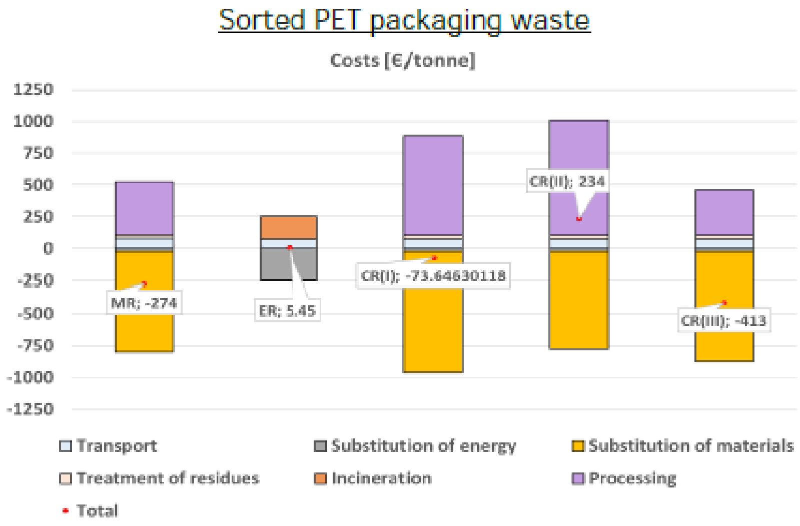


Figure 40: CO_2 emissions by different technologies [19]

Furthermore, Solvolysis is a promising technology for thermoset plastics and shows lower carbon emissions when compared to pyrolysis and gasification. It is a better alternative for recycling PA (nylon 6) and PLA when compared to mechanical recycling [16].

Figure 41 presents the cost analysis of sorted PET packaging waste processing between mechanical recycling, solvolysis and incineration. It can be understood that alkaline hydrolysis is a best alternative followed by mechanical recycling, partial glycolysis, incineration and hydrolysis-methanolysis. Similar results can be observed in Figure 23 for climate change impact.



MR: PET regranulate production; ER: incineration; CR-I: partial glycolysis; CR-II: hydrolysis-methanolysis; CR-III: alkaline hydrolysis

Figure 41: Cost analysis of Sorted PET packaging waste between different recycling methods[7]

In Figure 42, Figure 43, Figure 44 and Figure 45, PET packaging waste comprising of bottles and trays is considered. The different solvolysis processes considered are:

- CR-I: Partial glycolysis
- CR-II: Hydrolysis-methanolysis
- CR-III: Alkaline hydrolysis [7]

For Figure 42, CR-I is a better option than mechanical recycling. CR-I is also a better alternative when compared to the other solvolysis methods [7].

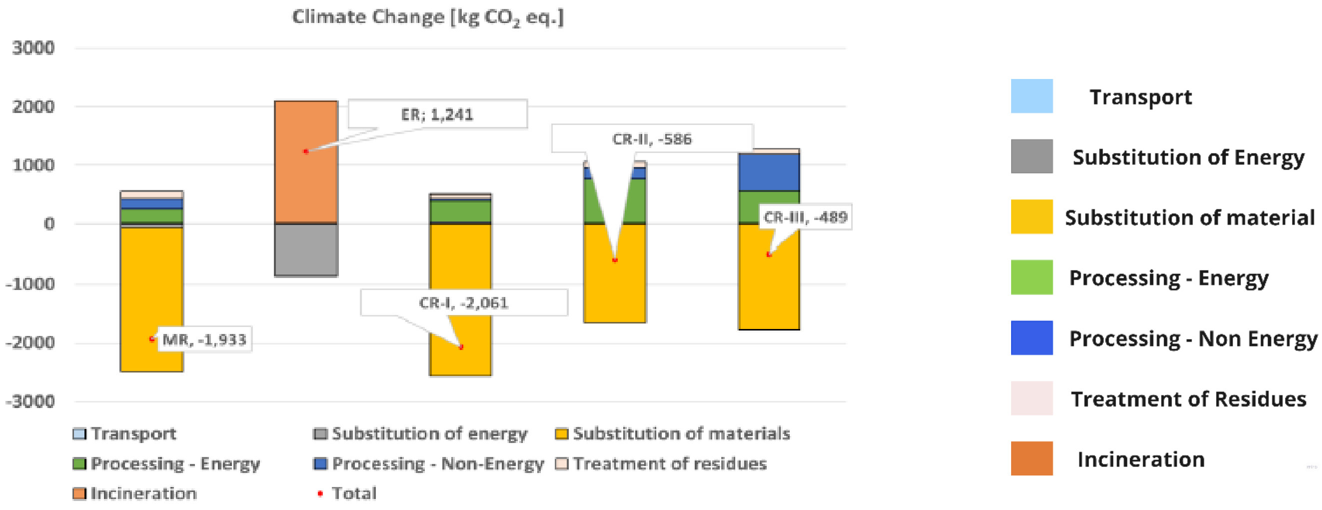


Figure 42:Comparison between Mechanical Recycling (MR), Energy Recovery (ER- incineration) and Chemical Recycling (CR) of 1 tonne of sorted mixed PO waste - Climate Change [7]

For Figure 43, it can be observed that CR-II has the highest impact due to the use of sodium hydroxide. But the results of CR-1 and mechanical recycling are relatively equal [7].

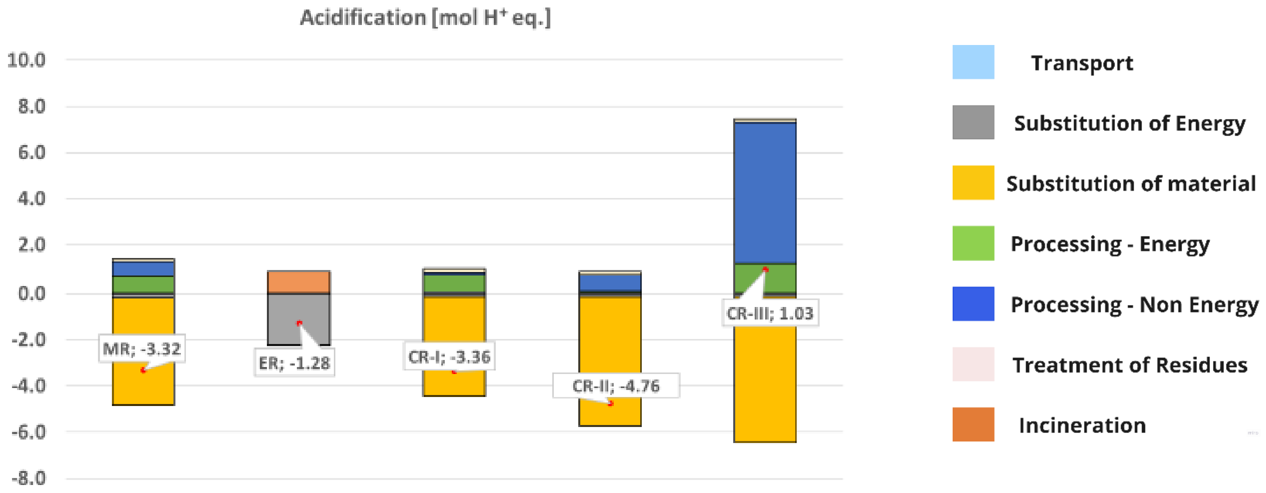


Figure 43:Comparison between Mechanical Recycling (MR), Energy Recovery (ER- incineration) and Chemical Recycling (CR) of 1 tonne of sorted mixed PO waste – Acidification [7]

For Figure 44, similar to the acidification, sodium hydroxide contributes to the significant impact of CR-III. CR-I has the highest net savings, but CR-II and mechanical recycling have similar values [7].

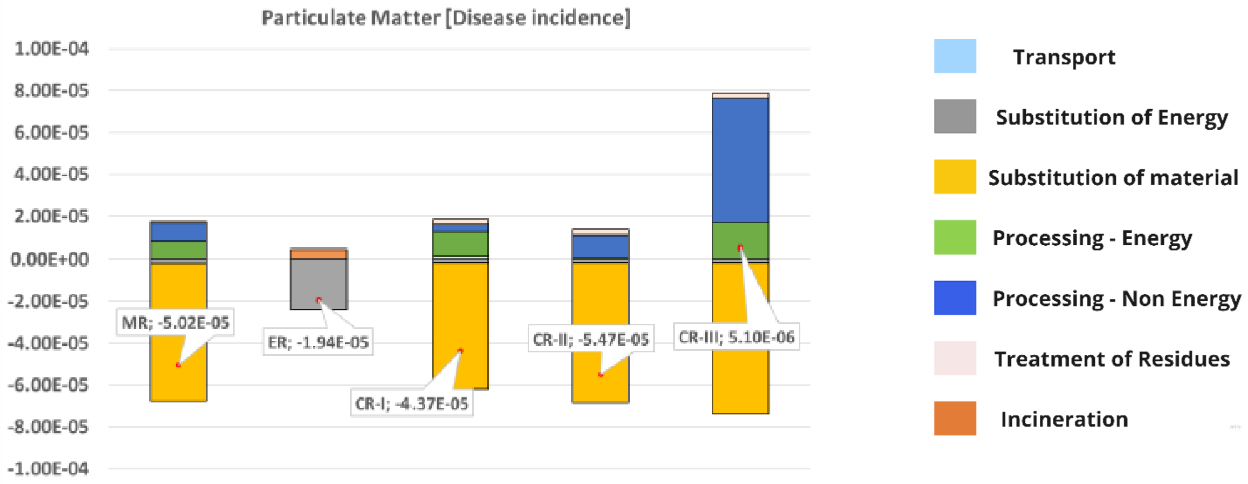


Figure 44: Comparison between Mechanical Recycling (MR), Energy Recovery (ER- incineration) and Chemical Recycling (CR) of 1 tonne of sorted mixed PO waste – Particulare Matter [7]

For Figure 45, here mechanical recycling is the best option followed by CR-I, CR-II and then CR-III.

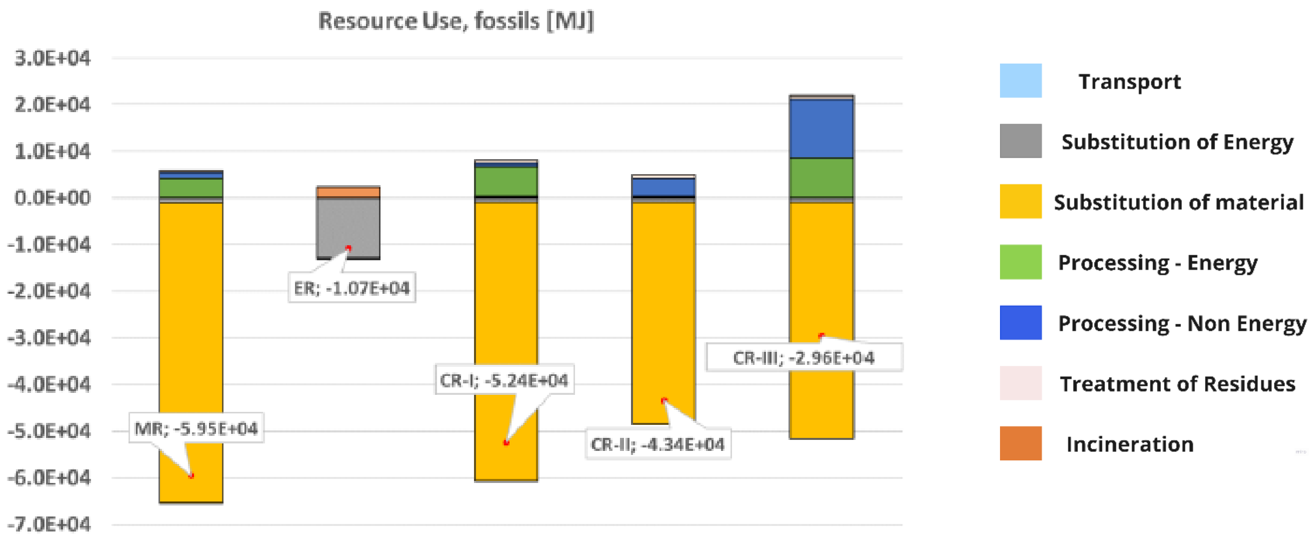


Figure 45:Comparison between Mechanical Recycling (MR), Energy Recovery (ER- incineration) and Chemical Recycling (CR) of 1 tonne of sorted mixed PO waste – Resource Use, Fossil [7]

Overall, electricity and heat consumption were the main impact contributors for mechanical recycling. For CR-I and CR-II, the main contributors were electricity consumption and processing of the waste incurred in the process [7].

6.5 References

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7. Dissolution

Another chemical recycling method is solvent-based recycling (SBR), which is also emerging as a subject of increasing relevance in plastic recycling. SBR comprises several techniques and is a widely researched topic [2][4].

Dissolution, also called as physical recycling, can be defined as a purification process through which the polymer present in mixed plastic waste is selectively dissolved in a solvent, allowing it to be separated from the waste and recovered in a pure form **without changing** its chemical make-up [13].

It is important to understand that Dissolution and Solvolysis are different technologies in the output they produce. Dissolution delivers ready polymers while solvolysis produces monomers that forms the basis of the plastic production.

7.1 Processes

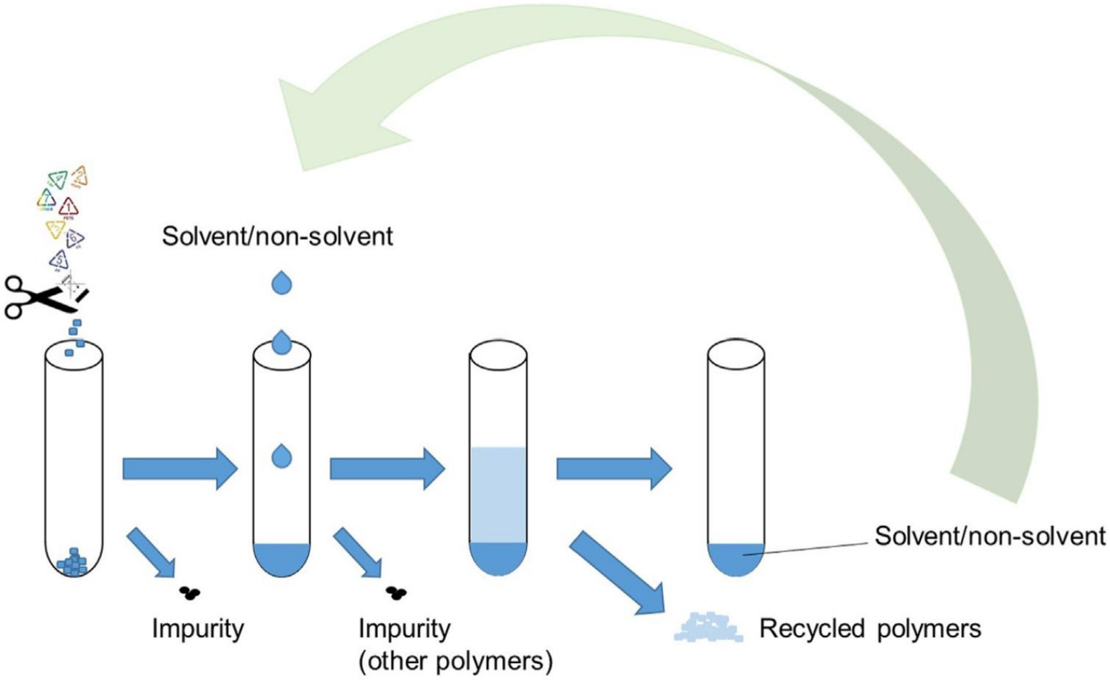


Figure 46: General Framework of Dissolution [15]

In Figure 46, the general principle of the process is depicted. A typical Dissolution recycling facility would include the following steps:

1. Purchase of plastic feedstock
2. Sorting and cleaning the targeted polymer
3. Chemical analysis of the feedstock
4. Dissolution process
    a. Impurity separation
    b. Filtration

    c. Recovery of the polymer by drying (distillation)
5. Quality check of the recyclate
6. Extrusion pelletization (compounding and granulation by extrusion and chopping)
7. Transport of the product [15]

Figure 47 provides a brief overview of the technology [24].

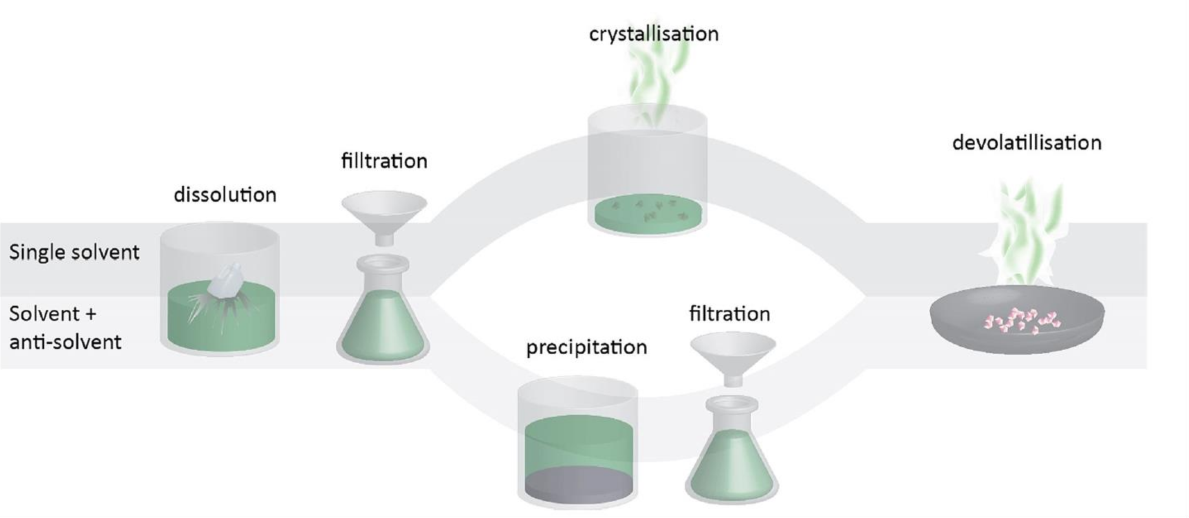


Figure 47: Overview of Dissolution process [24]

As the name suggests the main factor affecting the efficiency of the process is the combination of solvents and non-solvents used to separate the targeted polymers. To attain the optimal solvent/non-solvent combination, the following principles are considered:

- The polarity of the solvent and the polymer should be closer. This is concerning the solubility rule.
- Cohesion of the polymer affects the interaction of polymers with the solvent.
- The polymer and solvent solubility parameters must be similar or equal [26].

The Hansen solubility parameter (HSP) is considered to predict the possible suitable solvents for the process. HSP uses energy density from dispersion bonds (δ_D), energy from dipolar intermolecular force between molecules (δ_P), and energy from hydrogen bonds between molecules (δ_H) to find the distance between the solvent point to the center of the sphere (R_a) (Equation 1). The ratio of R_a and radius of the sphere (R_0) will provide the Relative Energy Difference (RED), indicating the extent of solubility. The limits are provided in Table 22 [26].

$$(R_a)^2 = 4(\delta_{D1} - \delta_{D2})^2 + (\delta_{P1} - \delta_{P2})^2 + (\delta_{H1} - \delta_{H2})^2 \qquad \text{Equation 1}$$

$$RED = \frac{R_a}{R_0} \qquad \text{Equation 2}$$

RED < 1	Soluble and high affinity; strong solvent

RED > 1	Non-soluble and low affinity, weak solvent
RED ~ 1	Boundary condition

Table 22: Extend of solubility using HSP [26]

It is important to understand that this theory also has limitations since several other parameters like electrostatic forces are not accounted for. Therefore, it is only used for predicting the best combination. Other operational factors like temperature, pressure, solvent viscosity, toxicity, and cost should be considered. Some common solvent combinations are explained in Table 23 [26].

Polymer	Strong Solvent	Weak Solvent
PS	Methyl Ethyl Ketone (MEK)	Methanol
PC	Dichloromethane (DCM)	Methanol
PE	Xylene	Propanol
PP	Xylene	n-hexane
PET	N-methyl-2-pyrrolidone (NMP)	-
ABS	Acetone	-
PVC	Cyclohexanone	n-hexane

Table 23: Common solvent combinations [26]

When the experiment is closely observed, a gel-like layer is seen to be forming around the polymer due to plasticization. This forces the polymer to infiltrate the solvent. Chain disentanglement caused by dissolution results in the movement of the polymer within the solvent. Through research, it can be observed that the presence of non-solvents in small portions can result in improved performance [9][10][26].

To gain more understanding of the process, consider LDPE as the target polymer in a plant with a capacity of 50 tonnes per day. The concentration of other plastics in the feedstock is 1%. The solvent combinations considered for the process are toluene/isopropanol. After shredding and cleaning the feedstock, they are dissolved in Toluene at a rate of 1890 kg/hr at 85 °C, and heated toluene is added. The experiment also takes into consideration the possible presence of isopropanol. To ensure proper dissolution, the solution was stirred for 30 min and filtered through 3 Ettlinger filters of size 80 μm. With the addition of isopropanol at 80°C, the polymer precipitates and is filtered again to remove the polymer. For safety reasons, nitrogen is used to occupy the reactor space. Finally, the polymer is filtered from the solvent/non-solvent solution using a rotary-drum under vacuum and then dried at 90ºC. In order to reuse the solvent and non-solvent, the solution is passed through a distillation column and then a condenser. This process recovers 1871 kg/hr of LDPE. After distillation, the solvent and non-solvent projected a recovery of 99%. Figure 48**Error! Reference source not found.** is a block diagram of the process [11].

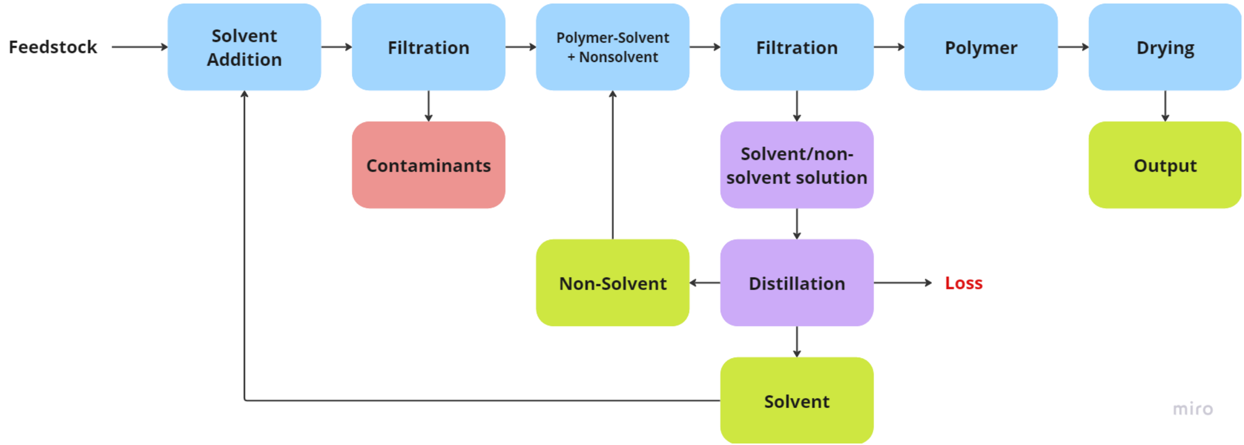


Figure 48:Block Diagram of the Dissolution process [11]

The advantage of this system over mechanical recycling is the potential to remove additives and other insoluble contaminants from the polymer. Common contaminants in plastic are stabilizers, plasticizers, lubricants, flame retardants, and pigments [22]. Apart from dissolution, several other additive extraction methods under investigation for plastic waste treatment, which are listed below:

1. Shake-flask Extraction:
    - A simple method where an appropriate solvent is used to dissolve the targeted additive in the solid polymer through agitation for a while. After the desired compound is extracted into the solvent, the solid matrix can be separated through filtration, centrifugation, or decantation.
    - Example: Phenolic compound like α-tocopherol is separated from LDPE using Tetrahydrofuran (THF) solvent in the darkness for 24 hours. The recovery is recorded as 82-86% [22].
2. Soxhlet Extraction:
    - This process is a complex version of Shake-flask Extraction.
    - An appropriate solvent is used to dissolve the targeted additive in solid polymer through a continuous boiling-condensation cycle.
    - This method is not adopted in the plastic industry but is widely used in the agricultural industry.
    - Example: Flame retardants like DecaBDE can be removed from PS and PE using the solvent toluene at -110°C for 6 hours. The recovery is recorded as -70% [22].
3. Ultrasonic Extraction:
    - This method is a separation powered by ultrasound, creating cavities in the solid matrix by agitating the additives. The cavities further enable the creation of bubbles, resulting in an unstable solid surface. This increases solvent diffusion.
    - This method is widely used in the food and pharmaceutical industries but it is still challenging to adopt in the plastic industry due to the requirement for processing large quantities.
    - Example: Removal of Bromide Flame Retardants (BFRs) from HIPS using 2-propanol /methanol (1:1) at 65°C for 60 mins. The recovery is recorded as 10-50% [22].
4. Microwave Assisted Extraction (MAE):

- This method is a separation powered by heating the solvent using microwave energy. The heat transfer is based on the dipole rotation (inductive heating) and ionic conduction (Joule heating).
- This is a relatively new technology and requires further optimization.
- Example: Removal of Azo dyes like Sudan IV, Disperse RED I from PVC using methanol at 120 °C for 20 mins. The recovery is recorded as 59.5–99.8% [22].

5. Supercritical Fluid Extraction (SFE):
    - This method follows the same principle as basic solid-liquid extraction but the solvent is supercritical fluid.
    - At critical condition (liquid and vapor phase is indistinguishable), would dissolve organic compounds from the matrix.
    - Supercritical-CO_2 is a relatively cheap and non-toxic solvent making the process 'greener' however, it still requires optimization.
    - Example: Removal of Hindered phenol (like Irganox 1010) and phosphite-type antioxidants (like Irgafos 168) from PMMA using Supercritical-CO_2 and methanol as a modifier at 0-90 °C and 45 MPa for 30 mins. The recovery is recorded as more than 75%. It is called hindered since they cannot react with oxygen [22].
6. Accelerated solvent extraction (ASE):
    - This method is the same as fluid extraction but at elevated temperatures and pressures for short duration and using small amounts of solvent.
    - Example: Removal of Hindered Amine Light Stabilizers (HALS) and phenolic antioxidants from PE using 2-propanol with THF at 80-110 °C and 10.3 MPa for 2-22mins. The recovery is recorded as higher than 97% [22].

The technological readiness level (TRL) of all these methods is provided in Table 24.

	Shake flask Extraction	**Soxhlet Extraction**	**Ultrasonic Extraction**	**MAE**	**SFE**	**ASE**	**Dissolution**
TRL	3-5	5-8	3-5	5-8	5-8	3-5	8-9
Other Application sectors	-	Agriculture	Pharmaceutical and food industries	-	Food industry	Food industry	NewCycling and Creasolv Process

Table 24: TRL of various types of additive extraction [22]

7.2 Dissolution Feedstock and Products

The feedstock considered here is household plastic waste, which is a mixture of different types of plastics. Polyolefins and PET are the most common polymers in the mix, along with small quantities of metal foil (mostly aluminum in beverage cartons and laminates in chips bags) and paper [5][6]. Dissolution has the ability to recycle all types of plastic in the feedstock but would require altering the combination of solvents/non-solvents depending on the polymers present. In order to analyse the composition of the feedstock, the Fourier Transform Infra-Red (FTIR) spectrophotometer is used [1].

For example, consider the target polymers Polyolefins, PVC, and PS [16]. Taking into consideration the thermodynamic properties of these 3 types of plastics it is possible to create a combination of solvents/non-solvents. Initial cleaning of additives like dyes, lubricants, oils, and plasticizers is done using non-solvents like methanol. Considering the chemical and economic aspects of the available solvents/non-solvents, it was concluded that at 100°C or higher temperatures, 85% xylene and 15% cyclohexane would be the optimal combination. The polyolefins will be present in the solution while a layer of PVC and PS is formed that can be separated [16].

This method is also practically possible with multilayered flexible plastic packaging. Consider the plastic food packaging comprising the 3 materials, PE, EVOH, and PET. Computational tools are used to select solvents that would help in deconstructing the feedstock plastics, layer by layer. This process is called Solvent-Targeted Recovery and Precipitation (STRAP). Figure 49 presents the basic idea of the process. After analysis, the following steps were followed to separate the polymers:

1. Dissolving PE - Toluene at 110°C for 4 hours
2. Dissolving EVOH - Dimethyl sulfoxide (DMSO) at 95°C for 30 mins and
3. Recovering PE and EVOH – lowering the temperature to 25°C and adding a certain proportion of acetone (anti-solvent), which precipitates PE. While water (antisolvent) is used to precipitate PET and EVOH.

After which distillation and filtration is performed to isolate the polymers [21].

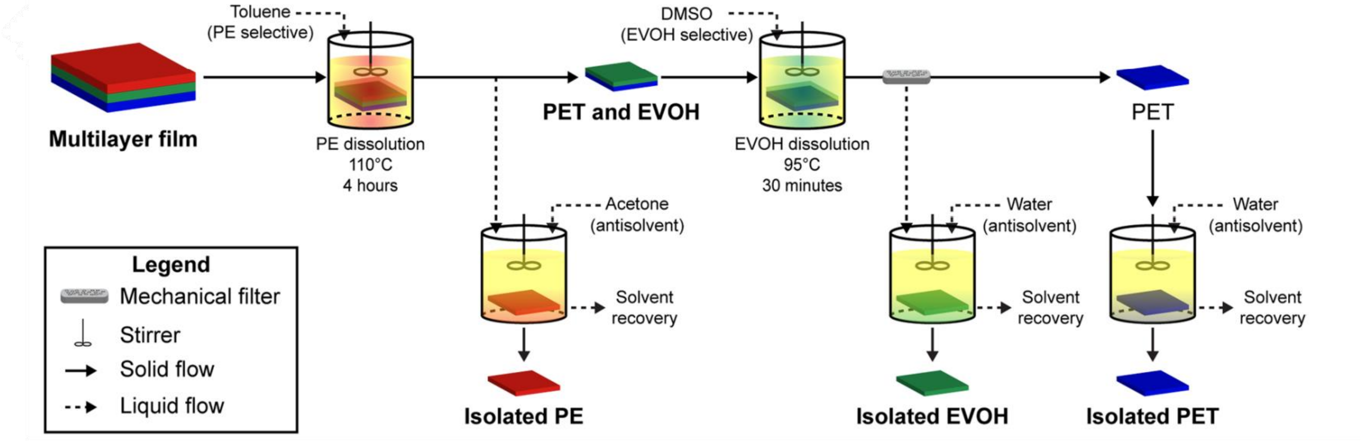


Figure 49: Overview of the STRAP process [21]

7.3 Applied Technologies

Obbotec is a Dutch chemical recycling company that does focus on recycling PP and PE through dissolution (SPEX). As presented in Figure 50, the company claims that dissolution is the solution to the problems faced by pyrolysis and mechanical recycling. They further cite CE-Delft as their external source, who argues that there is a 100% plastic-to-plastic yield through dissolution [12].

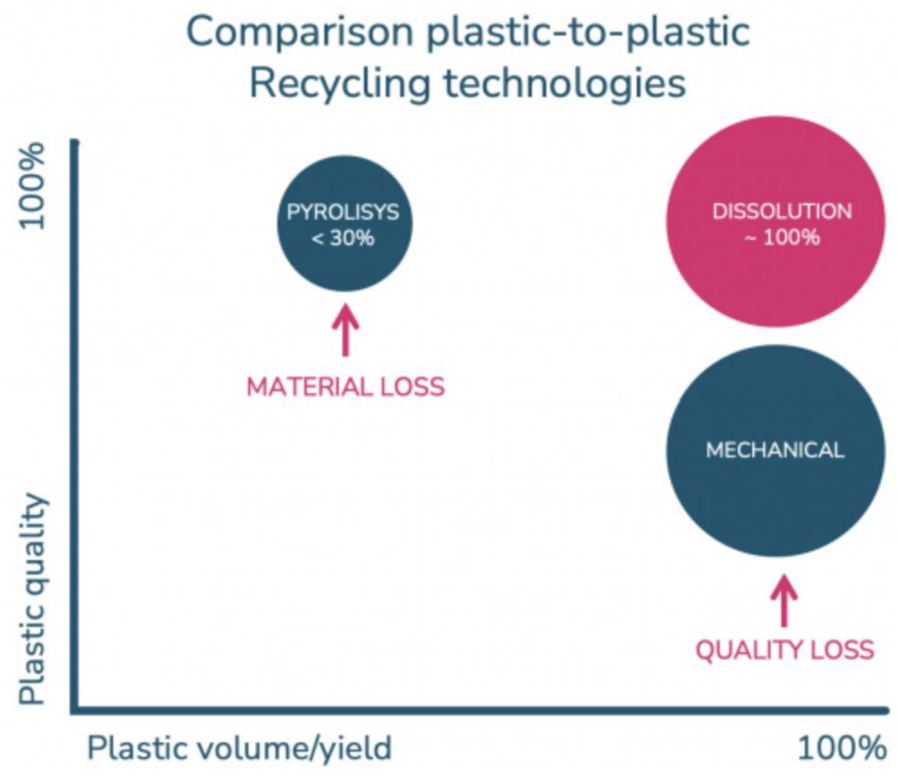


Figure 50: Obbotec viewpoint [12]

APK AG is a German dissolution company that enables the selective separation of polymers from mixed plastic waste using their technology, NewCycling. They have 2 products, which are LDPE granules and PA granules that can replace virgin LDPE and PA (for certain applications). However, their production capacity is limited. Since the company only mentions the processing of mixed plastic, it can be assumed that their target polymer is LDPE and PA [15].

CreaCycle GmbH is a German start-up founded in 2002 that designed the CreaSolv® Process in cooperation with the Fraunhofer Institute for Process Engineering and Packaging (IVV). The process is claimed to effectively solve the problems with contaminations and reduced recyclate quality of mechanical recycling [18][25]. Figure 51 is the overview of the process [18].

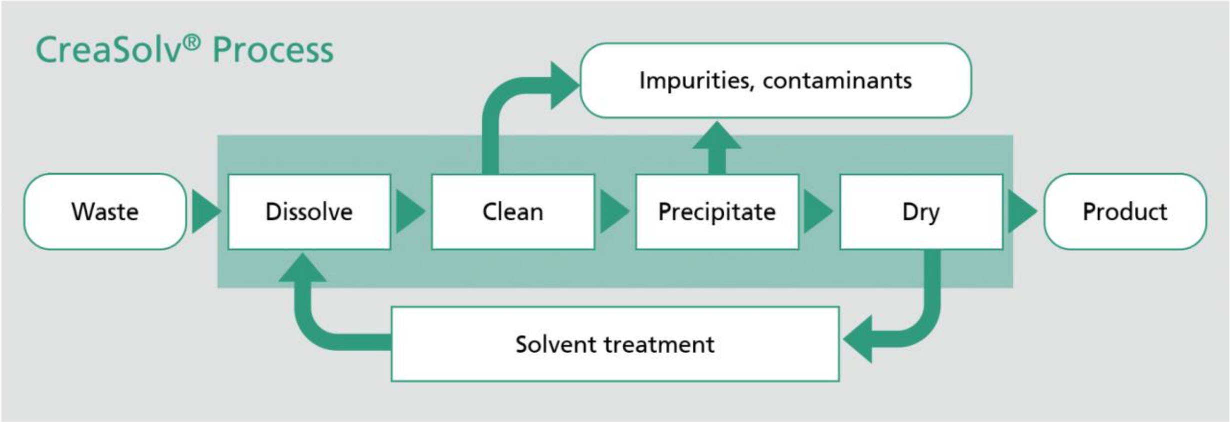
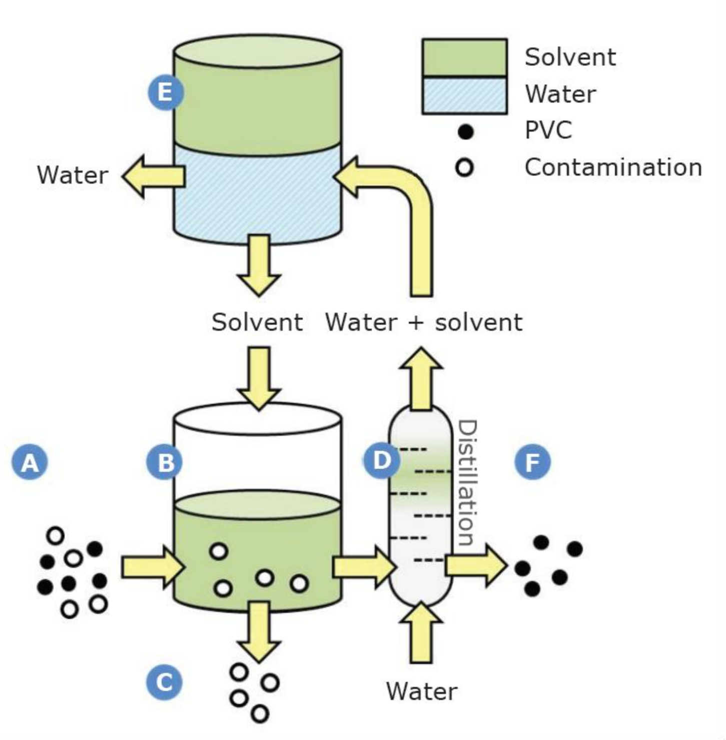


Figure 51: Overview of CreaSolv® Process [18]

The CreaSolv® technology can be used for the following waste materials:

- EoL vehicles and electronic waste- In September 2010 a collaborative project was started focusing on this group of waste in Europe and the production of plastic recyclate that complies with the legislation [18]. There is no further information provided for this project. They further focus on the recovery of WEEE streams [19].
- Packaging material- the technology has the ability to process both post-consumer and post-industrial waste. They have set up recycling plants in Indonesia in 2018 for Unilever. The plant has been functional since 2019 and produces LDPE recyclate. This plant has a capacity to process 3 metric tonnes of waste per day [18]. This project was considered to be an 'expensive failure' (as quoted by The Guardian) since collection and cleaning of the input was too expensive. In the December of 2019, Unilever stopped the collection which lead t the waste pickers burning the collected packaging material [3][8].
- EPS waste- there is an ongoing project to recycling this group of waste, PolyStyreneLoop project in Terneuzen, the Netherlands. The plant has a capacity to process 3,000 tonnes of Hexabromocyclododecane (HBCD)-containing material annually and the plant will start its operation in 2024 [14][18].
- Plastic composites- Several studies from Fraunhofer IVV claim that with the modification of the process metal-plastic composites can be recycled and little to no loss in quality was observed in both the plastic and metal [17].

There is another important Belgium company called **VinyLoop Ferrara SpA** which specializes in PVC waste using their technology called VinyLoop® Process. This company had a plant in Ferrara, Italy, and processed 10,000 tonnes/year [23]. They use Methyl ethyl ketone (MEK) as their solvent and n-hexane as the non-solvent. The process runs at 100ºC for 10 minutes with cellulose ether dispersant. Figure 52 provides an overview of the process. In this process, phthalate esters were used to plasticize PVC. This compound is toxic and was banned by the European Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) in 2015. Before the ban, the company was required to apply for a permit to use this compound which had time limit of 3 years. After 16 years of operation, the company closed in 2018 [20].



A. Collection of PVC waste

B. Selective dissolution of PVC

C. Filtration of contamination

D. Steam Distillation

E. Recovery of solvent

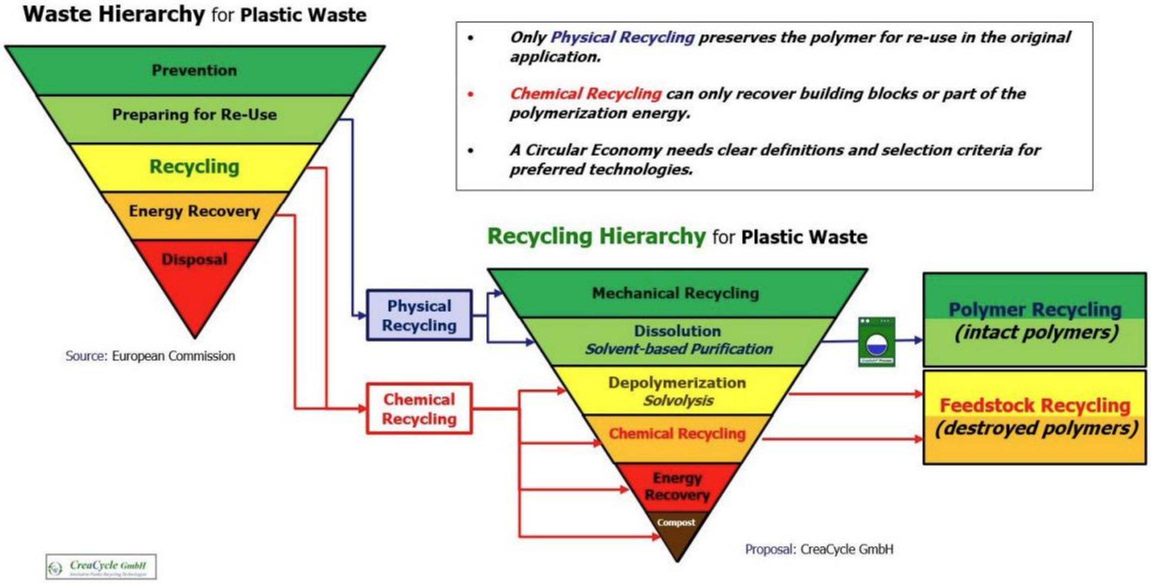
F. Recycled PVC

Figure 52: Overview of the VinyLoop® process 94[20]

These listed companies do not mention the solvent/non-solvent combination used for any feedstock specification.

7.4 Environmental Impacts

Dissolution is a solvent-based recycling method that does not break the targeted polymer structure. Figure 53 further explains the position of dissolution in the recycling industry [2]. It should be noted that recycling plastic waste through dissolution is still a widely researched topic but its environmental impacts are unclear. For Figure 53, dissolution is marked as green, this should be investigated further to actually confirm whether it is a better alternative.



- *Only Physical Recycling preserves the polymer for re-use in the original application.*
- *Chemical Recycling can only recover building blocks or part of the polymerization energy.*
- *A Circular Economy needs clear definitions and selection criteria for preferred technologies.*

Figure 53: Waste and Recycling Hierarchy by CreaCycle GmbH[2]

The process is said to have less environmental impact with respect to chemical recycling as observed in Figure 23. However, the major areas of environmental impact would be the solvent production, recycling treatment and EoL of solvent.

Figure 54, Figure 55, Figure 56, and Figure 57 is the comparison between mechanical recycling, energy recovery, and physical recycling for 1 tonne of sorted large-format PE film waste [4].

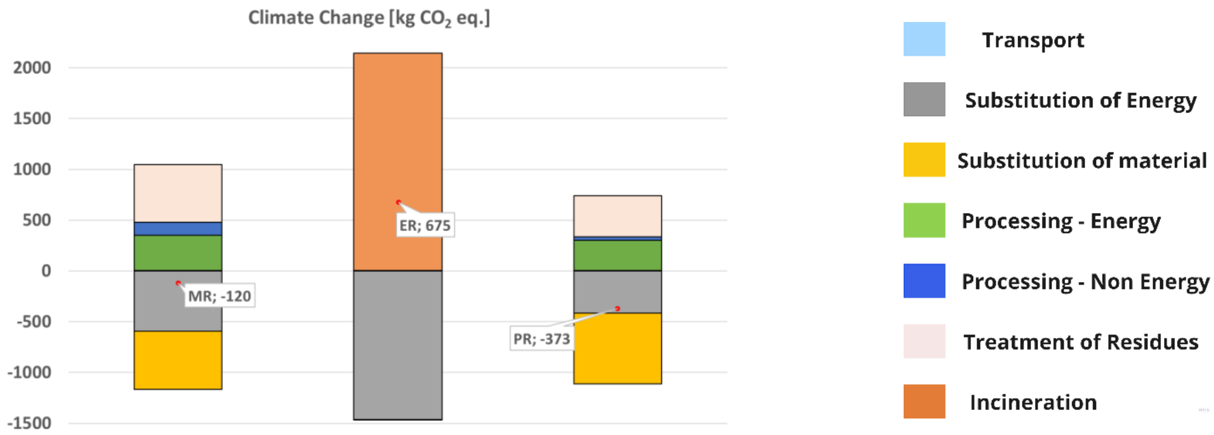


Figure 54: Comparison between Mechanical Recycling (MR), Energy Recovery (ER- incineration) and Physical Recycling (PR) of 1 tonne of sorted large-format PE film waste - Climate Change [4]

From Figure 54, it can be observed that physical recycling has higher net savings when compared to mechanical recycling. The figure also presents the highest contributing factor.

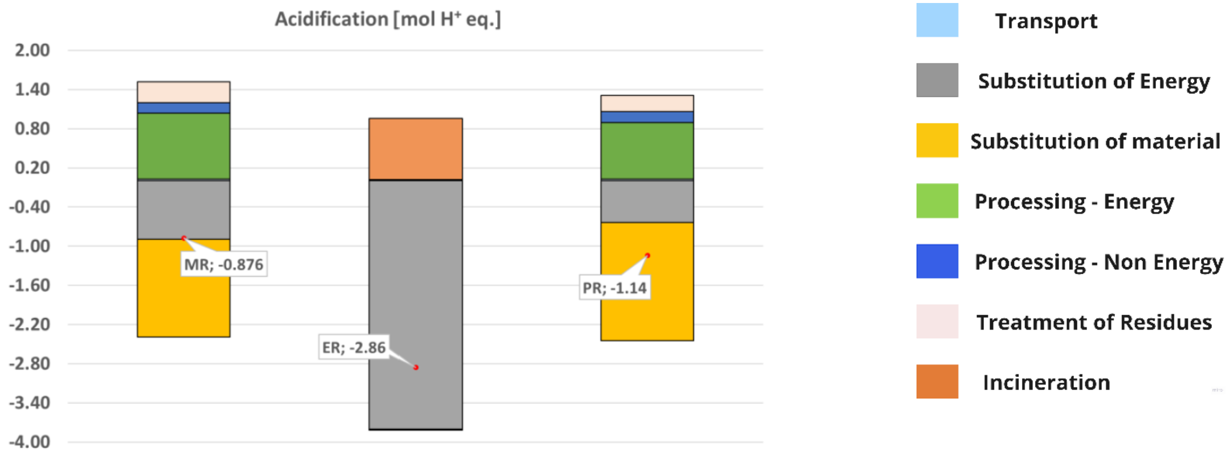


Figure 55: Comparison between Mechanical Recycling (MR), Energy Recovery (ER- incineration) and Physical Recycling (PR) of 1 tonne of sorted large-format PE film waste – Acidification [4]

In Figure 55, Figure 56 and Figure 57, incineration (energy recovery) has better results. This is because the dissolution process requires the use of solvents and the incineration process does not involve the use of energy [4].

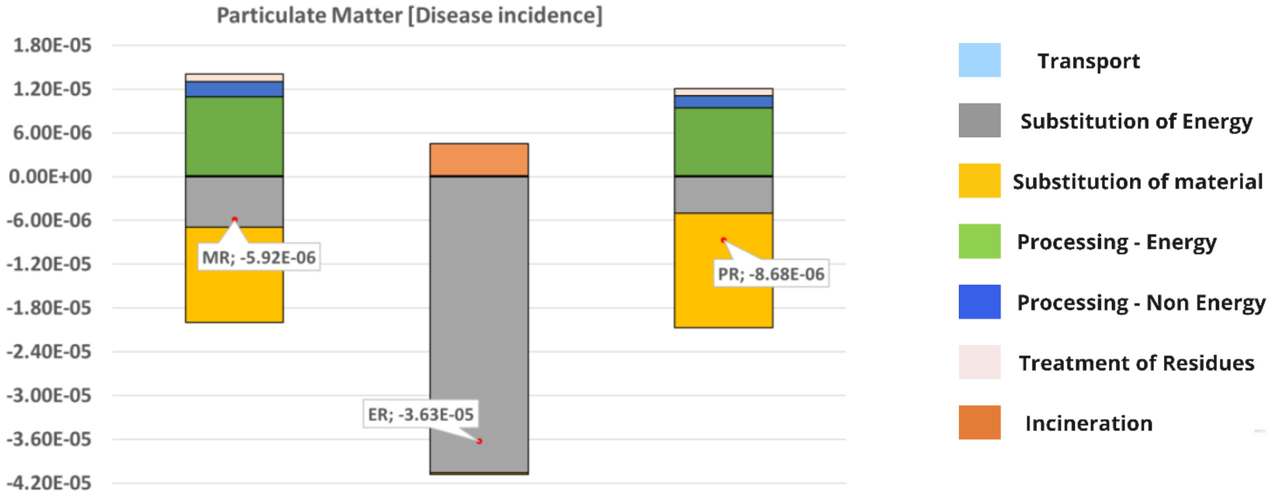


Figure 56: Comparison between Mechanical Recycling (MR R), Energy Recovery (ER- incineration) and Physical Recycling (PR) of 1 tonne of sorted large-format PE film waste - Particular Matter [4]

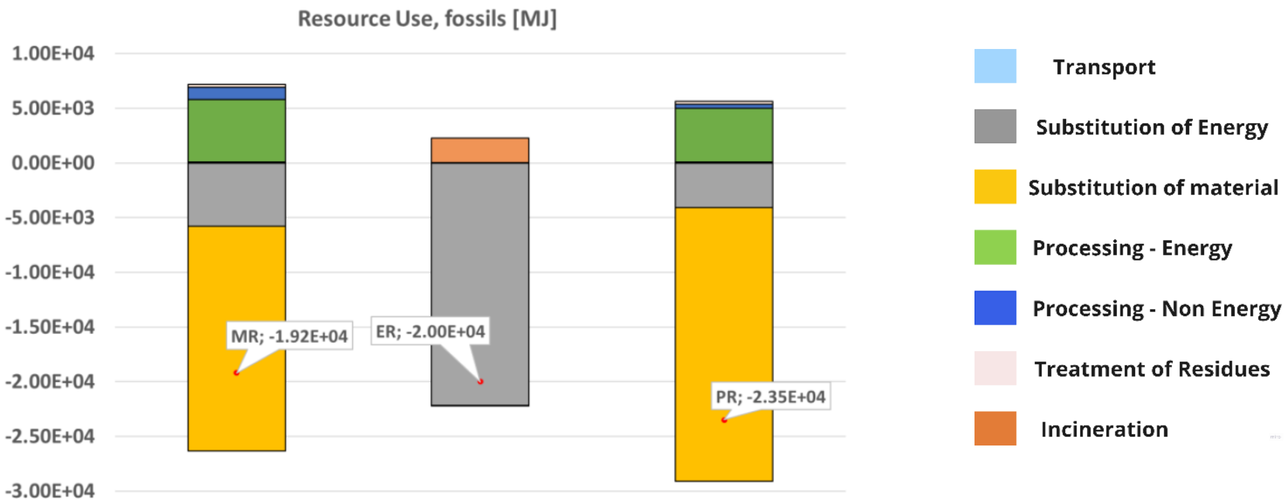


Figure 57: Comparison between Mechanical Recycling (MRR), Energy Recovery (ER- incineration), and Physical Recycling (PR) of 1 tonne of sorted large-format PE film waste - Resource Use [4]

In Figure 58, Figure 59, Figure 60, and Figure 61**Error! Reference source not found.**, the graph provides a comparison between dissolution and incineration for 1 tonne of post-industrial PE/PA multilayer film waste. The analysis focuses on post-industrial waste, which is relatively pure when compared to household waste. However, it is interesting to observe the environmental impact of recycling multilayered plastic which is a larger part of the problem [4].

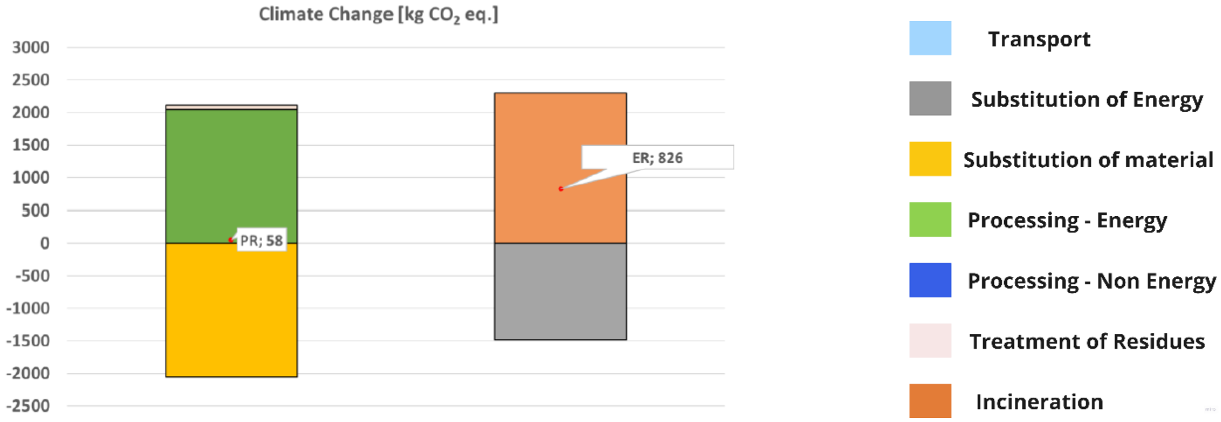


Figure 58: Comparison between physical recycling (PR) and incineration(ER) of 1 tonne of post-industrial PE/PA multilayer film waste - Climate Change [4]

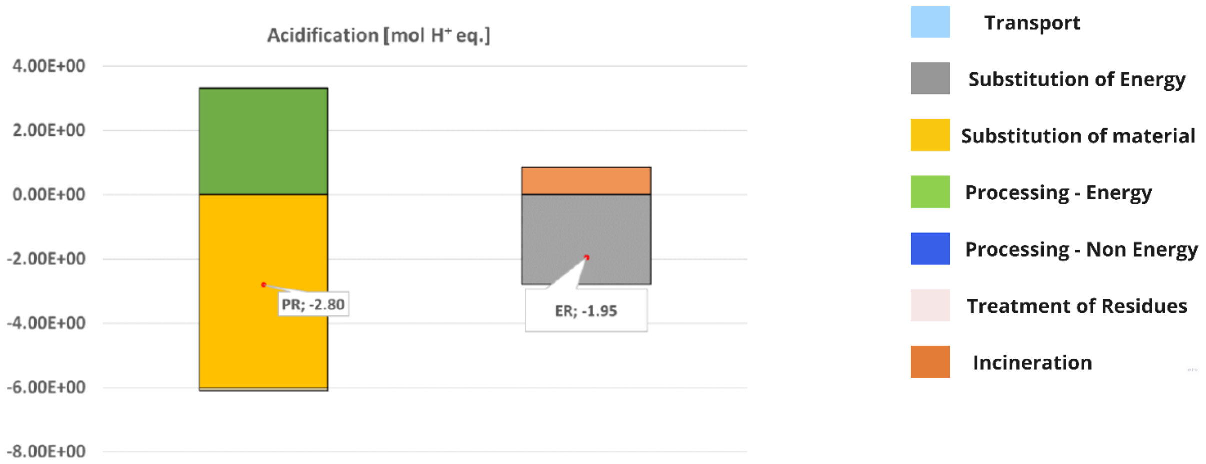


Figure 59: Comparison between physical recycling (PR) and incineration(ER) of 1 tonne of post-industrial PE/PA multilayer film waste – Acidification [4]

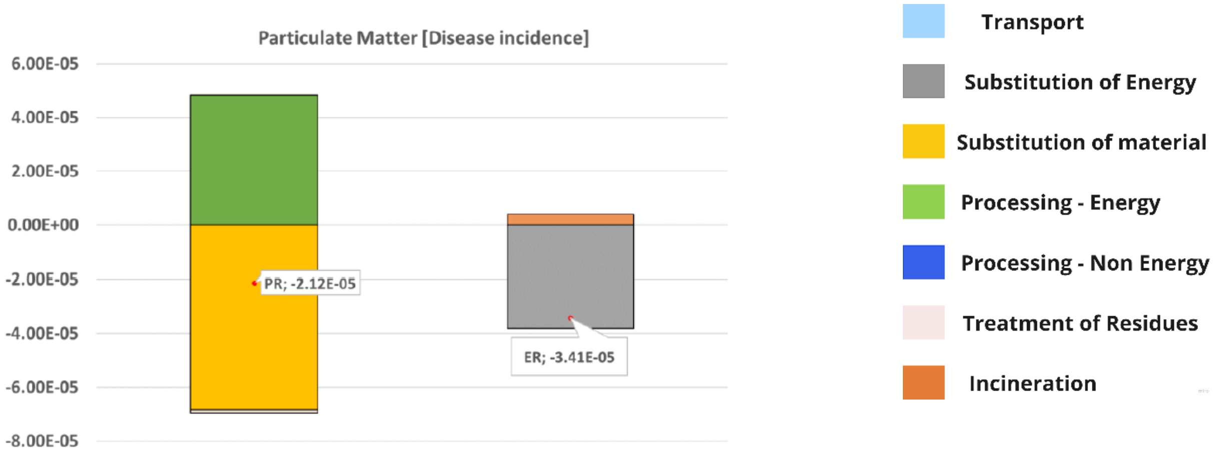


Figure 60: Comparison between physical recycling (PR) and incineration(ER) of 1 tonne of post-industrial PE/PA multilayer film waste – Particulate Matter [4]

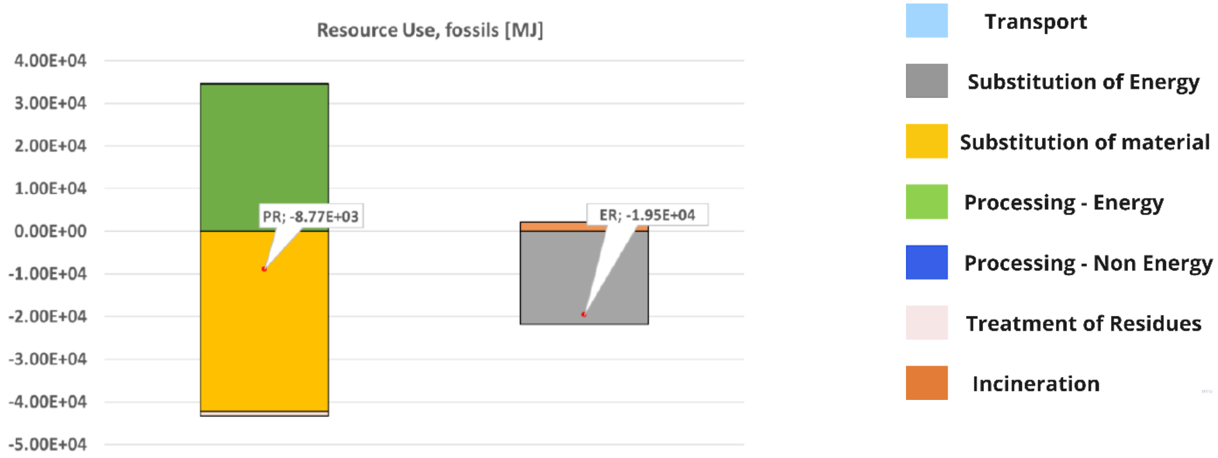


Figure 61: Comparison between physical recycling (PR) and incineration(ER) of 1 tonne of post-industrial PE/PA multilayer film waste – Resource Use [4]

Optimization of solvents/nom-solvents used can help reduce the overall environmental impact. For example, as mentioned above the use of supercritical CO_2 for the recovery of PMMA, PP, PE, PVC, and PET 93[1].

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8. Discussion

8.1 Pyrolysis

Despite this technology being commercially mature, it demands significant and sensitive optimization. After speaking to several experts in the field, it is clear that pyrolysis does not necessarily claim to use the residual stream from mechanical recyclers. However, they have higher tolerances towards contamination when compared to mechanical recycling. One of the experts in the field of chemical recycling mentioned that the pyrolysis process itself can be environmentally friendly but all these environmental gains are lost with the hydrogenation process that helps to make pyrolysis oil to a high quality. Experimenting with various combinations of reactors, catalysts and different blends of feedstock can help create a type of pyrolysis that is economically feasible/ profitable and environmentally friendly.

I believe that interesting partnerships like SPEAR (if done right) can create a middle ground for chemical and mechanical recycling. The combination of companies in this partnership would help develop the waste management system further in the future. In my opinion, this can also help in easier mass balance record keeping of the chemical recycling facility. The mechanical recycling facility could be considered as the pretreatment facility for the chemical recycling process. This pretreatment step not only seperate undesirable materials from the feedstock (like metals, stones, PVC) it would also remove mechanically recyclable plastic to produce non-food grade plastic. The remaining material in the feedstock, mostly multilayered packaging would enter the chemical recycling system. In other words, understanding carefully chosen the splitting of available feedstock can create a difference in the current doubts about chemical recycling entering the waste management sector. A company specialized in creating advanced equipment can constantly update sensors to monitor the composition of the feedstock heap. I believe that mechanical and chemical technologies should and can work together to close the loop for plastic with understanding that pyrolysis can only be a part of the solution for plastic waste, not the whole solution.

I would also argue that diesel and gasoline produced from pyrolytic oil should not be considered as a sustainable fuel source. After talking to an expert in a certification company, it was interesting to learn that the pyrolytic oils produced would have slightly different compositions. This points to the importance of feedstock specification. If companies are provided with the incentive to create sustainable fuel from plastic waste, this could lead to a large imbalance among the recyclers. Pyrolysis companies would want the best plastic waste feedstock for high-calorie fuel. Petrochemical companies would be happy to invest and help them acquire this ideal feedstock. Furthermore, both sources are fossil-based, the only difference is that virgin plastics have undergone some level of use phase before becoming fuel. In other words, it would be called advanced energy recovery.

8.2 Gasification

Opposite to pyrolysis, gasification is only widely used in treating biomass and other organic waste. I believe that the technology can become an advanced energy conversion process, a route for plastics that cannot be recycled mechanically or chemically. For it to become an advanced process, further optimization is required. Having analyzed the entire technology, I observed that the gaseous product (syngas) requires even more steps than pyrolysis to become polymers or chemicals from which plastics can be made. This contributes further negative environmental impact. On the other hand, it was interesting to see that in the current market, Synova offers a promising technology that combines pyrolysis and gasification.

In my judgment, I would not prefer the use of gasification as a recycling route for plastic. Despite the wide variety of plastics, it can process, it does not provide significant environmental gains when compared to the other technologies. In many LCAs with scenario evaluation, the technology showed little to no difference with incineration for heat.

However, the technology at the moment focuses on providing aviation fuel and there are big projects for the production of hydrogen. This could be a better allocation for the technology, reducing carbon emissions and also creating hydrogen from non-conventional sources. This is a different and innovative approach to reaching lower carbon emissions in the EU and creating a new fuel source, and this does align with the interests of the report. For this report, retaining all the carbon entering the system would count as recycling.

8.3 Solvolysis

This chemical recycling technology is very different from pyrolysis and gasification. I believe that being very specific with the input polymer can be an advantage as well as a disadvantage for the plastic waste problem. In my observation, the advantage would be the lack of competition with other chemical recycling technologies. After all, solvolysis considers polymers that are not favored by the previous chemical recycling technologies. The disadvantage would be the necessary inclusion of a good pre-treatment system to ensure the availability of clean and pure input streams for the system. Despite that, I believe that scaling up the process would help create a closed loop that is more polymer-specific instead of product-specific.

The conversion of monomer to polymer could increase the environmental impact compared to the dissolution process. I also observed that a lot of environmental impact assessments were regarding PET recycling and not PA, PC, or PU. This could be because the latter are available in smaller quantities in household waste. However, these polymers are more popular in the automotive and electronics industries. Change in consumer behavior in the recent decade has resulted in a rise in waste produced by these sectors. The constant need to keep up with the 'current trend' does increase the presence of more thermoset plastics that cannot be recycled in conventional ways. Another complication is the presence of flame retardants in plastics from those sectors. These impurities would dissolve into the solvent and catalyst that is used but retrieving them and treatment is a knowledge gap in the literature.

Overall, solvolysis can have a significant role in the recycling landscape. The technology could include PVC in its input feedstock, since it is a popular reject by pyrolysis and gasification.

8.4 Dissolution

I believe this technology has a wide potential for waste feedstock and can be used in combination with other chemical recycling technologies. When we consider processes like STRAP (as observed in 7.2 section), removal of EVOH from the waste stream and then using the PO-rich feedstock for pyrolysis can be the solution for closing the loop for multilayered or single-used food packaging. The same principle could be applied to the recycling of metal-polymer laminates by dissolving the polymers around the metal.

The major contributor to the environmental impact would be the solvent production and treatment for reuse. Other possible contributors will be treatment of contaminates from the solvent and disposal of the solvent. A possible alternative would be the use of natural solvents like D-limonene which is obtained from citrus fruits. One of the research questions that can be addressed would be: is it possible to use a more environmentally safe solvent/ non-solvent combination for the process? Neverthless, several sources state that dissolution still has lower environmental impact than pyrolysis and gasification, even after the inclusion of solvent production in the LCA.

Reading through the literature, I observed that the reuse of the solvent/non-solvent is possible but it does not mention how many cycles or times the same solvent/non-solvent can be used.

It is clear that feedstock composition is a very important aspect of the dissoltuion techniques as the solvent/non-solvent combination would vary according to the composition. This is a drawback when it comes to commercializing the technology. The feedstock entering the facility has to meet strict specifications and the rest of the feedstock would go out as residue. Again a process like STRAP would be able to solve a part of this problem by analyzing the feedstock and making the necessary combinations. Furthermore, there are discussions in which the technique is regarded more as a sorting technology and that it leaves purer feedstock streams for the other technologies.

Overall, in my opinion, dissolution can be the middle ground between chemical and mechanical recycling. But only if it operates under proper legislation, so that it does not engage in a societal useless competition with mechanical recycling as a subsidiary of the chemical recycling industy.

9. Conclusion

To conclude, of the 4 developing recycling technologies, I believe that dissolution has the highest potential to improve the recyclability of the feedstock that is currently hard to recycle. in my observation, dissolution is more flexible compared to pyrolysis and gasification. Although, solvolysis and dissolution are relatively similar, the output produced by dissolution requires fewer steps to produce a plastic product. This makes it a better option than solvolysis. During the thesis, dissolution will be studied further with chemical recycling company, Obbotec.

Table 25 provides an overview of all the technologies in the report. The scale considered here is provided in Figure 62. The level of allowable contamination in the feedstock is determined by feedstock sensitivity. Moreover, the quality of the product obtained from the process is relative to the quality of the feedstock entering the system. Here, it is assumed that the feedstock is relatively clean and pure, and that the target product are polymers.

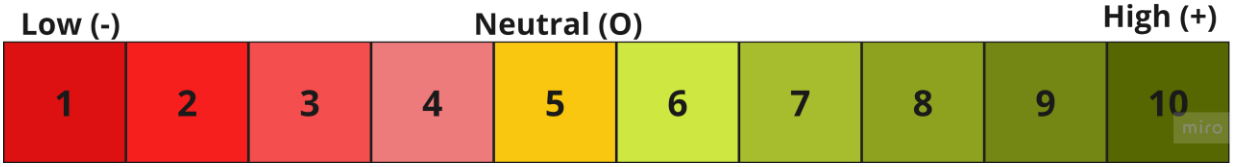

Figure 62: Scale

Characteristics	Pyrolysis	Gasification	Solvolysis	Dissolution
Range of treatable polymers	7-8	8-9	4-5	6-8
Types of Polymers	PO, PS, and very small quantities of PET and PVC	PO, PS, PA, PU, and small quantities of PET and PVC	PET, PLA, PC, PU and PA	Almost all types but with different solvents and catalyst
Multiple inputs in 1 cycle	8	9	3	5
Feedstock Sensitivity	4-5	2-3	7-8	3-4
Output	Naphtha/ fuel oil, wax, syngas	Syngas	Monomer, oligomers	Polymers
Quality of Output	7	5	8	9
Complexity of Technology	9	9	8	7-8
Cost	8	8	8	8
TRL	6-8	6-7	5-7	5-7

Table 25: Overview of all the technologies

Table 26, Table 27, and Table 28 gives an overview of the recycling effect the technology has on each polymer. Rigid plastics are considered to have additives while the flexibles are considered to be transparent (little to no additives present). +, O, and – are the weight indications.

Resource efficiency is the ability of the technology or technique to maximize the recovery of resources from the input feedstock. This would result in the minimized use of natural resources and energy.

Resource Efficiency (kg-product/kg-feedstock)

Polymer		Pyrolysis	Gasification	Solvolysis	Dissolution
LDPE	Rigid	O	+	-	+
	Film	+	+	-	+
HDPE	Rigid	O	+	-	+
PP	Rigid	O	+	-	+
	Film	+	+	-	+
PET		-	O	+	+
PVC		-	O	O	+
PS		O	+	O	+
PUR		-	O	+	+
Others	ABS, PC, PMMA, Nylon	-	O	+	+

Table 26: Resource Efficiency of the 4 Technologies based on polymers

Environmental Impact

Polymer		Pyrolysis	Gasification	Solvolysis	Dissolution
LDPE	Rigid	+	O	O	+
	Film	+	O	O	+
HDPE	Rigid	+	O	O	+
PP	Rigid	+	O	O	+
	Film	+	O	O	+
PET		-	O	+	+
PVC		-	O	O	+
PS		-	O	O	+
PUR		-	O	+	+
Others	ABS, PC, PMMA, Nylon	-	O	+	+

Table 27: Environmental Impact of the 4 Technologies based on polymers

Quality of Product

Polymer		Pyrolysis	Gasification	Solvolysis	Dissolution
LDPE	Rigid	+	+	+	O
	Film	+	+	+	O
HDPE	Rigid	+	+	+	O
PP	Rigid	+	+	+	O
	Film	+	+	+	O
PET		-	O	+	O
PVC		-	O	O	O
PS		O	+	O	O
PUR		-	O	O	O

Others	ABS, PC, PMMA, Nylon	-	-	+	O

Table 28: Quality of product of the 4 Technologies based on polymers

The efficiency at which the product is produced in dissolution is high but the quality of this product is still a topic under research.

Figure 63 provides the an overview of all the chemical and physical recycling companies existing in the Netherlands. The circled areas are hotspots for future chemical recycling development.

Figure 63: Chemical Recycling Landscape in the Netherlands

Appendix

A: Different reactors used for pyrolysis

1. Batch Reactor

Figure 64 provided is an example of a batch reactor using a stirrer. Inflow of feedstock (reactant) and outflow from the system only occurs before the reaction and after the reaction, respectively. It is a closed system and higher conversion rates can be obtained through longer reaction times. However, for consistent output quality it is important to ensure the reactants in each batch have the same specification. This reactor is suitable for small scale production [3][8].

This reactor has a simple design, low investment and controllable operating parameters. Reactions occur at a temperature range of 300-800°C. It is not preferred for a catalytic reaction due to the difficulty in separating the residue and catalyst in the end of the reaction [3][8].

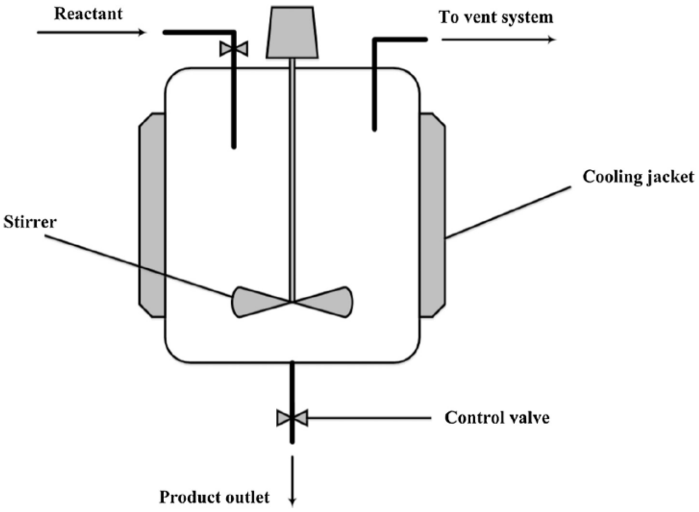

Figure 64: Example of a batch reactor [8]

2. Fluidized Bed

This type of reactor enables a continuous pyrolysis process at shorter durations of time. The fluidizing gases fluidize the particles increasing the heat and mass transfer rate. This reactor can be scaled up. Since the catalyst is placed on the distributor plate particles can have better access. The schematic diagram of the reactor is provided in Figure 65. The reaction in this reactor occurs at a temperature range of 290-850°C [3][6][8].

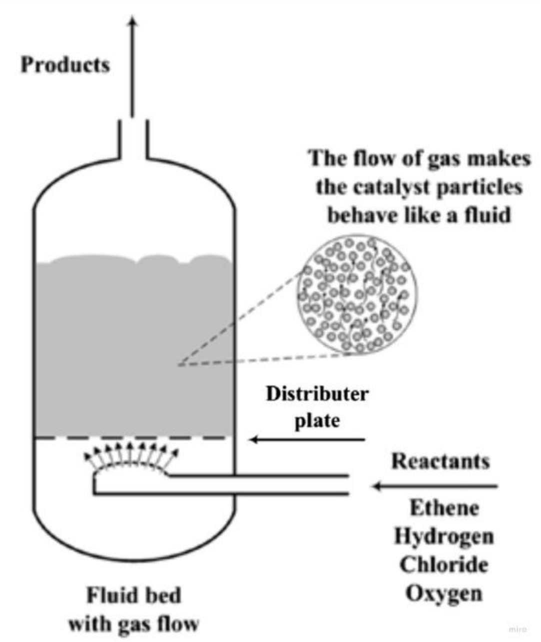

Figure 65: Schematic Diagram of Fluidized Bed Reactor[8]

3. Fixed Bed

Unlike fluidized bed reactor, the palletized catalyst provides limited contact area for particles since the reactor offers a static bed. This type of reactor is very often used in a two-step pyrolysis or two step gasifier operation. This reactor is a simple design but is difficult to commercialize. The reactor has inefficient temperature control. This reactor works at a temperature range of 400-800ºC. Figure 66 provides is a diagram of the reactor [3][6][8].

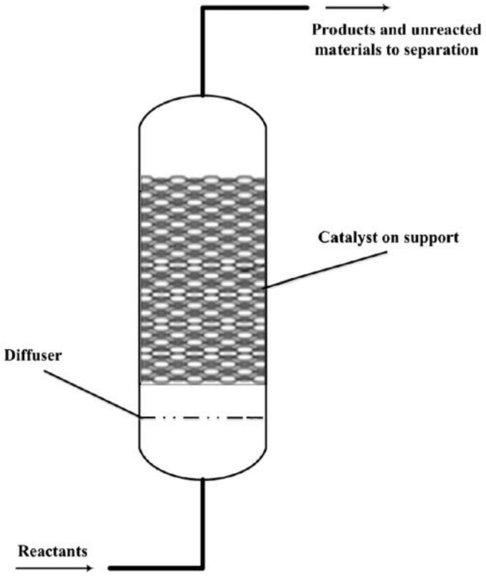

Figure 66: Fixed Bed Reactor [8]

4. Screw kiln

This reactor is also called as Auger kiln. As presented in Figure 67 a centered co-axial auger conveys the feedstock through the reactor. This enhances the particle mix and the heat transfer. This reactor enables good control of mass flow rate as well as less energy demand. This reactor is mostly used as pretreatment process and can be functioned at a temperature range of 200-520ºC. It is important to have proper maintenance to prevent breakdown from the continuous wear and tear of the auger [1][2][3][5][8].

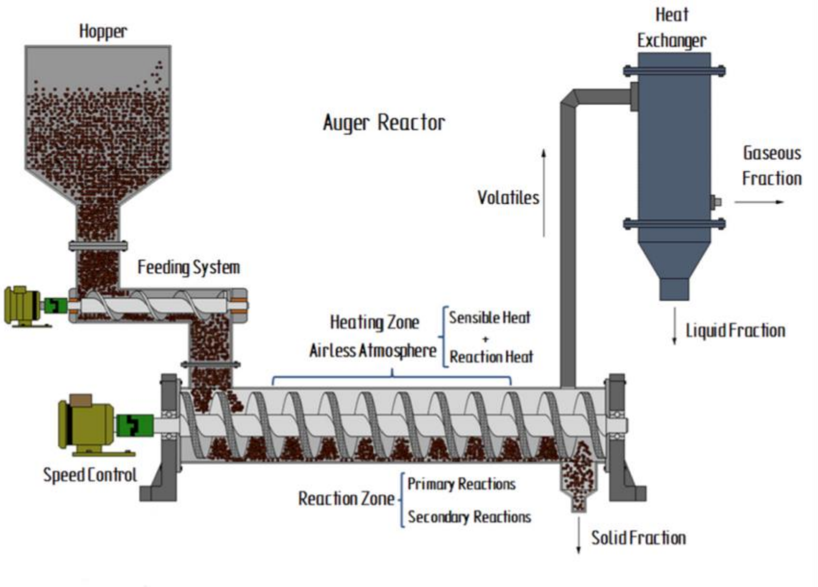

Figure 67: Pyrolysis process with auger reactor [2]

5. Rotary Kiln

This reactor is more robust and affordable. They are more popular for complex feedstock like waste tires and other industrial waste. Heat is supplied through external source to the walls of the reactor. This reactor creates low grade output and has limited operating parameters. Figure 68 provides a diagram of a rotary kiln, it is very similar in design to rotating drum to mechanical recycling [1][3][5][6][9] .

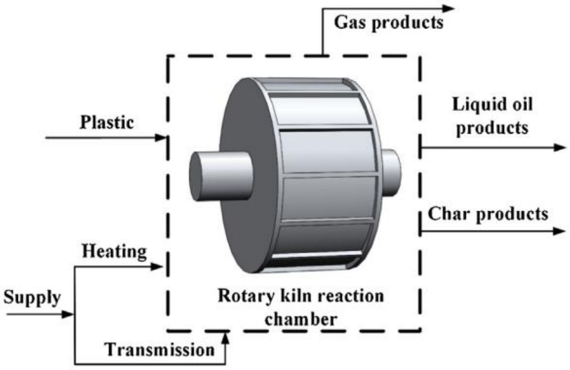

Figure 68: Rotary Kiln diagram [1]

6. Melting vessels or stirred tank reactors (STRs)

This reactor is used in the Smuda process in Poland and the Hitachi Zosen process. it is a continuous reactor used in the melt phase of the process. They have a relatively simple design. Heat is provided from an external source and there is a large stirrer to enhance mixing. Figure 69 provided is a diagram of the reactor. One of the main disadvantages of this reactor is the need for regular maintenance [5][7].

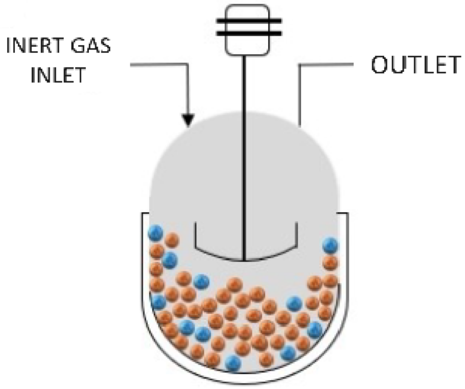

Figure 69: Diagram of STRs [4]

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