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Polystyrene Waste Pyrolysis: A Systematic Literature Review

.

Joaquín Farah Abedrabbo Campana

Ingeniería Química

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Joaquín Farah Abedrabbo Campana

Nombre del profesor, Título académico   **Daniela Almeida, PhD.**

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Nombres y apellidos: Joaquín Farah Abedrabbo Campana

Código: 137418

Cédula de identidad: 1723301006

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RESUMEN

La acumulación de residuos plásticos en el medio ambiente se ha convertido en una de las problemáticas mundiales más graves debido a que su consumo es masivo. El poliestireno (PS) constituye un gran porcentaje de esta acumulación plástica al poseer un sinnúmero de aplicaciones en productos de uso cotidiano. La pirólisis es una de las técnicas químicas que ha surgido para reciclar de manera efectiva este polímero. En los últimos años se han estudiado diferentes condiciones de operación para efectuar la pirólisis, como por ejemplo: tipos de reactores, rangos de temperatura, uso de catalizadores y combinaciones de materia prima. Se realizó una revisión sistemática literaria de las diferentes formas de aplicar pirólisis para el reciclaje de PS. Para la revisión, se utilizaron las bases de datos Science Direct y Taylor & Francis. Se identificaron 24 artículos que cumplieron con los criterios de inclusión. Los reactores discontinuos y semi-continuos fueron los más utilizados ya que los experimentos se realizaron principalmente a escala de laboratorio. Se encontró que, para la pirólisis de PS, existe un mayor rendimiento de productos líquidos en un rango de temperatura alrededor de los 500°C. Los campos de estudio en crecimiento son la pirólisis catalítica y la aplicación de co-pirólisis para mejorar las condiciones de operación y el rendimiento de los productos. Se demostró que la pirólisis es una forma efectiva de reciclar PS y de transformarlos en productos de alto valor agregado con el fin de reducir los impactos ambientales.

Palabras Clave: Pirólisis, Poliestireno Residual, Catalizadores, Reciclaje Químico.

ABSTRACT

Plastic accumulation in the environment has become a serious worldwide problem due to its massive consumption. Polystyrene (PS) makes up a large percentage of this plastic buildup, as it is used widely in many different applications. Pyrolysis has been a trending chemical technique for recycling this polymer. Different reactor types, temperature ranges, catalysts and feedstock combinations have been studied in recent years. A systematic literature review of the different ways of applying pyrolysis to PS recycling was performed. For this review the databases Science Direct and Taylor & Francis were used. 24 papers were identified that fulfill the inclusion criteria. Batch and semi-batch reactors were the ones most used, as experiments were performed mainly at laboratory scale. It was found that for PS pyrolysis, a higher liquid yield was found at around 500°C. The growing fields of study are catalytic pyrolysis and the application of co-pyrolysis to improve operating conditions and products yield. It was demonstrated that pyrolysis is an effective way to recycle PS into high value added products in order to reduce the environmental impacts.

Keywords: Pyrolysis, Polystyrene Waste, Catalysts, Chemical Recycling.

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INTRODUCTION

Nowadays, one of the biggest environmental issues is the accumulation of plastic waste throughout the world. Its massive production, low recycling rate and, especially, its long degradation time in nature is what makes plastic so harmful for the environment (Hu et al., 2020). A considerable amount of these plastic wastes consist of polystyrene (PS), because it is used on a large scale due to its wide variety of applications. PS is used for food protective packaging, in disposable food products, as composites for cares of computers or inner car parts (Bartoli et al., 2015), and in many more products used on a daily basis (Nisar et al., 2019). PS and most of other plastic wastes usually end up stockpiled under uncontrolled conditions in the environment or in municipal landfills which brings several problems to public health and the environment, causing negative impacts in marine ecology, water, soil and specially air quality, because it releases toxic gases such as NOx, COx and SOx (Uttaravalli et al., 2020). For these reasons, an efficient recycling treatment for PS is needed.

Conventional waste treatment for PS and other polymers has had insignificant or inefficient impacts on the previously discussed issues. For example, mechanical recycling, combustion or landfilling present low recovery rate, unsatisfactory quality resources and produces secondary pollution (Sun et al., 2020). Mechanical recycling presents a series of limitations. It requires direct remanufacturing through milling, washing, drying and molding, processes that will not be efficient in contaminated or degraded waste banning it from being reincorporated in the process cycle. Besides, most of the time plastic waste is a mixture of many plastic types. The implementation of separation processes in order to recycle them in mechanical ways may be an ineffective and expensive challenge (Bartoli et al., 2015). Another way to treat plastic waste is by chemical recycling. Some of the chemical methods used are gasification, liquefaction, catalytic cracking and pyrolysis, among others. Pyrolysis is being described as an ideal approach for polymer conversion to gaseous or liquid fuels and/or valuable products (Jiang et al., 2018), being the last two the most significant. This type of thermos-chemical conversion decompose plastics at temperatures between 400–600°C under an anaerobic atmosphere, in order to obtain gaseous and liquid high value products (Oh et al., 2018).

PS pyrolysis has been widely investigated in the last years in different operating conditions such as: type of reactor, temperature range, use of catalyst, application of co-pyrolysis by mixing PS with one or more feedstock and more. Research and investigation is often done in batch or semi-batch reactors as an initial baseline for future experiments (Çelikgöɟüs and Karaduman, 2015). Other researchers (Özsin and Pütün, 2018; Van Nguyen et al., 2019; Veses et al., 2020) used advanced reactor types such as Auger reactors, fluidized bed reactors and fixed bed reactors. As stated before, conventional pyrolysis usually goes from 400°C to 600°C. The use of catalysts or a microwave oven may reduce the optimal temperature in the range of 300°C to 350°C (Bartoli et al., 2015; Uttaravalli et al., 2020; Veses et al., 2020). Furthermore, other studies have shown an

improvement in pyrolysis products quality and yield by introducing other type of feedstock along with the PS. Co-pyrolysis of PS with biomass is being highly studied, because it enhances the pyrolysis product by gaining excellent characteristics similar to gasoline thanks to the plastic feed. While the addition of biomass reduces the formation of harmful compounds, such as benzenes, dioxins and furans (Stančin et al., 2021). Finally, co-pyrolysis between plastic types, mixing PS with other polymers, is also applied in order to change the selectivity of the products (Oh et al., 2018).

The purpose of this study is to perform a systematic literature review (SLR) on the state of the art of the pyrolysis of polystyrene waste, which serves as a guide for the treatment of polystyrene plastic waste via pyrolysis. This will help future researchers and scientists in order to identify gaps in the state of the art of PS pyrolysis or select the appropriate methods to reduce the environmental impact of PS residues.

METHODS

This review followed the PRISMA (Preferred Reporting Items for Systematic Reviews and Meta-Analyses) method to report a systematic literature review (SLR). The search command used in the established databases were "pyrolysis" AND "polystyrene" AND "waste" NOT "plastic waste" NOT ["plastic mixture" OR "plastic mix"]. These commands were chosen after a manual screening of the articles about PS pyrolysis, in order to exclude researches where polystyrene was not one of the principle feedstock in the pyrolysis process and was only part of a mixture of many plastics. It also ensures the use of residual PS by researchers. Search was performed in 2 databases: Science Direct and Taylor & Francis. The same command was used in both databases. The search was performed on September 28, 2020.

Papers need to provide enough information in the following inclusion criteria in order to be accepted in this review: operating conditions such as reactor type and optimal temperature, use of catalysts, application of co-pyrolysis with maximum two more feedstock besides PS and the pyrolytic products with major selectivity. This information was part of the data that was extracted manually, along with the authors, year, journal, keywords and results. As exclusion criteria, only papers published in English from 2015 to 2021 were elected.

The screening process was performed manually. First, all papers were briefly assessed by their tittle and abstracts. The ones that include PS as one of their main feedstock for the pyrolysis were fully reviewed. For example, there were articles that included Municipal Solid Waste (MSW) treatment with pyrolysis but PS only constituted a small percentage of this waste´s volume. Only the articles that presented all the inclusion criteria exposed previously were chosen to be part of the results of this SLR. In *Annex 1* a chart of the number of papers found on the searching process and the excluded during the screening process is presented.

RESULTS AND DISCUSSION

47 papers were identified after using the search commands in the established databases. After the manual screening, 24 papers were the ones that satisfied the inclusion criteria. The results presented in the retrieved papers are displayed in the following tables. The tables in this study are divided by: reactor type used in the experiments, catalysts applied, operating temperature range, co-pyrolysis feedstock and main products obtained. In

Annex 2 a complete table of the summarized results of all the retrieved articles can be found.

In *Table 1* we can see the different reactor types researchers used in order to carry out the chemical recycling of PS through pyrolysis. As most experiments were performed at a laboratory level, batch and semi-batch reactors were mostly used. If the type of batch reactor is specified, then it is included in the results as a separate result from those who do not specify the kind of batch/semi-batch reactor. The micro-pyrolyzer, the tubular furnace and the microwave oven are the batch type reactors that were specified by the authors. Also, continuous laboratory scale reactors were used in order to perform the PS pyrolysis. These are the fixed, fluidized and conical spouted bed reactors. On the other hand, there was one experiment that scaled up an Auger reactor to a pilot plant (Veses et al., 2020), which are commonly used for this purpose and are very effective for conducing fast pyrolysis. Prove that this Auger reactor was used to scale up the pyrolysis mechanism is that it processed 25 kg of plastic waste, while the rest only treated <200 g. Experiments made in micro-pyrolyzers (Adnan et al., 2015; Sophonrat et al., 2018; Sun et al., 2020, 2018) treated samples smaller than 1g. All samples were placed in a solid phase fed manually when using a batch reactor, while continuous reactors used mechanical devices to feed the solids, such as screw feeders (Van Nguyen et al., 2019; Zhang et al., 2015) or stirred hoppers (Veses et al., 2020). Absolutely all experiments used inert gases as carrier gases for purging non condensable gases and for sweeping products. Most of them used Nitrogen as the inert gas with the exception of three (Dorado et al., 2015; Patil et al., 2018; Xue et al., 2017) that used Helium.

Table 1. Reactor type used for PS pyrolysis

Reactor Type	Number of papers	Percentage	Authors
Batch / semi-batch	7	29%	(Çelikgöğüs and Karaduman, 2015; Déparrois et al., 2019; Hadi et al., 2017; Khaobang and Areeprasert, 2017; Nisar et al., 2019; Reshad et al., 2019; Shadangi and Mohanty, 2015)
Fixed bed reactor	4	17%	(Chai et al., 2020; Özsin et al., 2019; Özsin and Pütün, 2018; Stančin et al., 2021)
Fluidized bed reactor	2	8%	(Van Nguyen et al., 2019; Zhang et al., 2015)
Micro-pyrolyzer	4	17%	(Dorado et al., 2015; Oh et al., 2018; Patil et al., 2018; Xue et al., 2017)
Vertical tubular reactor	4	17%	(Adnan et al., 2015; Sophonrat et al., 2018; Sun et al., 2020, 2018)
Microwave oven	1	4%	(Bartoli et al., 2015)
Conical spouted bed	1	4%	(Artetxe et al., 2015)

Auger reactor	1	4%	(Veses et al., 2020)

Regarding catalytic pyrolysis of PS, *Table 2* illustrates the number of articles that applied catalytic pyrolysis for PS treatment. These articles represents 50% of the retrieved papers, while the other 50% studied non-catalytic processes (Artetxe et al., 2015; Bartoli et al., 2015; Déparrois et al., 2019; Khaobang and Areeprasert, 2017; Nisar et al., 2019; Özsin et al., 2019; Özsin and Pütün, 2018; Reshad et al., 2019; Shadangi and Mohanty, 2015; Sophonrat et al., 2018; Stančin et al., 2021; Van Nguyen et al., 2019). It is evident that there is not yet a catalyst or a group of characteristic catalysts commonly used for PS pyrolysis, being HZSM-5 zeolite the only catalyst that repeats once. This means there is still a wide field of research to find an optimal catalyst for this process. In fact, many of the selected papers had the main purpose to study alternative catalysts to optimize the pyrolysis process. For example, Activated Sewage Sludge Char was studied as a catalyst in the PS pyrolysis process, giving positive results by increasing the selectivity of high value liquid aromatic products (Sun et al., 2020).

Table 2. Catalysts used for PS pyrolysis

Catalyst Used	Number of papers	Percentage	Authors
HZSM-5 Zeolite	2	10%	(Dorado et al., 2015; Xue et al., 2017)
$ZnCl_2$–activated biochar	1	4%	(Sun et al., 2018)
Al-Al_2O_3	1	4%	(Adnan et al., 2015)
Spent FCC	1	4%	(Zhang et al., 2015)
Ni-CaO-C	1	4%	(Chai et al., 2020)
Sewage Sludge Char	1	4%	(Sun et al., 2020)
Al-MSU	1	4%	(Oh et al., 2018)
Red Clay	1	4%	(Patil et al., 2018)
CaO	1	4%	(Veses et al., 2020)
Kaolin-CuO/Kaolin	1	4%	(Hadi et al., 2017)
Cu/y-Al_2O_3	1	4%	(Çelikgöłüs and Karaduman, 2015)

Another reason why it is important to continue developing catalysts for this reaction is to reduce the operating condition such as temperature. As it is evident in *Table 3*, the most common operating temperature for PS pyrolysis is between 500 and 550°C because it is demonstrated that PS decomposes better at this range having maximum bio-oil yield (Özsin and Pütün, 2018; Shadangi and Mohanty, 2015). However, operating at this temperature range is energy intensive and the material requirements for the equipment are expensive. That is why investigations of catalytic pyrolysis of PS are needed, as it is shown that catalysts can reduce the operating temperature range to 300-380°C (Veses et al., 2020). Nine articles studied the pyrolysis at a wider temperature range between 400-450°C and 600-650°C. *Table 3* also reflects the most common yield for the products of interest defined by the authors. Similar ranges of liquid yield are obtained within these ranges, from 70 to 95% of the liquid fraction. Only two studies by (Chai et al., 2020) and

(Déparrois et al., 2019) carried out the pyrolysis process at much higher temperatures, 800°C and 900°C, respectively. The main interest in these investigations are the production of syngas and/or H_2 from the PS, which requires more energy, so a combination of pyrolysis with gasification was studied. This gaseous fraction reached a yield from 15 to 25%.

Table 3. Operating temperature range for PS pyrolysis

Temperature Range	Number of papers (Percentage)	Products of interest (yield)	Authors
300-380	2 (8%)	Liquid (80-90% w/w)	(Bartoli et al., 2015; Veses et al., 2020)
400-450	4 (17%)	Liquid (70-80% w/w)	(Adnan et al., 2015; Hadi et al., 2017; Khaobang and Areeprasert, 2017; Nisar et al., 2019)
500-550	11 (46%)	Liquid (85-95% w/w)	(Artetxe et al., 2015; Çelikgöɬüs and Karaduman, 2015; Oh et al., 2018; Özsin et al., 2019; Özsin and Pütün, 2018; Patil et al., 2018; Reshad et al., 2019; Shadangi and Mohanty, 2015; Sophonrat et al., 2018; Sun et al., 2018; Van Nguyen et al., 2019)
600-650	5 (21%)	Liquid (80-90% w/w)	(Dorado et al., 2015; Stančin et al., 2021; Sun et al., 2020; Xue et al., 2017; Zhang et al., 2015)
700	0 (0%)	-	-
800	1 (4%)	Gas (15 – 20% w/w)	(Chai et al., 2020)
900	1 (4%)	Gas (20 – 25% w/w)	(Déparrois et al., 2019)

One of the main purposes of studying PS pyrolysis is to obtain high value products. 6 investigations of the retrieved articles studied the pyrolysis of pure PS (Artetxe et al., 2015; Bartoli et al., 2015; Çelikgöɬüs and Karaduman, 2015; Hadi et al., 2017; Khaobang and Areeprasert, 2017; Nisar et al., 2019), while the rest studied PS combined with other feedstock in co-pyrolysis (*Table 4*). These studies proved that using PS as a feedstock in co-pyrolysis improves the yield of the liquid fraction of products, in quantity and quality (Stančin et al., 2021). In *Table 5* we can see the different main products obtained by the co-pyrolysis with PS. Main products were defined as the 5 (or less) products with major yield or the ones that are expressed explicitly by the authors. They also have a yield higher that 1%. This is because there are cases in which the percentage of styrene is so big that the other products yields are negligible. 14 articles were only interested in the liquid fraction of the pyrolytic products (Adnan et al., 2015; Artetxe et al., 2015; Bartoli et al., 2015; Çelikgöɬüs and Karaduman, 2015; Hadi et al., 2017; Khaobang and Areeprasert, 2017; Oh et al., 2018; Özsin et al., 2019; Özsin and Pütün, 2018; Patil et al., 2018; Shadangi and Mohanty, 2015; Stančin et al., 2021; Sun et al., 2018; Xue et al., 2017), while Déparrois was the only one interested solely in the gaseous fraction(Déparrois et al., 2019). Only three articles were the only ones interested in the solid fraction (bio-

char) along with the liquid fraction of the pyrolytic products, where the three of them reported a solid yield near 30%(Reshad et al., 2019; Van Nguyen et al., 2019; Zhang et al., 2015). The rest of authors reported the liquid and gaseous products with major yield. Light hydrocarbons such as methane, ethylene, propylene and butene along with hydrogen, CO_2 and CO are the main pyrolytic gases products. As expressed before, PS promotes the production of the liquid fraction. The gaseous products are included in *Table 5* in those papers were the gases were declared as the main product of study by the authors. As styrene is the monomer of PS, most of the papers reported it as the main product obtained, combined with aromatic compounds such as benzene, toluene, ethylbenzene, xylene, naphthalene, among others. These compounds are widely used as raw materials, solvents and additives in many industries, such as chemical, cosmetic, pharmaceutical, petrochemical, etc (Sun et al., 2020). In *Table 5* the categories that include its derivatives such as benzene derivatives, incorporates all its derivatives with minor yield, while the derivatives with major yield are stated as an independent category, e. g., ethylbenzene. Also some non-aromatic main products are reported in *Table 5* such as Acetic Acid and Benzoic Acid. These products are obtained by co-pyrolysis. It is evident that co-pyrolysis has generated greater interest in researchers as only 25% of the pyrolysis studies were conducted with pure PS, while 75% percent of researchers used biomass, polymers, or both as combined feedstock with PS. Shadangi and Van Nguyen obtained the Acetic Acid by combining PS with karanja and niger seeds biomass or with pine sawdust, respectively (Shadangi and Mohanty, 2015; Van Nguyen et al., 2019). Oh et al obtained Benzoic Acid by mixing PS with another polymer, PET (Oh et al., 2018). One problem solved by co-pyrolysis is that it reduces the selectivity of the aromatics produced mainly by PS pyrolysis. It is true that these aromatic compounds are high value products, but some of them are also very harmful and toxic for people and the environment. Co-pyrolysis reduces the yield of polycyclic aromatic hydrocarbons (PAHs), especially when PS is combined with biomass (Stančin et al., 2021). When styrene is not a product of interest, it is also a viable option to mix PS with other types of polymer such as polyethylene and/or polypropylene to increase the yield of other high value product that normally would have lower yield, such as bicyclic aromatics like naphthalene (Sun et al., 2020).

Table 4. Co-pyrolysis of PS with other feedstocks

Co-pyrolysis feedstock		Number of papers	Percentage	Authors
Biomass	Cellulose	1	4%	(Dorado et al., 2015)
	Walnut Shell and Peach Stones	2	9%	(Özsin et al., 2019; Özsin and Pütün, 2018)
	Lignin	1	4%	(Zhang et al., 2015)
	Pine Sawdust	2	9%	(Chai et al., 2020; Van Nguyen et al., 2019)
	Karanja and Niger Seed	1	4%	(Shadangi and Mohanty, 2015)
	Rubber Seed Cake	1	4%	(Reshad et al., 2019)
	Grape Seed	1	4%	(Veses et al., 2020)

	Paper Waste	1	4%	(Déparrois et al., 2019)
	Beech, Oak and Fir Sawdust	1	4%	(Stančin et al., 2021)
Polymer	PE & PP	2	9%	(Sun et al., 2020, 2018)
	PE	1	4%	(Xue et al., 2017)
	PET	2	8%	(Adnan et al., 2015; Oh et al., 2018)
Combined Feedstock (Biomass & Polymer)	Dealkaline lignin and LDPE	1	4%	(Patil et al., 2018)
	PE and Paper Waste	1	4%	(Sophonrat et al., 2018)

Table 5. Main products reported from PS pyrolysis

Main products reported		Number of papers	Authors
Liquid	Styrene	19	(Adnan et al., 2015; Artetxe et al., 2015; Bartoli et al., 2015; Çelikgöłüs and Karaduman, 2015; Dorado et al., 2015; Hadi et al., 2017; Khaobang and Areeprasert, 2017; Nisar et al., 2019; Oh et al., 2018; Özsin et al., 2019; Özsin and Pütün, 2018; Patil et al., 2018; Reshad et al., 2019; Sophonrat et al., 2018; Stančin et al., 2021; Sun et al., 2020; Van Nguyen et al., 2019; Zhang et al., 2015)
	Toluene	12	(Adnan et al., 2015; Artetxe et al., 2015; Bartoli et al., 2015; Çelikgöłüs and Karaduman, 2015; Dorado et al., 2015; Nisar et al., 2019; Oh et al., 2018; Patil et al., 2018; Shadangi and Mohanty, 2015; Sophonrat et al., 2018; Xue et al., 2017; Zhang et al., 2015)
	Benzene derivatives	17	(Adnan et al., 2015; Artetxe et al., 2015; Chai et al., 2020; Dorado et al., 2015; Khaobang and Areeprasert, 2017; Oh et al., 2018; Özsin et al., 2019; Özsin and Pütün, 2018; Patil et al., 2018; Reshad et al., 2019; Shadangi and Mohanty, 2015; Sophonrat et al., 2018; Stančin et al., 2021; Sun et al., 2020, 2018; Xue et al., 2017; Zhang et al., 2015)
	Ethyl-benzene	11	(Adnan et al., 2015; Artetxe et al., 2015; Çelikgöłüs and Karaduman, 2015; Dorado et al., 2015; Khaobang and Areeprasert, 2017; Oh et al., 2018; Patil et al., 2018; Sophonrat et al., 2018; Stančin et al., 2021; Veses et al., 2020; Xue et al., 2017)
	Naphtalene	8	(Dorado et al., 2015; Hadi et al., 2017; Özsin and Pütün, 2018; Stančin et al., 2021; Sun et al., 2020, 2018; Xue et al., 2017; Zhang et al., 2015)
	Phenyl derivatives	11	(Adnan et al., 2015; Artetxe et al., 2015; Bartoli et al., 2015; Çelikgöłüs and Karaduman, 2015; Hadi et al., 2017; Özsin and Pütün, 2018; Shadangi and Mohanty, 2015; Sophonrat et al., 2018; Stančin et al., 2021; Sun et al., 2018, 2020)

	Phenol derivatives	4	(Özsin et al., 2019; Özsin and Pütün, 2018; Patil et al., 2018; Reshad et al., 2019)
	Acetic Acid	3	(Reshad et al., 2019; Shadangi and Mohanty, 2015; Van Nguyen et al., 2019)
	Propanone	1	(Nisar et al., 2019; Stančin et al., 2021)
	Benzoic Acid	1	(Oh et al., 2018)
	Tetrafluoro hydrazine	1	(Shadangi and Mohanty, 2015)
	Propanediol	1	(Khaobang and Areeprasert, 2017)
	Formamide	1	(Reshad et al., 2019)
	Hydroxymethyl	1	(Khaobang and Areeprasert, 2017)
	Methane	4	(Chai et al., 2020; Nisar et al., 2019; Sophonrat et al., 2018; Veses et al., 2020)
	CO_2	3	(Chai et al., 2020; Sophonrat et al., 2018; Veses et al., 2020)
Gas	Propene	3	(Khaobang and Areeprasert, 2017; Nisar et al., 2019; Veses et al., 2020)
	H_2	2	(Chai et al., 2020; Veses et al., 2020)
	Butene	1	(Nisar et al., 2019)
	Ethylene	2	(Dorado et al., 2015; Nisar et al., 2019)
	CO	2	(Chai et al., 2020; Veses et al., 2020)
	Pentane	1	(Nisar et al., 2019)
	Syngas	1	(Déparrois et al., 2019)

CONCLUSIONS

In this SLR the state of the art of the pyrolysis and co-pyrolysis of PS has been retrieved. Systematic research in the chosen databases gave 47 related articles that passed through a manual screening in order to establish the ones that fulfilled the inclusion criteria. In total, 24 studies have been identified between 2015 and October 2020 that satisfied these criteria. Every study proved the effectiveness of pyrolysis as a chemical recycling method for PS. Pyrolysis application obtained high value products, whether if liquids, gaseous or solid products were the ones of interest. It was evidenced that PS promotes the yield of liquid products, reason why most papers studied obtaining these fraction. Different reactor types and operating conditions were analyzed in order to understand its effect on the process. The analyzed operating conditions were: continuous or batch operations, temperature range, catalysts used and the composition of the feedstock as in co-pyrolysis. The majority of reactors employed were batch and semi-batch reactors. The optimal temperature range found was from 500 to 550°C for non-catalytic processes, as it showed a higher yield of liquid products compared to other temperature ranges. Regarding the catalysts used, it is fair to say that in this field there is still a wide potential for studying more catalysts since few of them were used and there is not a clear preference over one of them. It is interesting to evidence the new trend of applying combined feedstock in co-pyrolysis processes. Co-pyrolysis of PS brings many positive outcomes to the process as it increases the liquid product yield, decreases the production of toxic and harmful substances, allows the recycling of other polymers, not only PS, and extends the life cycle

of organic waste (biomass). Most of the studies were performed at a laboratory scale but others proved that this chemical technique is applicable at an industrial level. It is important to continue studying the different ways to apply pyrolysis in the treatment of non-degradable waste in order to optimize the process. In this way, an economically viable and large-scale solution can be found, as these studies have shown that it is a promising technology for treating PS and valorizing its products. This could boost the treatment of many of these contaminant polymers being one of the many solutions needed to reduce the anthropogenic environmental pollution.

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ANEXXES

Annex 1: Number of papers in searching and screening process

Title-ABS-KEY ("pyrolysis" AND "polystyrene" AN

Year: 2015-2021

Science Direct: 90 papers   Taylor & Francis: 2 papers

Research and review articles

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Science Direct: 45 papers   Taylor & Francis: 2 papers

Manual Screening

Science Direct: 22 papers   Taylor & Francis: 2 papers
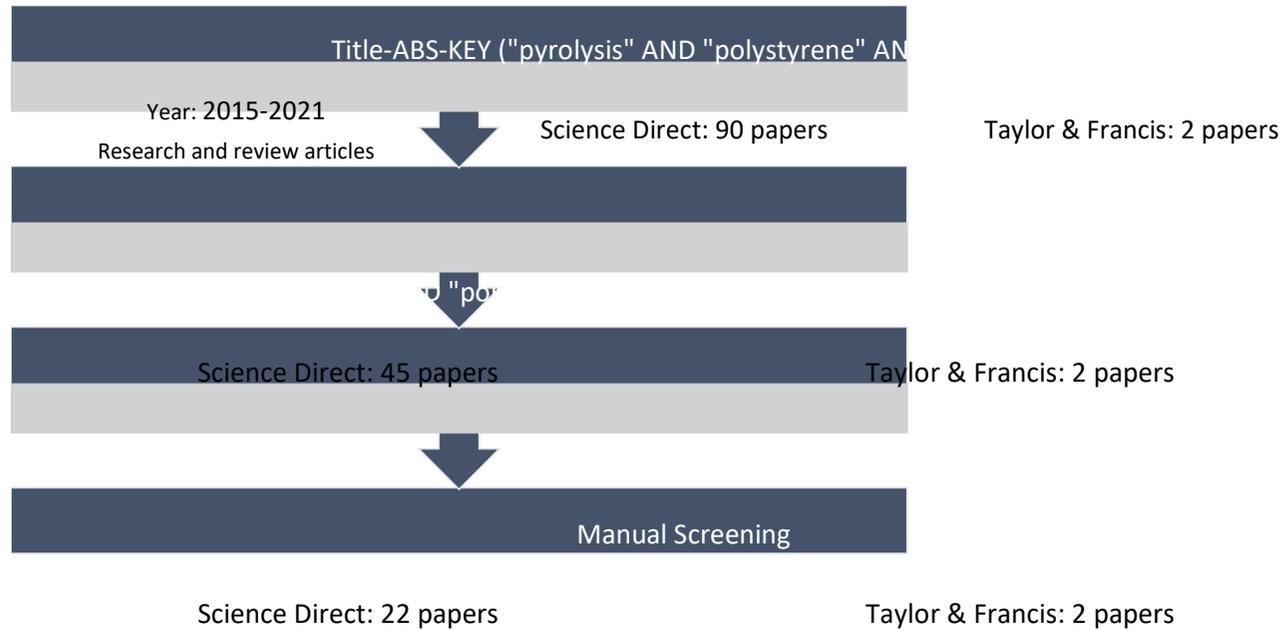
Annex 2: Complete information from each paper

N°	Article Name	Reactor Type	Catalyst	Temperature	Co-pyrolisis	Main Products	Authors
1	Thermal Catalytic Pyrolysis of Polystyrene Waste Foams in a Semi-Batch Reactor	Semi-batch	Cu/y-Al$_2$O$_3$	500°C	No	Styrene Toluene Ethylbenzene Phenyls	(Çelikgöⱡüs and Karaduman, 2015)
2	Effect of neat Kaolin and CuO/Kaolin on the yield and composition of products from pyrolysis of polystyrene waste	Batch	Kaolin – CuO/Kaolin	450°C	No	Styrene Naphthalene Phenyls	(Hadi et al., 2017)
3	Co-pyrolysis and synergistic effect analysis of biomass sawdust and polystyrene mixtures for production of high-quality bio-oils.	Fixed-bed	No	600°C	Biomass sawdust (beech, oak and fir)	Styrene Naphthalene Ethylbenzene Benzenes Phenyls	(Stančin et al., 2021)

#	Title	Reactor	Catalyst	Temperature	Feedstock	Products	Reference
4	Syngas production from co-pyrolysis and co-gasification of polystyrene and paper with CO2	Semi-batch	No	900°C	Paper waste	Syngas	(Déparrois et al., 2019)
5	Fuel production from waste polystyrene via pyrolysis: Kinetics and product distribution	Batch	No	410°C	No	Methane Ethylene Propene Butene Pentane Styrene Toluene Propapone Methane	(Nisar et al., 2019)
6	From laboratory scale to pilot plant: Evaluation of the catalytic co-pyrolysis of grape seeds and polystyrene wastes with CaO	Auger	CaO	380°C	Grape seeds	H_2 CO CO_2 Styrene Ethylbenzene	(Veses et al., 2020)
7	Thermal and Co-pyrolysis of rubber seed cake with waste polystyrene for bio-oil production	Semi-batch	No	500°C	Rubber seed cake	Styrene Benzenes Phenols Formamide	(Reshad et al., 2019)

#	Title	Reactor	Catalyst	Temperature	Feedstock	Products	Reference
8	Improvement of bio-crude oil properties via co-pyrolysis of pine sawdust and waste polystyrene foam	Fluidized bed	No	500°C	Pine Sawdust	Acetic acid, Bio-char, Styrene	(Van Nguyen et al., 2019)
9	A comparative study on co-pyrolysis of lignocellulosic biomass with polyethylene terephthalate, polystyrene, and polyvinyl chloride: Synergistic effects and product characteristics	Fixed-bed	No	500°C	Wallnut shell and peach stones	Acetic acid, Bio-char, Styrene, Benzenes, Phenyls, Phenols	(Özsin and Pütün, 2018)l
10	Co-pyrolysis of Karanja and Niger seeds with waste polystyrene to produce liquid fuel	Semi-batch	No	550°C	Karanja and niger seed	Naphthalene, Toluene, Benzenes, Phenyls, Acetic Acid, Tetrafluorohydrazine	(Shadangi and Mohanty, 2015)

11	Co-pyrolysis of lignin and plastics using red clay as catalyst in a mycro-pyrolizer	Micro-pyrolyzer	Red clay	500°C	Dealkaline lignin and LDPE	Styrene Phenols Toluene Ethylbenzene Benzenes	(Patil et al., 2018)
12	Catalytic pyrolysis of polystyrene and polyethylene terephthalate over Al-MSU-F	Batch	Al-MSU-F	500°C	PET	Styrene Benzoic Acid Toluene Ethylbenzene Benzenes	(Oh et al., 2018)
13	Stepwise pyrolysis of mixed plastics and paper for separation of oxygenated and hydrocarbon condensates	Vertical Tube	No	500°C	Polyethylene and paper waste	CO_2 Methane Styrene Toluene Ethylbenzene Benzenes Phenyls	(Sophonrat et al., 2018)
14	Investigation on thermal decomposition and kinetics study of recovered oil from electronic waste by	Semi-batch	No	450°C	No	Styrene 1, 3 propanediol Hydroxymethyl	(Khaobang and Areeprasert, 2017)

	thermogravimetic analysis					Ethylbenzene	
15	Selective production of aromatics from waste plastic by using sewage sludge derived char catalyst	Tubular Furnace	Activated Sewage Sluge Char	600°C	Polyethylene and polypropylene	Benzenes Styrene Benzenes Naphthalene Phenyls Styrene	(Sun et al., 2020)
16	Depolymerization of polystyrene at reduced pressure through a microwave assisted pyrolysis	Microwave oven	No	300°C	No	Toluene Phenyls	(Bartoli et al., 2015)
17	Experimental study on pyrolysis/gasification of biomass and plastics for H2 production under new dual-support catalyst	Fixed bed	Ni-CaO-C	800°C	Pine Sawdust	Benzenes Methane H_2 CO_2 CO	(Chai et al., 2020)

No	Title	Reactor	Catalyst	Temperature	Feedstock	Products	Reference
18	Catalytic pyrolysis of black liquor lignin by co-feeding with different plastics in fluidized bed reactor	Fluidized bed	Spent FCC (Spent fluidized catalytic cracking catalyst)	600°C	Lignin	Styrene; Benzenes; Toluene; Naphthalene; Bio-char	(Zhang et al., 2015)
19	Styrene recovery from polystyrene by flash pyrolysis in a conical spouted bed reactor	Conical spouted bed	No	500°C	No	Styrene; Toluene; Benzenes; Ethylbenzene; Phenyls	(Artetxe et al., 2015)
20	Environmental-friendly production of carbon fiber from isotropic hybrid pitches synthesized from waste biomass and polystyrene with ethylene bottom oil	Fixed bed	No	500°C	Wallnut shell and peach stones	Styrene; Phenols; Benzenes	(Özsin et al., 2019)
21				600°C	Polyethylene	Benzenes	

	Title	Reactor	Catalyst	Temp	Feedstock	Products	Reference
	Effect of catalyst contact mode and gas atmosphere during catalytic pyrolysis of waste plastics	Micro-pyrolizer	HZSM-5-zeolite			Ethylbenzene Toluene Naphthalene Styrene Benzenes	(Xue et al., 2017)
22	Effect of polyethylene terephthalate on the catalytic pyrolysis of polystyrene: Investigation of the liquid products	Quartz glass	Al-Al$_2$O$_3$	450°C	PET	Toluene Phenyls Ethylbenzene Benzenes	(Adnan et al., 2015)
23	Effect of Zn-Cl2-activated biochar on catalytic pyrolysis of mixed waste plastics for producing aromatic-enriched oil	Tubular Furnace	ZnCl$_2$-activated biochar	500°C	Polyethylene and polyproplylene	Phenyls Naphthalene	(Sun et al., 2018)
24	Origin of carbon in aromatic and olefin production products derived from HZSM-5 catalyzed co-pyrolysis of cellulose and plastics via isotopic labelling	Micro-pyrolyzer	HZSM-5-zeolite	650°C	Cellulose	Styrene Toluene Naphthalene Ethylbenzene	(Dorado et al., 2015)

Benzenes

Ethylene

Propene