Current Trends in Waste Plastics' Liquefaction into Fuel Fraction: A Review

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Abstract: Polymers and plastics are crucial materials in many sectors of our economy, due to their numerous advantages. They also have some disadvantages, among the most important are problems with the recycling and disposal of used plastics. The recovery of waste plastics is increasing every year, but over 27% of plastics are landfilled. The rest is recycled, where, unfortunately, incineration is still the most common management method. From an economic perspective, waste management methods that lead to added-value products are most preferred—as in the case of material and chemical recycling. Since chemical recycling can be used for difficult wastes (poorly selected, contaminated), it seems to be the most effective way of managing these materials. Moreover, as a result of this kind of recycling, it is possible to obtain commercially valuable products, such as fractions for fuel composition and monomers for the reproduction of polymers. This review focuses on various liquefaction technologies as a prospective recycling method for three types of plastic waste: PE, PP and PS.

Keywords: plastic waste; liquefaction; fuels; quality standards

1. Introduction

Access to cheap energy carriers is crucial for the development of many sectors of the economy worldwide. The constantly growing demand for these carriers contributes to the depletion of the world’s oil, gas and coal resources. This growing demand is observed in both developed and developing countries. According to the International Energy Agency report [1], the world’s total consumption of crude oil was at 150.1, 169.3 and 153.5 exajoules, while natural gas consumption was 57.2, 69.7 and 68.2 exajoules, in 2010, 2019 and 2020, respectively. The recorded reduction in fuel consumption in 2020 was caused by the global COVID-19 pandemic. The increasing demand for energy carriers will entail an increase in the prices of these goods. According to the Report of U.S. Energy Information Administration (EIA) [2], the price of oil in November 2021 was 81 USD per barrel, while in the corresponding period of 2020 it was 43 USD. Over the course of 2021, oil prices increased due to the use of global oil reserves at an average of 1.4 million barrels per day. The successive coronavirus waves during the global pandemic situation have contributed greatly to the imbalance in the use and price of oil resources [3,4]. Despite the slowdown in global oil consumption due to concerns about other COVID-19 variants, the EIA predicts that prices per barrel will remain at a similar level as in 2021.

The growing demand for and rising prices of energy have led to a crisis in the fuel market and the search for substitute fossil fuel carriers. The second reason for replacing fossil fuels with raw materials from renewable sources is the global trend of decarbonizing economies [5]. The aim of decarbonization is to counteract severe climate change, including global warming [6]; as recommended by the Intergovernmental Panel on Climate Change, to avoid the aggravation of the negative effects of climate change, a temperature rise limit of 1.5 °C should be achieved [7].
One way of minimizing the effects of the energy and climate crisis is to, inter alia, move away from a linear economy (a vision called Cradle-to-Grave (CtG)), in which the last stage of a product’s life is waste, in favor of a circular economy (CE). The CE treats waste as a valuable raw material and is based on the Cradle-to-Cradle (CtC) model. It is a global strategy for sustainable development, which is assumed to be renovating or regenerative in nature [8]. It replaces the ‘end of life’ concept with the renovation/regeneration of the use process and moves towards the use of renewable energy. It aims to minimize the amount of generated waste, and products, materials and raw materials should remain in the economic cycle for as long as possible [9].

At present, we cannot imagine life without petroleum-based polymers and plastics. Their advantages, such as ease of shaping, non-toxicity, low density, non-conductivity, good mechanical strength or very high corrosion and acid resistance, means that these materials have become very common in the economy and people’s daily life [10]. The constantly growing demand for polymers has led to their continuous increase in production, which, in 2020, amounted to 367 million Mg worldwide [11]. Polymer-based materials are characterized by some disadvantages, such as a lower heat resistance, hardness and mechanical strength in comparison with metals. However, the most important drawbacks of these materials are their non-biodegradable, environmentally unfriendly and, in most cases, non-recyclable nature [12]. In many cases, the useful life of products made of plastic materials is very short, ranging from one day to three years [13]. After this time, they become waste, the decomposition time of which is disproportionately long and may last for up to 300–500 years, as is the case with a plastic bottle [14].

At present, many groups of polymers are known, but the category of large-volume polymers (mass-produced) includes: polyethylene (PE), sometimes differentiated into low-density (LDPE) and high-density (HDPE) material, polypropylene (PP), polyvinyl chloride (PVC), polystyrene (PS), polyethylene terephthalate (PET). These polymers are the main components of plastics, which also contain additives modifying the properties of the final material (e.g., dyes, stabilizers, flame retardants, foaming agents, fillers). In 2020, the largest end-use market of plastic materials was packaging (40.5%) and building/construction (20.4%) sectors. The third biggest market was the automotive industry sector (8.8%) [11].

Plastic waste (PW) mainly derives from industrial activities or consumer residue. Post-industrial PW is usually clean, free from organic or other contamination, and often monomaterial or its composition is well known. In turn, post-consumer PW most often contains different mixed plastics, the composition of which is unknown, and is contaminated with organic fractions or other materials (paper, metal, textiles) [15]. The largest share (over 61%–17.8 M t) is common packaging waste, such as plastic bags, foil, trays for packing and storing food, thermal dishes, cups and bottles for beverages. The share of individual plastics in the packaging waste stream is as follows: PE > PP > PET >> PS > PVC [16].

2. Plastic Waste Management

The problem with the management of plastics waste is already global, but the situation is improving every year. This is evidenced, inter alia, by the annual data published in the report of the Plastics Europe Foundation, which indicates that, in the European Union in 2020, compared to 2006, recycling of plastic waste increased by almost 118%, energy recovery through incineration increased by 77% and the amount of waste sent to landfills decreased by over 46% [11]. In 2020, over 29 million tonnes of post-consumer plastic waste were collected in European Union countries. Unfortunately, as much as 23.4% of them went to landfills, and only 34.6% was subjected to typical recycling. A total of 42% of collected waste was utilized through energy recovery through incineration (energy recycling) [11]. This form of recycling (in accordance with the principle of waste management hierarchy [17]) should only be used as a last resort for waste that is not suitable for other forms of recycling, such as depolymerization, material or chemical recycling. Sadly, the above data show that waste incineration is the most common and dominant form of PW management, which unfortunately leads to the complete elimination
of plastic material from the economy and makes it impossible to use this material in any other way. In addition, large amounts of harmful and toxic compounds are generated during incineration [18].

The still relatively low level of PW recycling (depolymerization, material and chemical recycling) results from the complexity of the processing methods, significant energy demand or/and unsatisfactory quality of the obtained products. The best method for managing plastics is their depolymerization to monomers (input ingredients for the production of plastics). However, this method is applicable, with good efficiency, to a few, selected polymers (polyethylene terephthalate, polymethyl methacrylate, polystyrene) [19–21]. In addition, the raw material must be clean and free from any additives of other materials. Unfortunately, this method cannot be applied to polyolefins, which accounts for approximately 70–76% of the waste plastic stream [22].

In the case of polyolefins, the best method for their management is material (mechanical) recycling to regranulate. This method is considered the most environmentally friendly due to the low value of CO$_2$ emissions compared to other methods [23], but it is not free from drawbacks. The feedstock for processing must be very well selected and clean, and unfortunately the material loses quality with each subsequent processing cycle. In addition, the use of different types of plastics on various parts of packaging (e.g., labels, caps, packaging) and the use of additives and fillers for plastics make it difficult to recycle and recover individual groups of materials and reduce the quality of the obtained final products [24,25]. Post-industrial plastics (such as cuttings and trimmings from production, runners from injection moulding or granulation residues) are best-suited for such recycling because they have a known and homogeneous composition and contain few impurities [26,27].

Regarding post-consumer PW, which is a complex mixture of different plastics and other materials, a sorting process should be carried out to obtain separate components should. Selected components, depending on their quality, can be mechanically recycled (for example, into outdoor furniture, flower pots, elements of terraces), directed to chemical recycling or sent to incineration [28]. However, due to the difficulty of completely separating the individual materials and contaminations of post-consumer waste, chemical recycling methods seem to be the most appropriate for their management [29]. Figure 1 shows a schematic diagram of the main directions of plastic waste management.

![Figure 1. The plastic waste management recycling technologies.](image-url)
this article focuses on a review of the methods of converting plastics to hydrocarbons, which could be used as components of liquid fuels. Figure 2 shows the main directions of the thermochemical conversion of polyolefins and polystyrene to hydrocarbons, most frequently encountered in the literature.

Figure 2. The main directions of thermochemical conversion of polyolefins and polystyrene to hydrocarbons.

3. Pyrolysis

One of the methods of converting waste plastics to hydrocarbon fractions is pyrolysis. This enables the transformation of high-molecular compounds, such as waste plastics, into compounds with much shorter carbon chains. It is considered a promising method for the conversion of addition polymers such as polyethylene and polypropylene (polyolefins) [31,32]. It offers the opportunity to recycle this polyolefin stream, which cannot be economically managed in conventional mechanical recycling, thus avoiding their incineration and the generation of hazardous substances such as dioxins and furans [33,34]. The pyrolysis oil (a mixture of waxes and a liquid fraction) obtained as a result of pyrolysis can be used as a substitute for heavy fuel oil or undergo further processing, e.g., in the petrochemical industry [35,36]. Furthermore, as shown in Reference [37], large-scale pyrolysis is economically viable. For example, in the case of an investment in installation that processes 100,000 kg/h of waste plastics, income is generated within the first year and has a positive net present value. The advantage of pyrolysis is that pre-segregated, mixed and contaminated plastic waste with both organic and inorganic material can be subjected to this process [38,39].

The pyrolysis process is based on the thermochemical decomposition of various materials of organic and synthetic origin at elevated temperatures and in an oxygen-free atmosphere. Typically, the process is carried out at temperatures in the range of 500–800 °C and, in the case of plastics, it follows four types of mechanism: end-chain scission or depolymerization, random-chain scission, chain stripping and cross-linking [40]. The main products of the pyrolysis process are pyrolysis oil, gaseous products and the solid fraction (char). On average, depending on the technology used, 45–50% of the oil fraction, 35–40% of the gaseous fraction and 10–20% of char is obtained in the process [41]. It was generally found that with the increase of the process temperature, the yield of the liquid fraction increases, while the yield of the solid fraction decreases [42]. However, for selected plastics (e.g., for PE over catalyst), it is possible to obtain a liquid fraction in an amount exceeding even 90% [43,44]. The high propensity of plastics to generate significant amounts of oil fraction during pyrolysis is the result of high volatile matter and low ash content in relation to other materials (e.g., biomass). These two parameters are the key factors influencing the pyrolysis oil yield [45].

Due to the process conditions (vapor residence time in the reactor, temperature, raw material heating rate), pyrolysis is divided into three types [46,47]:

- Slow pyrolysis—process temperature from 350 °C to 550 °C, heating rate from 1 to 10 °C/min, extended steam residence time, where char is the main product’s first bullet;
- Fast pyrolysis—the process temperature usually ranges from 500 °C to 700 °C, the raw material heating rate is above 100 °C/min, and the vapor residence time is usually within a few seconds; the main product is the liquid fraction, and in the case of polyolefin, pyrolysis also waxes;
- Flash pyrolysis—the process temperature usually exceeds 700 °C, the heating rate of the raw material >200 °C/s, and the vapor residence time is in the millisecond range.

In addition to the process time, pyrolysis can also be divided depending on other conditions of the process (e.g., presence of a catalyst, type of gas) or the type of supporting equipment [48].

The composition of pyrolysis oil depends not only on the process conditions, but also on the type of waste plastic in the raw material. A higher yield of aromatic hydrocarbons is obtained when PS and PET are pyrolyzed. On the other hand, PP and PE produces oil that is rich in paraffins, olefins and waxes based on aliphatic hydrocarbons. Wax is an intermediate product, mainly composed of long-chain hydrocarbons (C20+) with a high boiling point. In order to transform it into fuel products, it is necessary to separate it after pyrolysis and subject it to further cracking [46]. The pyrolysis oil also requires further processing (e.g., distillation, refining, hydrogenation) to improve its properties, due to the content of unsaturated hydrocarbons [49–51].

It should also be considered that even well-sorted waste for fuel production (PE, PP and PS) may contain contaminants in the form of other plastics, e.g., polyvinyl chloride (PVC). The presence of this plastic will result in the formation of chlorine compounds (including hydrogen chloride) during the recycling process. These compounds will have a corrosive effect on apparatus components and poison the catalyst [52]. Since the proportion of PVC admixture is generally low, in order to eliminate the harmful effect of chlorine, chlorine-binding compounds such as NaHCO₃, CaO, CaCO₃, Na₂CO₃, Ca(OH)₂ can be fed to the reactor with the feedstock [53].

Plastics, among the additives, may contain flame-retardant compounds. These additives are usually bromine or chlorine derivatives, e.g., chlorinated paraffins, boric acid; polybrominated diphenyl ethers, tetrabromobisphenol, tris(2-chloroethyl)phosphate, hexabromocyclohexane [54]. These compounds are generally not added to packaging, which has the largest share in the plastic waste stream, while they may be included in EPS waste from construction. The degradation of bromine compounds can lead to the formation of organo-bromine compounds and bromine hydrogen, whose action is similar to that of chlorine compounds. HBr can be disposed of in a manner analogous to hydrogen chloride. Another method to inactivate bromine compounds is the use of suitable catalysts during pyrolysis, e.g., metal oxides (e.g., ZnO, Fe₂O₃, La₂O₃, Cu₂O, Sb₂O₃, Al₂O₃, [55–57]), calcium and iron-based composites [58,59], zeolites, molecular sieves, red mud, or natural zeolites [15,60].

The reactor also plays an important role in the pyrolysis process [61]. The type of reactor used affects the process control, mass and heat exchange, mixing, liquid and gas phase flows, retention time, etc. There are many ways to classify pyrolysis reactors. According to the method of carrying out the process, there are batch reactors, semi-batch reactors and reactors with continuous flow. In turn, due to their construction, fixed bed, fluidized bed (bubbling and circulating) and conical spouted bed reactors (CSBR) can be distinguished, among others. Another criterion for the division may be, for example, the method of heat energy supply: to the interior via an inert gas or material, through the external walls via flue gas or electricity, or via internal heating elements [62–64]. Examples of studies focused on plastic waste pyrolysis using different reactors are shown in Table 1. The main advantages and disadvantages of pyrolysis reactors are presented in Table 2.
### Table 1. Examples of reactors for polymer pyrolysis.

| Type of Reactor      | Type of Feedstock Materials | References |
|----------------------|-----------------------------|-------------|
| Batch reactor        | PS, PE, PP and PET          | [15]        |
|                      | HDPE                        | [31]        |
|                      | Plastic medical wastes      | [65]        |
| Semi-batch reactor   | PS, HDPE, LDPE, PP          | [66]        |
|                      | PE                          | [67]        |
|                      | Polyolefin                  | [68]        |
| Continuous reactor   | Plastic waste from landfill | [69]        |
|                      | HDPE                        | [70]        |
| Fixed bed reactor    | PP, HDPE, LDPE              | [71,72]     |
|                      | HDPE                        | [73]        |
| Fluidized bed reactor| LDPE                        | [74]        |
|                      | PP, PE                      | [75]        |
|                      | PE                          | [76]        |
| CSBR                 | HDPE, LDPE, PP              | [77]        |
|                      | HDPE, LDPE, PP, PS, PET, PMMA| [78]        |
|                      | PE                          | [79]        |

### Table 2. The main advantages and disadvantages of pyrolysis reactors [33,45,62].

| Type of Reactor      | Advantages                                                                 | Disadvantages                                                                 |
|----------------------|---------------------------------------------------------------------------|--------------------------------------------------------------------------------|
| Batch reactor        | • High conversions of feedstock.                                          | • Variability of product from batch to batch;                                  |
|                      |                                                                           | • High labor costs per batch;                                                  |
|                      |                                                                           | • Problem with adoption for large-scale production.                           |
| Semi-batch reactor   | • Possibility of simultaneous addition of reagents and removal of the product; | • High labor costs per batch;                                                  |
|                      | • Flexibility of adding reactants over time.                              | • Problems with adoption for large-scale production.                          |
| Fixed-bed reactor    | • Simple and reliable construction.                                       | • Keeping the size and shape of the raw material particles relatively constant;|
|                      |                                                                           | • Limited accessibility of the catalyst surface area during the reaction;     |
|                      |                                                                           | • Low heating rate;                                                          |
|                      |                                                                           | • Non-uniform temperature inside the polymeric material.                     |
| Fluidized-bed reactor| • Better access to the catalyst than in the fixed-bed reactor;           | • Small particle size of the raw material;                                   |
|                      | • Large reaction surface;                                                 | • Problem with separating char from bed material;                            |
|                      | • Higher degree of cracking than in the fixed-bed reactor;                | • It is easy to defluidize bed when melted plastic sticks on it.              |
|                      | • Uniform temperature distribution;                                       |                                                                                 |
|                      | • Excellent mixing properties;                                            |                                                                                 |
|                      | • Better consistency of the process conditions;                           |                                                                                 |
|                      | • Less frequent loading of raw material and the associated process shutdown;|                                                                                 |
|                      | • Easy catalyst regeneration without unloading.                            |                                                                                 |
### Table 2. Cont.

| Type of Reactor                  | Advantages                                                                 | Disadvantages                                                                                   |
|----------------------------------|-----------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------|
| Rotary kiln reactor              | • More efficient in heating raw materials than a fixed-bed reactor;         | • Slow heating rate provides a significant amount of char to the products;                      |
|                                  | • Good mixing of raw material;                                              | • Mainly applicable to conventional pyrolysis.                                                   |
|                                  | • Yields uniform pyrolytic products;                                       |                                                                                                |
|                                  | • Possibility of adjusting the residence time;                             |                                                                                                |
|                                  | • Simple maintenance;                                                      |                                                                                                |
|                                  | • Possibility of feeding the raw material with different particle sizes.   |                                                                                                |
| Stirred tank reactor             | • Good temperature control;                                                | • Tendency to build up char deposits on the walls;                                               |
|                                  | • Easy to construct and operate;                                           | • Low conversion rate per volume;                                                               |
|                                  | • Uniform heat distribution.                                               | • Poor agitation;                                                                                |
|                                  |                                                                            | • Require frequent maintenance.                                                                |
| Conical spouted bed reactor      | • Good mixing;                                                             | • Problem with catalyst feeding;                                                                |
|                                  | • Possibility of using raw material with a large particle size distribution;| • Problem with catalyst entrainment;                                                            |
|                                  | • High heat transfer;                                                      | • Deposition of products on the catalyst;                                                       |
|                                  | • Protects against defluidization caused by melted plastic;                | • The reactor requires many pumps (high operating costs).                                       |
|                                  | • Relatively simple construction;                                          |                                                                                                |
|                                  | • Extremely short residence time of the polymers in reactor avoids secondary|                                                                                                |
|                                  |   reactions;                                                               |                                                                                                |
|                                  | • Lower pressure drop in comparison with other fluidized bed reactor.      |                                                                                                |

In general, regardless of the type of reactor that is used, the conventional pyrolysis of polyolefins produces a liquid product of poor quality, which is almost impossible to use as a fuel component. To overcome the problems associated with this type of pyrolysis, new technologies have been developed and are still being developed, that enable better-quality liquid products to obtained from the thermal conversion of waste plastics. In addition to conventional pyrolysis, the process can be carried out using catalysts, in a hydrogen atmosphere, as well as using microwave- and plasma-assisted processes, as shown in Figure 3.

![Figure 3. Pyrolytic methods of plastic conversion.](image-url)
3.1. Catalytic Pyrolysis

A catalyst is a substance whose presence in a mixture of reagents increases the reaction rate. It is involved in a chemical reaction, but is reconstituted during the process. Catalysts make it possible to lower the reaction temperature, speed it up and increase the selectivity of the product, and, therefore, have been widely used in industry and scientific research. Therefore, catalytic pyrolysis has an advantage over the conventional process and enables the production of a product with higher added value, such as hydrocarbons with a chain length (C8–C16) typical for jet fuel [80].

Catalysis can be carried out homogeneously (catalyst and reagents are in the same phases) or heterogeneously (catalyst and reactants are in different phases). Lewis acids, e.g., AlCl₃, TiCl₃, TiCl₄ and FeCl₃, as well as molten metal tetrachloroaluminates [M(AlCl₄)n], where (M = Li, Na, K, Mg, Ca or Ba; n = 1 or 2), can be used as homogeneous catalysts in the thermal decomposition of plastics [81,82]. However, due to the easier separation of the catalyst from the product, heterogeneous catalysis has found a much wider application in PW cracking. In the pyrolysis of plastics, nanocrystalline zeolites (HZSM-5, HUSY [84,85], HBeta [86] and HMOR [87]) are most often used as heterogeneous catalysts, but are also used as fluid catalytic cracking (FCC) catalysts [88–90] and silica-alumina catalysts [91]. Activated carbon (pure or impregnated with transition metals) can also be used as a catalyst for the process [92]. During the two-stage process of thermal and catalytic cracking, the life of the catalyst can be extended [93].

The use of a catalyst avoids waxes in the liquid product, but can also reduce the liquid fraction in favor of the gaseous fraction. For example, the authors of [94] investigated the thermal decomposition of PE and PP with and without a catalyst. The process was carried out in a batch reactor at a temperature of 450 °C. During pyrolysis without the PE catalyst, the main product was wax, at 80%. With PP, the main product was liquid in the amount of 85.5%. The use of the ultra-stable Y zeolite (USY) in the ratio 1:10 for both polymers resulted in a high yield of liquid products (PE—71%, PP—82%). The product of catalytic pyrolysis was a liquid mixture of hydrocarbons in the case of PE—C5–C39 compounds, and PP—C5–C30 compounds.

The use of a catalyst not only determines a better cracking of polymers and a lower reaction temperature, but also has an impact on the kind of compounds (naphthene, aromatics, paraffins) in the product. The authors of [95] investigated the influence of various catalysts (ZSM-5, USY, SBA-15 (SiO₂) -supported different metal catalysts) on the composition of HDPE pyrolysis products. They found that some metals (e.g., Cs, Co, Cu) in the metal/SBA-15 catalytic system do not favor the cracking processes, as the product has a high content of C23–C30 hydrocarbons (waxes, from 17% to 36%). Other metals in this system showed a higher cracking capacity of HDPE to C5–C12 hydrocarbons, such as the Al/SBA-15 catalyst (yield approx. 63%). However, aluminum showed a very high selectivity to aromatic compounds (over 45%). Zinc, on the other hand, resulted in a product with a relatively high content of short-chain hydrocarbons (approx. 41% of C5–C12) and low aromatics (4.1%). The zeolite catalysts studied by the authors (ZSM-5, USY), compared to the catalysts based on SBA-15, showed a high cracking efficiency towards C5–C12 hydrocarbons (approx. 90%), but the main components of the oil were aromatic hydrocarbons (over 80%). These hydrocarbons are not desired in such large amounts in the fuel fractions.

The research described in Reference [96] showed that the pyrolysis of plastics with the participation of the zeolite 5Fe/B-ZSM-5 catalyst leads to a product containing the highest amount of light hydrocarbons in the C5–C12 range; however, it has a significant predominance of aromatic compounds (76.9%). Similar results were obtained by the authors of [97]. The cause of olefin aromatization may be the strong acidity of the zeolites, which facilitates aromatization during the catalytic cracking of waxes due to the Diels–Alder reaction [95]. The number of works on catalytic pyrolysis is very high; Table 3 presents a list of selected research works in this area.
Table 3. Selected research works in the area of catalytic pyrolysis of plastic wastes.

| Material       | Catalyst                                      | Conditions                                      | Liquid Product                  | Reference |
|----------------|-----------------------------------------------|-------------------------------------------------|---------------------------------|-----------|
| PE             | Ultra-stable Y (USY) zeolite                  | Batch reactor Temparature 450 °C                | Yield 71%                       | [94]      |
|                |                                                | Polimer/catalyst ratio 10:1 Reaction time 50 min| C5–C39 compounds                |           |
| PP             | Ultra-stable Y (USY) zeolite                  | Batch reactor Temparature 450 °C                | Yield 82%                       | [94]      |
|                |                                                | Polimer/catalyst ratio 10:1 Reaction time 45 min| C5–C30 compounds                |           |
| LDPE           | Zeolite CAT-2                                 | Batch reactor Polimer/catalyst ratio 10:1       | Yield (-96% without catalyst: 24% C7–C12, 30% C13–C20, 46% C21–C40, 52% with catalyst: 100% C7–C12) | [98]      |
|                |                                                | Temparature 460 °C Nitrogen atmosphere          |                                 |           |
| PP             | Zeolite CAT-2                                 | Batch reactor Polimer/catalyst ratio 10:1       | Yield (-86% without catalyst: 44% C7–C12, 33% C13–C20, 23% C21–C40, 58% with catalyst: 100% C7–C12) | [98]      |
|                |                                                | Temparature 460 °C Nitrogen atmosphere          |                                 |           |
| HDPE, LDPE, and PP | Zeolite CAT-2                                 | Batch reactor Polimer/catalyst ratio 10:1       | Yield (for 34% PP and 66% PE):   | [98]      |
|                |                                                | Temparature 460 °C Nitrogen atmosphere          | -64% without catalyst: 36% C7–C12, 32% C13–C20, 32% C21–C40, 68% with catalyst: 100% C7–C12 | |           |
|                |                                                |                                                  | Yield (for 66% PP and 34% PE):   |           |
|                |                                                |                                                  | -84% without catalyst: 46% C7–C12, 31% C13–C20, 23% C21–C40, 63% with catalyst: 100% C7–C12 | |           |
| HDPE           | Y-zeolite impregnated with transition metal (Ni, Fe, Mo, Ga, Ru and Co) | Fixed bed reactor Two-stage process (pyrolysis/catalysis) Temperature both processes 600 °C Reaction time 30 min | Yield of oil: without catalyst—69% with Y-zeolite—45% with metal/Y-zeolite—below 40% Y-zeolite with and without metal causes greater production of aromatic hydrocarbons | [97]      |
| LDPE           | FCC catalyst silica alumina                    | Semi-batch pyrolysis reactor Fluidizing gas—nitrogen Amount of catalyst 5% Temperature 500 °C Reaction time 60 min | Yield of oil—93.5% where: C6–C9—20.7% C10–C15—64.7% C16–C19—12.2% >C20—2.4% | [91]      |
The authors of [91] for the decomposition of LDPE used a catalyst with a lower acidity (FCC catalyst silica alumina). They obtained light hydrocarbon fractions (C10–C15) with high efficiency (64.7%). GCMS analysis showed that the obtained oil contains similar compounds to diesel fuel (but with a significant number of alkenes), some aromatic hydrocarbons and over 4.5% oxygenated compounds. Blends containing from 20% to 80% pyrolysis oil and diesel fuel were tested in a four-stroke, single-cylinder DI diesel engine. The authors found that a blend containing 20% pyrolytic oil could be used as a diesel fuel without any engine modifications. Recently, works on the possibility of using liquid fractions from the conversion of plastic waste as a fuel component have become very common. These works concern the influence of such a fraction in fuel, e.g., on:

- Engine work (engine parameters, process of combustion) [99–101];
- Emissions, including LCA [102–107];
- Combability with fuel components [103,108,109].

The oils obtained in the process as a result of classical and catalytic pyrolysis contain unsaturated hydrocarbons, which are chemically unstable. For this reason, according to the authors of the article, many studies prematurely conclude that the oil fraction of plastics may be a component of conventional fuels. In most of the studies, the obtained fuel fractions were not hydrogenated (thus having poor stability) and/or were not tested for compliance with fuel standards. To use such fractions as fuel components, they must be hydrogenated, and the fuel mixtures are tested for all standard parameters [110,111]. Hydrogenation can be accomplished by:

- Classical hydrogenation;
- Hydro-pyrolysis (as well as hydrocracking and hydrogenolysis).

3.2. Stabilization of Pyrolysis Oil with Hydrogen

Classical hydrogenation is carried out in a hydrogen atmosphere, under high pressure and in the presence of the catalyst [112–114]. Due to their high costs, most installations are located on the premises of re-refineries. The process consists of saturation with multiple hydrogen bonds between carbon atoms. In turn, the hydro-pyrolysis of plastics is a thermal decomposition carried out under a hydrogen atmosphere where, apart from the hydrogenation of multiple bonds, a single bond is broken between carbon atoms and hydrogenation with the participation of a metallic catalyst (monofunctional) takes place. A variation in the process is hydrocracking, where a bifunctional metal or acid catalyst is used [115]. These reactions can be performed without or in the presence of solvent as a liquid phase promoting heat and mass exchange. For example, research on HDPE conversion using hydrogenolysis was carried out in Reference [116]. The process was carried out at a temperature of 220 °C, under a hydrogen pressure of 0–60 bar, with the Ru/C catalyst, in different solvents. Within an hour of the process, under 30 bar and in the presence of n-hexane, approx. 92% efficiency of the liquid fraction was obtained (60.8% jet-fuel and 31.6% lubricant-range hydrocarbons). In turn, in Reference [117], LDPE conversion studies were carried out without the presence of a solvent. The process was carried out at a temperature of 200 °C, at a pressure of 20 bar of H2 and in the presence of a Ru/C catalyst. After 16 h of reaction, the n-alkanes were obtained in a yield of up to 45%. The authors of [118] studied the catalytic depolymerization of PP, in the presence of a Ru/C catalyst, in the absence of solvent. The process was carried out at 200–250 °C, with a hydrogen pressure of 20–50 bar. The investigated catalyst was found to be effective in the conversion of PP to C5–C32 liquid hydrocarbons with an efficiency of about 68%. As in the case of catalytic pyrolysis, in hydrogenolysis, the type of catalyst affects the reaction efficiency and the yields of individual hydrocarbon fractions [119–121]. It should be mentioned that the hydrogenolysis process of waste plastics can be used to produce not only liquid fuels, but also gaseous fuels, such as methane [122].

Due to the high cost of hydrogen, which is the main barrier to its use in the process, other hydrogenation methods are being sought. One of them is the use of tandem catalysis,
which uses two or more different catalysts coupled together. Hydrogenolysis conducted under such conditions speeds up polymer conversions compared to a monofunctional process [123]. In tandem catalysis, the metal/acid system catalysts are used. The acid catalyst is responsible for breaking bonds between carbon atoms, while the metal catalyst is responsible for the hydrogenation and minimization of catalyst coking. Therefore, the synergy of catalysts is one of the factors determining the high yields of the liquid fraction. Such studies were carried out in Reference [124], where chain and branched liquid alkanes were obtained from LDPE with a yield of up to 85% in temperature ca. 250 °C, in 2 h. The process was carried out under hydrogen atmosphere (pressure 30 bar), using Pt/WO₃/ZrO₂ and HY zeolite as catalysts.

Another example of this process is the tandem hydrogenolysis/aromatization, where, during aromatization, hydrogen is generated, which is then used in the hydrogenolysis process [125,126]. This reaction can then be carried out in a single reactor without solvent and hydrogen. For example, tandem hydrogenolysis/aromatization of PE leads to alkylaromatics and alkynaphthenes [127].

An innovative approach to the conversion of PW and hydration of the liquid fraction is the technology developed by Handerek Technology [128]. The polyolefin thermolysis process is carried out in a reactor, operating on the principle of reactive distillation, filled with Raschig rings. The process is not isothermal; the temperature varies along the axis of the reactor in the range of 360–450 °C. Gravity moves the plastic down the reactor, where it thermally decomposes. In the final step, the resulting product vapor is hydrogenated at a temperature above 320 °C under atmospheric pressure. The reaction gas in both processes is syngas. The mixture of waste plastics (PE and PE) was subjected to liquefaction and hydrogenation. From the 6 kg of waste plastics, six liters of liquid product (with boiling points below 360 °C) and 0.1 kg of solid phase (char) were received; the rest were gases. The liquid fraction from the thermolysis process contained 40.6% saturated compounds, 59.4% unsaturated compounds (49.1% alkenes, 8.4% alkynes and 1.9% aromatic compounds). Hydrogenation of this fraction resulted in a significant increase in the content of saturated compounds (to 83.5%) and a decrease in the content of unsaturated compounds (to 16.5%). The solid fraction contains char and mineral impurities that were introduced into the installation together with the raw material, and it may be used as a solid fuel. The gaseous fraction consists of combustible compounds (e.g., methane, ethane) and can be used as a heat carrier to the reactor or as a substrate for the production of syngas. Thus, the process becomes self-sufficient.

The authors have shown that this technology is very effective due to the use of a novel reactor solution, operating on the principle of reactive distillation (under non-isothermal conditions). This made it possible to obtain a stable light liquid product, containing no waxes (without using a catalyst). The studies also showed that it is possible to conduct hydrogenation with syngas under atmospheric pressure.

### 3.3. Microwave Pyrolysis

The thermal energy needed for the degradation of polyolefins in the pyrolysis process can be delivered by microwave radiation. Compared to conventional electrical heating, where temperature distribution and heat transfer are carried out by convection, radiation and conduction, the microwaves pass through the heated particle of the material and are converted into thermal energy inside it [129]. For this reason, microwave heating is faster, runs throughout the entire volume of the heated material and is a non-contact process [130,131]. Materials subjected to microwave pyrolysis are characterised by their differing susceptibility to radiation; therefore, this process is used in the case of materials that absorb radiation. Plastics have low dielectric constants; therefore, a special microwave absorbent (e.g., silicon dioxide, activated carbon, graphene) was added to the microwave pyrolysis process. This absorbent reduces the pretreatment before pyrolysis and the process time, improves the heating efficiency and increases the efficiency of the process [132,133]. The efficiency of the process can be additionally increased by adding metal (e.g., copper,
iron, aluminum) [134,135]. Another way of increasing the process efficiency is to use different types of carbon materials as susceptors. These materials absorb electromagnetic energy and convert it into thermal energy [136]. It should be mentioned that, in this method, polymers are usually introduced without cleaning to facilitate the absorption of microwaves, since dust, moisture and debris help absorb microwaves.

Due to its many advantages, the microwave-assisted process is the subject of much research. The work available in the literature relates to [137–140]:

- The general principles of microwave pyrolysis;
- The influence of parameters on the process efficiency (e.g., microwave power, time and temperature, type of material (absorber, reactor, catalyst));
- Co-pyrolysis possibilities;
- Kinetic models of the process;
- The properties of the obtained products (fractions).

In Reference [141], the authors conducted research on the ex situ catalytic upgrading (with MgO) of oil vapors from the microwave pyrolysis process of the low-density polyethylene. The ex situ catalytic upgrading of vapors resulted in a lower yield of liquid fraction in comparison with the non-catalytic process. The main product was gasoline fraction, which contained up to 96% of the hydrocarbons. This fraction consists of appropriately 40% aromatic and 60% aliphatic hydrocarbons, while the fraction obtained during the process without a catalyst contained 10% aromatic and 30% aliphatic hydrocarbons. Similar results were obtained in Reference [142], where the microwave pyrolysis process of LDPE was carried out with the use of the ZSM-5 catalyst. About 88% of the gasoline fraction (containing valuable aromatic hydrocarbons) and the gas fraction containing ethylene, ethane and hydrogen were obtained. Based on this research, it was found that the highest efficiency of the liquid fraction was obtained at a temperature of 450 °C and the reagent to catalyst ratio of 2, while the gas fraction was obtained at the temperature of 375 °C and the reagent to catalyst ratio of 4.68. The higher temperature and the higher ratio of the reactants to the catalyst favored the formation of a large number of monocyclic aromatic hydrocarbons. Conversely, maintaining a high temperature with a low reagent-to-catalyst ratio resulted in the formation of polycyclic hydrocarbons.

The above studies focused on the microwave pyrolysis of only one of the polyolefins. In other works, scientists researched the microwave pyrolysis of various types of plastic mixture, including the plastic fraction of waste from electric and electronic equipment [134,143,144]. For example, in Reference [145], the research material was a mixture of plastics waste (from industrial sorting plants and household activities) and carbon black, which, as a dielectric, increased the temperature of the microwave pyrolysis process. There are also some papers on the co-pyrolysis of plastics with biomass mixtures [146–148] or waste oils from cooking [149]. Table 4 presents an overview of the work on microwave pyrolysis and the co-pyrolysis of various types of plastic. As the data in the table show, the process can be carried out for different types of waste plastics and their mixtures with, e.g., biomass. Depending on the type of raw material, process conditions (power, temperature, time), type of catalyst and susceptor, the process efficiency varies. However, according to the research, it is possible to obtain liquid hydrocarbons, which can be used to produce fuel components. The microwave pyrolysis technology is not widespread and still requires a lot of research [134]. Reference [150] showed that the cost of producing oil from the pyrolysis process, which can be a component of or substitute for fossil fuel, is cheaper than diesel oil. For this reason, this technology should be developed and applied on an industrial scale.
Table 4. Comparison of research works on the conversion of various types of plastic into hydrocarbon fractions using microwave pyrolysis and co-pyrolysis.

| Type of Plastic/Material | Type of Catalyst/Absorber | Process Parameters | Pyrolysis Oil Yield (%) | Oil Composition | Reference |
|------------------------|--------------------------|--------------------|--------------------------|-----------------|-----------|
| HDPE                   | AC, molecular sieves     | HDPE to AC ratio from 100:60 to 100:330, heating power combinations (20–40% of the maximum power of 900 W) | 87.8          | 82.4% C7 and C20 | [151]    |
| LLDPE                  | HZSM-5                   | Catalyst to feedstock 5–20%, catalytic temperature 550 and 500 °C | 84.1%         | 98.0% gasoline-range hydrocarbons (70.4–72.3% mono-aromatics) | [152]    |
| LDPE                   | ZSM-5                    | Pyrolysis temperature 480 °C, catalytic temperature 250–500 °C, ZSM-5 to plastic ratio from 1:4.68 to 1:1.32, time 10 min, power 0.7 kW, N₂ gas | 24.4–32.6 | >94% aromatics; 74.7–88.5% C8–C12 MAHs | [142]    |
| HDPE                   | AC                       | Pyrolysis temperature 400–600 °C | 27.3–54.9 | >90% for C ≤ 21, ~45–58% normal aliphatics; ~35–45% aromatics | [153]    |
| LDPE                   | Silicone carbide, MgO    | Pyrolysis and catalytic temperature 350–550 °C, MgO to plastic ratio from 1:15 to 1:3, plastic to absorber ratio 0.03:1, time 20 min, vacuum | 24.2–38.5 | 79.5–96.0% gasoline fraction; ~15–50% MAHs | [141]    |
| PS                     | Carbon, silicon carbide  | Time 28 min, temperature 574 °C, pressure N₂ flux, power 3 kW, PS to absorber ratio 0.03:1, time 20 min, vacuum | 94.3          | 40.5–71.9% styrene, 5.9–18.4% α-methylstyrene, 6.2–10.9% toluene | [154]    |
| Waste PS               | Tire, carbonaceous char  | Power 1.2–6.0 kW, PS to carbon ratio 2.0–0.5, reaction time 13–82 min, temperature 364–578 °C, anoxic | 86.5          | 93.9% single-ring aromatic compounds (C₆–C₁₀), 66.0% styrene | [155]    |
| Waste: PS, PP, PS + PP | Carbon, AC               | Power 0.18–0.9 kW, polymer to an absorber ratio 10:0.5–10:2, time 10–20 min | 83.3–86.1 | 67.6% styrene | [144]    |
| LDPE                   | NiO, zeolite HY, silicon carbide | LDPE to HY ratio 20:1, 15:1, 10:1, 5:1, pyrolysis temperatures 450–600 °C, catalysis temperatures 350–500 °C, HY to NiO 15:1, 10:1, 5:1, 3:1, time 20 min, power 1.8 kW, vacuum | 56.5          | >92% C₅–C₁₂ gasoline fraction; 34.6–46.6% aromatics; 26–30% isomerized aliphatics | [132]    |
| LDPE                   | ZSM-5                    | Pyrolysis and catalytic temperature 375 °C, ZSM-5 to plastic ratio 1:10 | 64.4          | 97% C₈–C₁₆ aromatics | [156]    |
| LDPE, torrefied rice straw | ZSM-5                  | Temperature 309–590 °C, ratio catalyst to feedstock from 3.9% to 11.04% | 24.5–29.8 | ~80% gasoline fraction; 26.5–40.2% long-chain hydrocarbons and cyclic hydrocarbons | [147]    |
| Corn derived plastic bags | Iron powder, carbon powder | Power 1.2–3 kW, temperature 617–808 K, plastic bags to absorber ratio 2.02–2.39 | 28.4–47.5 | Mainly oxygen compounds, 9.6–13.3% aromatic hydrocarbons, 2.2–7.1% aliphatic hydrocarbons | [157]    |
| Type of Plastic/Material | Type of Catalyst/Absorber | Process Parameters | Pyrolysis Oil Yield (%) | Oil Composition | Reference |
|--------------------------|----------------------------|--------------------|-------------------------|----------------|-----------|
| HDPE                     | AC, molecular sieves       | HDPE to AC ratio from 100:60 to 100:330, heating power combinations (20–40% of the maximum power of 900 W) | 87.8 | 82.4% C7–C20 | [151] |
| LDPE                     | Chestnut shell (CNSACC)    | Carbonization temperature 850 °C, catalytic temperature 550 °C, CNSACC to LDPE ratio 1.0 | - | 95.9% aromatics | [158] |
| PP                       | Talk, ZSM-5               | Pyrolysis temperature 620 °C | 48.9 | 73.5% gasoline fraction (45.0% aromatic hydrocarbons and 24.6% isomerized aliphatic) | [70] |
| Wastes PS                | AC                         | Power 450 W, PS to AC ratio 10.0:5–10:3, temperature 500 °C, time 5.5 min | 80.7–93.0 | 26.8% benzene derivatives, 23.2% condensed ring aromatics, 8.4% alkenes | [159] |
| LDPE                     | AC, zeolite catalyst       | Atmospheric pressure, temperature 300–550 °C, time 45–90 min, plastic to absorber ratio 1:1, catalyst to plastic ratio 1:1, N₂ gas | 28.1 | 19.0% hydrocarbons | [160] |
| Plastic waste from WEEE | Carbon, iron              | Power 3 kW, in a nitrogen environment, plastic to absorber ratio 2:1, temperature 386–450 °C, time 30–60 min, N₂ gas | 76.6 | 117.7 mg/mL of styrene and 25.6 mg/mL of xylene | [143] |
| HDPE, PP                 | Chopped tire, carbon       | Power 1.2–6 kW, time 33–260 min, temperature 702–872 K, plastic to absorber ratio from 0.5:1 to 2.5:1 | 27.6–83.9 | <88.4% aliphatic hydrocarbons, <20.32% aromatic hydrocarbons | [161] |
| HDPE                     | Carbon, silicon carbide    | Temperature 400–550 °C, absorbent to HDPE ratio 10:1 and 3.3:1, power 3–5 kW, time 60–100 min, N₂ gas | 34.7–73.4 | C8–C35 | [162] |
| PS, PP, LDPE             | Iron                       | Power 500–2500 W, temperature 250–800 °C, time 19 min | 28.1–88.7 | Aromatic and aliphatic hydrocarbons (C8–C16) | [163] |
| LDPE, lignin             | HZSM-5, MgO, silicon carbide | Power of 750 W, pyrolysis temperature 450–600 °C, lignin to LDPE ratio (only lignin, 3:1, 2:1, 1:1, 1:2 and only LDPE), MgO to HZSM-5 ratio (only MgO, 1:2, 1:1, 2:1 and only HZSM-5), feedstock to catalyst ratio (only feedstock, 1:2, 1:1 and 2:1), vacuum | 22.8–38.5 | ~30–85% aromatic compounds, ~15–55% phenolic compounds | [164] |
| Waste cooking oil (WCO), waste polyolefins (WP) | AC                         | Power 800 W, WP to WCO ratio 1:2, 1:5, 1:1, 1:5:1, 2:1, time 20 min, temperature <450 °C, N₂ gas, vacuum | 24.0–62.0 | 50% C13–C24 hydrocarbons | [165] |
| Wheat straw, rice husk, expanded PS, waste PP | Graphite                   | Power of 600 W, biomass to plastic ratio 1:1, temperature 450 °C, N₂ gas, | 51.5–64.9 | 50.5–93.7% aromatic hydrocarbons, <27.1% cycloalkanes and alkanes | [166] |

AC—activated carbon, MAHs—monocyclic aromatic hydrocarbons, WEEE—plastic fraction of waste from electric and electronic equipment.
3.4. Plasma Pyrolysis

The pyrolysis process can also be plasma-assisted [167,168]. In plasma pyrolysis, the necessary energy for the process is provided by the thermal or electric current and electromagnetic radiations [169]. Compared to conventional and microwave pyrolysis, plasma pyrolysis is characterized by a higher energy density and temperature (that is better controlled), better reaction kinetics, greater energy efficiency and lower CO₂ gas emissions to the environment (not the combustion of conventional fuel during the process) [170,171]. Despite its many advantages, this technology also has disadvantages, such as a low TRL and high energy demand [115].

Depending on the gas temperature, plasma pyrolysis can be [172,173]:

- High-temperature (thermal), where electrons, ions and particles are in thermodynamic equilibrium and have the same temperature, at approx. 10⁶–10⁸ °C; this is method used to obtain mainly gaseous products;
- Cold (non-thermal) electrons, ions and particles are not in thermodynamic equilibrium and have different temperatures of approx. 10⁴–10⁶ °C, while the gas is at room temperature).

This process may be used for biomass [174,175] and municipal waste (including plastic [171,176] and rubber [177] wastes) conversion. Due to the very high energy demand, for economic reasons, this process is mainly used to neutralise hazardous medical waste at the larger scale [178–180]. Despite its drawbacks, this process is being studied. Due to its high temperature, during the processing of plastics by plasma pyrolysis, energy from these materials is mainly recovered in the form of synthesis gas [181,182]. This gas can be used to generate the necessary electricity to power plasma devices, which reduces its consumption [181,183]. The synthesis gas mainly consists of carbon monoxide and hydrogen and may be used for fuel production (such as methanol, diesel oil) [183,184] or hydrogen extraction [171].

Plasma pyrolysis technology is approx. 28–60% more expensive compared to energy recovery technology by waste incineration [185]. For this reason, the available literature focuses on the search for and optimization of economically and energy-efficient technologies for the plasma pyrolysis of plastics, including the selection of the following systems: plasma generator (torch), reactor, plasma working gas [186]. In Reference [187], research was carried out on the processing of plastic waste (PP, PE, PVC, Acrylonitrile Butadiene Styrene (ABS)) into hydrogen, using the developed twin DC thermal plasma torch. It was found that the concentration of hydrogen in the resulting gaseous product ranged from 0.75% (PE) to 70.5% (ABS), while the concentration of CₓHᵧ ranged from 21.9% (PVC) to 46.3% (PE). The results are consistent with the results obtained in [188], where a gas containing up to 75% of hydrogen in the process from plastic waste (PP, PE, PVC, ABS) was obtained.

In Reference [189], research on LDPE conversion was carried out using plasma pyrolysis at the temperature of 625–860 °C. It was shown that the use of direct current thermal plasma circuit in the process allows for a liquid fraction with an efficiency of approx. 57% to be obtained (where the major product was butyl-benzene), and approx. 37% of the gaseous fraction. The process produces up to 6% of tar, and the obtained products are more stable compared to conventional pyrolysis.

In Reference [172] the cold plasma technology for the thermal decomposition of HDPE, PP, PET and their mixtures was used. The tests were carried out with the use of various catalysts (zeolites, sulphated zirconia, Ni/Al₂O₃, char derived from the pyrolysis of biomass), in nitrogen atmosphere, at the temperature of 500–700 °C. The cold plasma pyrolysis with thermal and catalytic pyrolysis were compared. It was found that, during thermal pyrolysis HDPE, carried out at the temperature of 500 °C, the highest amount of liquid fraction was obtained (in which 92% were mainly C₂₀⁺ and C₁₂–C₂₀ hydrocarbons). With the increase in the process temperature, as well as with the addition of the catalyst, the amount of the gaseous fraction significantly increased at the expense of the liquid fraction (approx. 40% of the liquid fraction at 700 °C and approx. 25% with the catalyst
at 600 °C). Conducting the cold plasma pyrolysis reaction provided an indirect share of the liquid fraction compared to the thermal and catalytic processes. The plasma process can be applied not only to classical pyrolysis, but also to hydrogenolysis. These studies were carried out by the authors of the paper [190]. The thermal decomposition of HDPE by non-thermal plasma-assisted hydrogenolysis was studied in the presence of 5% catalyst (Pt/C and SAPO), at plasma power 60–90 W and hydrogen partial pressure 0–101 kPa. The results showed that it is possible to obtain light alkanes (mainly CH₄, C₂H₆ and C₃H₈) with 95% selectivity.

The technologies discussed above, used to convert PW to hydrocarbons, have various advantages and disadvantages (Table 5), and research is still being conducted to improve them.

Table 5. The main advantages and disadvantages of technologies used to convert PW to hydrocarbons.

| Process                     | Drawback                                                                 | Advantage                                                  |
|-----------------------------|--------------------------------------------------------------------------|------------------------------------------------------------|
| Conventional pyrolysis      | • Very broad product range.                                               | • Lower sensitivity to contamination with other materials. |
|                             | • High temperature required;                                             |                                                            |
|                             | • High content of waxes.                                                 |                                                            |
| Microwave-assisted pyrolysis| • Low microwave absorption and conductivity of PW;                        | • More even heat distribution in liquids;                   |
|                             | • Necessity of using susceptors.                                         | • Heat runs throughout the entire volume of material.      |
| Plasma-assisted pyrolysis   | • Low TRL;                                                               | • High energy density;                                     |
|                             | • Very high energy demand;                                               | • Better reaction kinetics and greater energy efficiency   |
|                             | • High costs.                                                            | than conventional pyrolysis.                               |
| Catalytical cracking         | • Difficulty in recovering the catalyst after use;                       | • Reduction in the reaction temperature;                   |
|                             | • Increased operating costs;                                             | • Promotion of decomposition reaction;                     |
|                             | • Quick deactivation of the catalyst due to the deposition of carbon     | • Improvement in the product quality.                      |
|                             |   matter and poisoning with elements (chlorine, sulfur).                 |                                                            |
| Hydrogenolysis              | • Difficulty in recovering the catalyst after use;                       | • Very good quality of liquid product;                     |
|                             | • Increased operating costs;                                             | • Reduction in the reaction temperature.                   |
|                             | • High pressure.                                                         |                                                            |

4. Patents Review

Patents are also an important source of information on the methods and technologies used to convert plastic waste into energy carriers. Patents often illustrate the latest technical and technological solutions within a given field of knowledge. In this review, the authors focused on patents from recent years related to the liquefaction of polyolefins and polystyrene. The number of patents on this subject is quite significant and varies from year to year depending on interest. For example, in 2009, fewer than 10 patents were granted related to polyolefin recycling, and, in 2011, 30 were granted [26]. The analysis of patents shows that this topic is still very popular among researchers and inventors. The frequent disadvantages of many solutions are the manual loading of the feed into the reactor, or solutions that significantly impede the transition to a continuous process, which is often a condition for industrial implementation. Other disadvantages include poor heat transfer in the waste raw material itself, low conversion efficiencies, the incorporation of multiple steps, and the cost and contamination of consuming catalysts [191].

Often, patents state that the end product is fuels. As is well known, commercial fuels contain only insignificant amounts of unsaturated hydrocarbons, and the thermal
decomposition products of polymers contain a lot of alkenes. Without the hydrogenation process, the use of such products as fuels is not possible. Therefore, it would be more correct to write that plastic waste is converted into hydrocarbon fractions. Below, the authors describe a few selected patents; a comparison of them is presented in Table 6.

The patent application [192] describes the multi-stage conversion of plastic waste into hydrocarbon fractions. PW melting and decomposition processes are carried out separately. The molten material is pyrolyzed in an oxygen-free atmosphere in an agitated pyrolysis chambers at 390–410 °C. The obtained pyrolysis gases are introduced into the contactor with condensation elements. In this contactor, the long-chain gas components are condensed and recycled for further pyrolysis. The condensation of long-chain hydrocarbons takes place on downwardly sloped plates for the run-off of the condensate. The plates include apertures to allow for the upward progression of pyrolysis gases. The short-chain components leave the contactor in gaseous form (in the temperature ranging from 240 °C to 280 °C) and are distilled in the distillation column. The thermal decomposition process is carried out without the use of catalysts. This is one of the few patents that has been commercialized. Unfortunately, the patent does not state whether and how the hydrogenation of the multiple bonds of the resulting liquid product is carried out.

Another example of the catalytical conversion of PW waste to fuel is described in the patent application [193]. According to this document, the thermal decomposition of waste plastic is carried out in a temperature in the range from 350 °C to 450 °C and in a slight negative pressure in the range from 0.0010 psi (0.00007 bar) to 0.030 psi (0.00207 bar). The catalysts used in the process belong to the group of FCC catalysts, Y-zeolite and ZSM-5 zeolite. The thermal decomposition of the waste plastic is realized in the rotary kiln reactor with the helical baffles attached to the inner wall. The obtained gases are then subjected to four-stage sequential cooling to a temperature in the range from −5 °C to −15 °C. The final products are a gaseous fraction comprising C1 to C4 hydrocarbons and the liquid fraction (fuel). Due to the use of a mixture of the catalyst and materials as the feedstock, it is necessary to separate the catalyst from the char and its regeneration after the process. The use of a catalyst and the operations related to its recovery increase the costs of the entire technology.

Table 6. Comparison of different patented processes for the conversion of PW to hydrocarbon fractions.

| Substrate/Product | Conditions of Thermal Decomposition | Process Description | Reference |
|-------------------|-------------------------------------|---------------------|-----------|
| Waste hydrocarbon material such as plastics/fuel | - Thermal decomposition process: pyrolysis;  
- Process is carried out without the use of catalysts;  
- Oxygen-free atmosphere (in nitrogen);  
- Process temperature: 390–410 °C;  
- Agitated (with the use of a double helical agitator with a central screw) pyrolysis chambers. | - Process steps:  
  o Melting the PW material 300–320 °C;  
  o Pyrolysis of molten material;  
  o Condensation of long-chain hydrocarbons in a contactor and returning them to the pyrolysis chamber;  
  o Distillation of pyrolysis gases (at temperature 260–280 °C) from the contactor in a distillation column into fuels (temperature of a bottom section of the column 210–230 °C; the top of the column approx. 100 °C);  
  o Heavy hydrocarbons fractions are sent to vacuum distillation. | [192] |
| Substrate/Product                     | Conditions of Thermal Decomposition                                                                 | Process Description                                                                 | Reference |
|---------------------------------------|------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|-----------|
| Waste plastics PE, PP, PS, PET, EPDM  | • Continuous process;                                                                                 | • Process steps:                                                                     | [192]     |
|                                       | • Thermal decomposition process: catalytic pyrolysis;                                                  | o Mixing the waste plastic feed and a catalyst in a feed hopper;                    |           |
|                                       | • Carrier gas: nitrogen, argon or the product gas;                                                    | o Thermal decomposition of waste plastic in the rotary kiln reactor,                |           |
|                                       | • Process temperature: 350–450 °C;                                                                    | o Four-stage sequential cooling.                                                   |           |
|                                       | • Slight negative pressure in the range of 0.0010 psi (0.00007 bar) to 0.030 psi (0.00207 bar);       | • The hydrocarbon vapors must pass through the cyclone in order to separate the residual catalyst and char from their stream; |           |
|                                       | • Catalysts: belong to the group of FCC catalyst, Y-zeolite and ZSM-5 zeolite;                        | • After the process, it is necessary to separate the catalyst from the char and its regeneration. |           |
|                                       | • The weight ratio of the feed to the catalyst: from 1:0.153 to 1:1.5.                                 |                                                                                     |           |
| Plastic material/diesel fuel          | • Semi-continuous process;                                                                            | • Process steps:                                                                     | [194]     |
|                                       | • Thermal decomposition processes: pyrolysis (at 390–410 °C), catalytic conversion (at 220 °C or greater on catalytic plates); | o Melting the PW material;                                                          |           |
|                                       | • Pressure in pyrolysis chamber: 1.08 bar,                                                            | o Pyrolysis of melted PW at the process temperature; material in the pyrolysis chamber is agitated. |           |
|                                       | • Oxygen-free atmosphere (in nitrogen);                                                                | o Catalytic conversion (cracking and reforming) of gaseous products from pyrolysis to diesel fuel hydrocarbons; |           |
|                                       | • Pyrolysis chamber provided with an agitator.                                                         | o Distillation and condensation of the final product.                               |           |
| Plastic material (PP, PE), light and heavy distillates/fuels | • Batch process;                                                                                      |                                                                                     | [191]     |
|                                       | • Thermal decomposition process: pyrolysis;                                                             |                                                                                     |           |
|                                       | • Temperature from 90 °C to 550 °C;                                                                   |                                                                                     |           |
|                                       | • Oxygen-free atmosphere;                                                                             |                                                                                     |           |
|                                       | • Atmospheric pressure;                                                                               |                                                                                     |           |
|                                       | • Whole process time from 18 h to 28 h.                                                                |                                                                                     |           |
|                                       | • The process is one step;                                                                            |                                                                                     |           |
|                                       | • PW is grounded into powder form or chips and loaded into the de-polymerization reactor (column thermal cracking reactor) with additives; |                                                                                     |           |
|                                       | • Melting and gasification of plastic material takes place in the same reactor;                        |                                                                                     |           |
|                                       | • The reactor works in the temperature range from 90 °C to 550 °C;                                    |                                                                                     |           |
|                                       | • Reactor temperature program:                                                                        |                                                                                     |           |
|                                       | o 90–140 °C moisture removal;                                                                         |                                                                                     |           |
|                                       | o 140–220 °C purging the reactor and removing oxygen;                                                  |                                                                                     |           |
|                                       | o 220–290 °C melting of the plastic material;                                                          |                                                                                     |           |
|                                       | o 350–320 °C initial gasification stage;                                                                |                                                                                     |           |
|                                       | o Increasing from 350 °C to 400 °C and holding for 8 h;                                                |                                                                                     |           |
|                                       | o 400–440 °C pet coke (byproduct) forming process;                                                     |                                                                                     |           |
|                                       | o Increasing to 480–550 °C and holding for 4 h—plastic melt transforms into a gaseous form.            |                                                                                     |           |
|                                       | • Fractionation.                                                                                      |                                                                                     |           |
Another example of a patent describing the conversion of PW waste to fuel is Reference [191]. The liquefaction process is based on pyrolysis. The process is carried out in one stage in a column reactor. The shredded PW is mixed with additives in a ratio of 10:1. These additives are used to improve heat absorption and can include crude oil, synthetic oil, synthetic sludge or synthetic heavy oil, which are recovered from the depolymerization plant after distillation. During the process, the temperature is regulated (from 90 °C to 550 °C) using a temperature controller. It is gradually increased and maintained at a certain level depending on the stage of the process. The product obtained in the final step is
fractionated into different hydrocarbon groups by condensation in a condenser comprising of a honeycomb structure.

In turn, patent [194] concerns the conversion of plastics to hydrocarbons characteristic of diesel fuel. Before the process, the input material is subjected to a pre-treatment, which is fragmentation. The process includes melting the PW material, the pyrolytic decomposition of melted waste material, catalytic conversion of thermolysis products via cracking and reforming to hydrocarbons of appropriate chain length (from C8 to C25), as well as the distillation and condensation of the final product. Catalytic processes are carried out in a catalytic tower analogous to that used in the petrochemical industry—unsaturated bonds are hydrogenated.

Similarly to patent [192], patent application [195] has been commercialised. The described process and apparatus relate to the technology based on the pyrolysis of a mixture of plastic raw materials into petroleum products such as naphtha, distillate (e.g., diesel) and gas oil (e.g., heavy oil and wax). The process is carried out in a reactor comprising several successive and adjacent zones arranged along the horizontal axis of the reactor. These zones are controlled independently. There is a temperature gradient in the reaction zone of the reactor from the lower surface that contacts the raw material to the upper surface, which is provided with an exit port, and may vary widely, for example from about 50 °C to 450 °C. The fed raw material moves along the horizontal axis of the reactor that is undergoing pyrolysis. The gaseous products that leave the reactor vessel are condensed and collected for further processing.

A different approach to the degradation of polyolefins is presented in patent [196]. The presented method enables the decomposition of polyolefins without a catalyst into hydrocarbons with chains no longer than those found in diesel fuel (boiling up to 360 °C). An additional advantage of the technology is the process of catalytic hydrogenation and isomerization in the synthesis gas atmosphere under atmospheric pressure. The final products are typical fuel fractions. Unlike many other methods, the process is continuously carried out in a moving-packed tower flow reactor. Polyolefin waste is mixed with the heated elements of the reactor packing. The surface of the elements is covered with a thin layer of plasticized polymer material, and this charge is introduced into the reaction chamber. The temperature in the chamber changes along its axis (highest at the bottom and lowest at the top). The process is carried out in the countercurrent flow of synthesis gas under atmospheric pressure.

In contrast, patent [197] describes a method of pyrolysis of plastics assisted by a catalyst (activated bauxite). In this solution, as in Reference [196], only hydrocarbon vapors with a certain maximum boiling point can leave the reactor space. The boiling point of the product vapors is controlled by a scrubber that is located at the outlet of the reactor. The scrubber is a packed scrubbing column with packing. In the scrubber, the reaction chamber gas product is brought into contact with a hydrocarbon scrubbing liquid (temperature below 350 °C). Hydrocarbons with a boiling point above the scrubbing liquid condense and are returned to the reaction chamber with the liquid. Behind the scrubber, various devices enable the recovery of various components of the hydrocarbon gas product, such as a fractionation column to condense diesel range hydrocarbons, a condenser to condense petrol range hydrocarbons, and a gas compression and cooling device to condense liquid petroleum gas range hydrocarbons. A portion of the hydrocarbons from the fractionation column (diesel oil fraction) is used as the scrubbing liquid. The obtained raw fuels are then subjected to extraction processes to purify them. The patent does not describe whether and how the hydrogenation of the multiple bonds is carried out. The presented purification of products by extraction makes the process quite complex, which probably increases the costs.

The review shows that there are still ongoing works on the improvement in the technology and technological equipment for the recycling of plastics (PP, PE, PS) to fuels. This work is largely focused on the development of a continuous process, which greatly facilitates its implementation in industrial conditions. Much work is still based on simple
pyrolysis, which leads to a poor-quality product with no chance of application to fuel channels. After distilling the fuel fraction from such a product, the obtained residue requires further processing. The use of a catalyst in the process makes it possible to obtain hydrocarbon fractions of better quality, but entails the costs of purchasing the catalyst, its separation after the process from the char, and regeneration. The best solution seems to be to carry out the process of recycling heavy hydrocarbon vapors to the reactor (non-isothermal process or with the condensation of vapors of long-chain compounds). In this way, relatively light hydrocarbon fractions, boiling up to a certain temperature, are obtained. The light product, unfortunately, contains significant amounts (about 60%) of unsaturated compounds and, despite the declarations of the inventors, according to the authors of this article, cannot be used as a fuel. It must be hydrogenated for such purposes.

Regardless of the method used to destroy the polyolefins, whether continuously, semi-continuously or batchwise, and with or without a catalyst, the by-products are the gaseous fraction of light hydrocarbons, which are most often used to heat the process (in some cases as a carrier gas), and the solid fraction (char). Char contains non-volatile substances during the process, such as inorganic compounds (fillers, pigments, catalyst residues), uncracked polymers, carbon as a product of dehydrogenation, and the products of secondary polycondensation reactions [198]. This can be used to produce activated carbon (adsorbents), additives to epoxy resins, fuel briquettes, cement additives or additives in the production of epoxy composite [199,200]. It can also provide a source of various metal elements that can be recovered as a result of appropriate treatment [201,202]. The high degree of unsaturation of the liquid fraction components is responsible for the unpleasant, pungent smell and instability manifested by the darkening of the product and the formation of resin-like substances. This limits the use of this product as a fuel component. Therefore, further processing is necessary.

In conclusion, the advantages of the technologies presented in the presented patents include:

• The use of various types of waste polyolefins, including mixed and contaminated;
• Obtaining hydrocarbons with a small mass distribution and short carbon chains (up to C20–C22—in the case of catalytic processes, the process with the recycling of heavy hydrocarbon vapors or the process using reactive distillation), which is possible to use in the production of liquid fuel components;
• The possibility of running the process continuously (in some cases);
• Obtaining chemically stable fractions thanks to the application of a cheap hydrogenation process (in the case of one patent).

Despite the fact that, for many years, research was carried out on the conversion of waste polyolefins to fuels, these technologies are still imperfect and have disadvantages, including:

• The manual loading of the feed into the reactor;
• Conducting the process in batch mode;
• Poor-quality product from the conventional pyrolysis process (e.g., high wax content, large dispersion of hydrocarbon masses);
• No hydrogenation process that chemically stabilizes the product and allows it to be used as a fuel component;
• High costs related to the use and regeneration of catalysts and product purification;
• High complexity of some processes.

5. Industrial Examples of Polyolefins Waste Conversion

Despite the many developed and patented technologies used for converting waste polyolefins into hydrocarbons, few have been implemented. This results, among others, from the complexity of these processes, their long reaction times, high energy demand or the poor quality of the obtained products [203]. A report from 2021, prepared by Closed Loop Partners [204], on plastic recycling technologies on the American and Canadian markets, indicates that only four of the recycling methods analyzed by the company have technologies with technology readiness levels (TRL) of level 8: Plastic Energy, Enerkem,
Brightmark and JEPLAN. The technology of the Japanese company JEPLAN is intended
for the recycling of polyethylene terephthalate; therefore, it is not discussed in this article.

In turn, the authors of [29] assessed the TRL of various technologies for the chemical
recycling of waste plastics. They analyzed the following technologies: thermal cracking
(conventional pyrolysis), plasma pyrolysis, microwave-assisted pyrolysis, catalytic cracking,
hydrocracking, conventional gasification, plasma gasification and pyrolysis with in-line
reforming. Their research shows that the highest degree of technological readiness is
demonstrated by three technologies: pyrolysis, catalytic cracking and gasification. Other
technologies are not yet sufficiently ready and require further work. One of the reasons
for the implementation of these technologies was the lower operating temperatures of the
installation and their lower sensitivity to the quality of the raw material. High temperatures
generate higher installation costs and higher costs to provide the necessary energy for the
process. On the other hand, the presence of catalysts (e.g., in hydrocracking) is associated
with greater sensitivity to charge contamination, particularly polyvinyl chloride admixtures.
As reported in Reference [205], a high energy consumption, reaching 5–20% of the calorific
value of the polymer waste input, has become the main reason for the failure of the
development of pyrolysis technologies on an industrial scale. However, start-ups are
currently emerging that are trying to modernize and improve these technologies. Some
of the pyrolysis-based industrial installations that are used to convert waste polylefins to
hydrocarbon fractions are still working and some are presented below.

In the technology of British company Plastic Energy [206], the input material is a mixture
of PP, PE and PS. Waste plastics do not require washing or separation into individual
types. A Thermal Anaerobic Conversion (TAC Technology) has been patented [192] and
its product is TACOIL, which can replace crude oil. The product is distilled into three
fractions: raw diesel, light oil and synthetic, gas components. Naphtha and diesel are sold
to refineries, and gaseous products are used to power the installations. From one tonne
of plastic waste, about 850 L of TACOIL is obtained. Plastic Energy has two operational
plants, in Seville and Almeria, Spain, which have been operational since 2015 and 2017,
each of which can process 5000 tonnes of plastic annually [207].

In the technology of the Canadian company Enerkem, the PW is first converted into
synthesis gas (syngas). The syngas is then transformed (in a catalysed process) into fuels
and chemical products [208]. As this technology is beyond the scope of this article, it is not
discussed in more detail.

The American company Brightmark has partnered with RES Polyflow, an Ohio-based
energy company that has patented [195] the processing of plastics. The companies are
building a commercial-scale plastic recycling facility in Ashley, Indiana, with a capacity of
100,000 tonnes of plastic waste per year [209]. The process is expected to be 93% efficient.

A slightly different technology was patented and implemented by BioCollection. The
company undergoes conversion of the contaminated PE by an accelerated thermal oxidative
decomposition (ATOD) process [210]. The process is performed catalytically in the presence
of an oxidant (e.g., oxygen, nitric oxide, nitric acid (V)), at a temperature of from 60 °C to
200 °C and for a period of from 30 min to 30 h. The product is a mixture of various high-
value chemical compounds and contains, inter alia, succinic, oxalic, glutaric, adipic, pimelic
and azelaic acids, or their esters or salts. The resulting organic acids are intermediate
chemicals that are used in the production of materials used, among others, in the clothing,
electronics and automotive industries.

In 2018, the international company BASF launched the ChemCycling project. The aim
of this project is plastic waste consisting of, e.g., PE, PP, PS by pyrolysis to pyrolysis oil.
The oil is then further processed, just like crude oil [211]. In the same year, the Austrian
company OMV built a pilot plant at the Schwechat refinery, in which it implemented the
proprietary ReOil® technology. This technology enabled the processing of waste plastics
such as polyethylene, polypropylene and polystyrene into a pyrolytic shell. The plant has
a processing capacity of up to 100 kg per hour, which is equivalent to 100 L of synthetic
crude oil. Plastics are crushed, mixed with a high-boiling solvent and heated in a reactor.
The process is a two-stage process—the materials melt at 200 °C, and the depolymerization process takes place at temperatures above 390 °C. A solvent reduces the viscosity and improves the heat transfer. After distilling the solvent, the obtained product is further processed in the refinery [212,213].

Cynar Plc installed its first full-scale plant in County Laois, Ireland in 2008. The company implements pyrolysis-based waste processing technology which converts a wide range of end-of-life plastics into hydrocarbons (similar to diesel oil). The plastic (chipped PE, PP, PS) is pyrolyzed at 370–420 °C, and the pyrolysis gases are condensed in a two-stage condenser to produce a distillate [214]. The distillates are collected in tanks. The raw diesel is further refined in another distillation column, where it is distilled into the main three products: diesel, kerosene and light oil. The 1 ton of PW is converted into to 1000 L of fuels (700 L of diesel, 200 L of light oil and 100 L of kerosene). The process also produces about 60 L of gaseous products, and the remaining char is about 5% [215]. The gaseous product is cleaned and used in the furnaces that heat the pyrolysis chambers.

Alphakat’s KDV technology is a catalytic process that enables the conversion of waste plastics to diesel oil. The input to the process may also be waste oils or biomass. Catalytic depolymerization of the fragmented feed occurs in reactor turbines at temperatures from 270 °C to 350 °C under the influence of a catalyst in the process of oil suspension and circulation. The patented catalyst used in this process has a double function: it catalyzes the reaction, facilitating the formation of valuable products, and works as ion exchanger, retaining the hetero-atoms such as halogens, phosphorus, nitrogen and heavy metals from raw material, and transforming them into inorganic compounds. This process is conducted under low pressure (0.9 bar). The by-products are CO₂, water, light gas and small amounts of solids [216]. The test facility is located in Eppendorf, Germany. At present, Alphakat is starting a project in Cyprus (Koshi Village Project), under which it will process wood biomass into biofuel [217].

6. Conclusions

The authors have provided an extensive review of the current state of the knowledge in the field of processing plastic liquefaction to fuel fractions as energy carriers. This review shows that thermocatalytic processing technologies are the most common. The authors did not analyze the methods of biological conversion of plastics, because these methods are at a very early stage of research, and the possibility of their industrial use cannot be determined. As part of the review, the progress in research and development was taken into account, as well as the patent status of selected technologies and examples of industrial use of these technologies. The existing technologies for the processing of waste plastics generally focus on material and energy recovery. The material recycling processes do not cover all types of plastics and, as a result, lead to the degradation of the functional properties of the recycled waste material. This results in the generation of waste that cannot be further recycled. Direct energy recycling also does not cover all groups of plastic wastes and has significant environmental burdens related to the nature of the technological processes. In the field of processing waste plastics into liquid and gaseous energy carriers, the research into pyrolysis processes is well-developed. The analysis of the state of the research into and application of these processes showed their development. However, the research mainly focused on the efficiency and effectiveness of these processes.

On the basis of the review of modern technologies for the liquefaction of waste plastics and their mixtures to liquid fuel fractions, it can be concluded that most existing solutions require further improvement, in terms of both economics and technology. These imperfections result in stagnation of the development of industrial technologies for the chemical recycling of PW. In most of the analyzed studies, no environmental impact assessment of these processes, especially the Life Cycle Assessment (LCA), was found. Depolymerization processes additionally require hydrogenation from external sources, which brings an additional environmental burden. For this reason, according to the authors, technologies where chemical stabilization of the obtained products is carried out in the process
of decomposition should be regarded as promising. Such technologies, despite the need for the refinement of process conditions (pressure, catalyst recovery), include tandem hydrogenolysis/aromatization, where, during aromatization, hydrogen is generated and used in the hydrogenolysis process. The technology with the greatest potential for commercial development, in which the problems of high pressure and catalyst recovery from the reaction mixture have been eliminated, is the thermolysis of plastics, discussed in Reference [128]. In this solution, the saturation of multiple bonds is conducted under atmosphere pressure, with hydrogen from the synthesis gas, using the catalytic effect of carbon monoxide. This technology results in fuel fractions which, when added to conventional fuels, yield products that meet the standards for motor fuels (EN 590 and EN 228). These technologies are part of a new direction called petrosynthesis, as defined and described in Reference [218]. Petrosynthesis is the latest area of research aimed at leading to a closed production cycle and use of industrial waste. This mainly focuses on carbon dioxide, but the thermolysis of plastic waste could be an element of petrosynthesis processes, leading to the production of saturated hydrocarbon fractions for various applications, forming part of the Circular Economy.

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