

Article

Fixed Bed Batch Slow Pyrolysis Process for Polystyrene Waste Recycling

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Abstract: This study evaluates the potential of recycling polystyrene (PS) plastic wastes via a fixed bed (batch) slow pyrolysis reactor. The novelty lies in examining the reactor design, conversion parameters, and reaction kinetics to improve the process yield, activation energy, and chemical composition. PS samples were pyrolyzed at 475–575 °C for 30 min under 10–15 psi. Process yield and product attributes were evaluated using different methods to understand PS thermal degradation characteristics better. The results show that PS decomposition started within 2 min from all temperatures, and the total decomposition point of 97% at 475 °C at approximately 5 min. Additionally, analytical results indicate that the average necessary activation energy is 191 kJ/mol. Pyrolysis oil from PS was characterized by gas chromatography–mass spectrometry. The results show that styrene was produced 57–60% from all leading oil compounds (i.e., 2,4-diphenyl-1-butene, 2,4,6-triphenyl-1-hexene, and toluene), and 475 °C has the major average of conversion effectiveness of 91.3%. The results show that the reactor temperature remains the main conversion parameter to achieve the high process yield for oil production from PS. It is concluded that pyrolysis provides a sustainable pathway for PS waste recycling and conversion to value-added products, such as resins and polymers. The proposed method and analytical results are compared with earlier studies to identify directions for future studies.



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Keywords: plastic waste; polystyrene; slow pyrolysis; thermochemical conversion; pyrolysis oil

1. Introduction

1.1. Motivation and Challenges

Plastic materials from petroleum-based resources play an essential role in daily life due to their unique properties, such as low weight, high strength, and extreme durability. The top plastic applications are electronic devices, medical equipment, cars, care products, and packaging. However, plastics are synthetic and composed of large molecules that make them difficult to recycle. Proper recycling methods can address the existing challenges, especially negative environmental impacts, such as marine and land pollution, resource depletion, and soil contamination. The United States (U.S.) Environmental Protection Agency (EPA) reported in 2018 that approximately 265 million metric tons (MMT) of municipal solid wastes were generated in the U.S., accounting for 32.4 MMT of plastics. Only 2.80 MMT of high-density polyethylene (HDPE) and polyethylene terephthalate (PET) were recycled, 5.1 MMT were utilized for energy recovery, and 24.5 MMT ended up in landfills [1]. EPA estimated an average of eight MMT of plastic waste worldwide is in oceans and freshwater waters due to inadequate recycling infrastructure [1]. Recycling and converting various plastic wastes to value-added products can reduce environmental pollution and create a recycled plastic market for producing petroleum-derived products (e.g., gasoline, diesel, fuel oil, and lubricants). Due to global recycling efforts, approximately 25 million barrels of

oil are expected to be replaced with recycled plastics by 2025. During the last decade, the total plastic recycling investment has been up to \$100 billion annually [2,3]. Incineration, burning at high temperatures, is a standard plastic waste recycling process at landfills for energy (heat or power) recovery [4]. Sikdar et al. (2020) reported that low-density polyethylene (LDPE), HDPE, polypropylene (PP), and polystyrene (PS) are the most utilized and efficient sources for the recycled plastics market due to their kinematic viscosity, which is comparable to petroleum-based lubricants [5].

1.2. Background

Due to their versatility, the increasing demand for synthetic plastics also raises plastic pollution concerns. Millions of tons of plastic waste end up in oceans, rivers, and terrestrial ecosystems due to poor recycling management, causing degradation to all ecosystems. Prior studies have reported that plastic waste will continue to grow from approximately 236 to 417 MMT from 2016 to 2030 at the current disposal rates. The main plastic recycling methods are mechanical, chemical, biological, and composting. Chemical recycling is an advanced form of recycling technology that can reduce the amount of plastic disposal in ecosystems and provides two significant advantages: selectivity and low energy requirement [6]. Chemical recycling can also produce high-quality raw materials for new products, decreasing the demand for fossil fuels and other nonrenewable resources. Chemical deconstruction can be classified to selective and non-selective methods (Figure 1). The selective process includes catalytic depolymerization and solvent-based reactive depolymerization. The non-selective process includes thermal depolymerization [7–9].

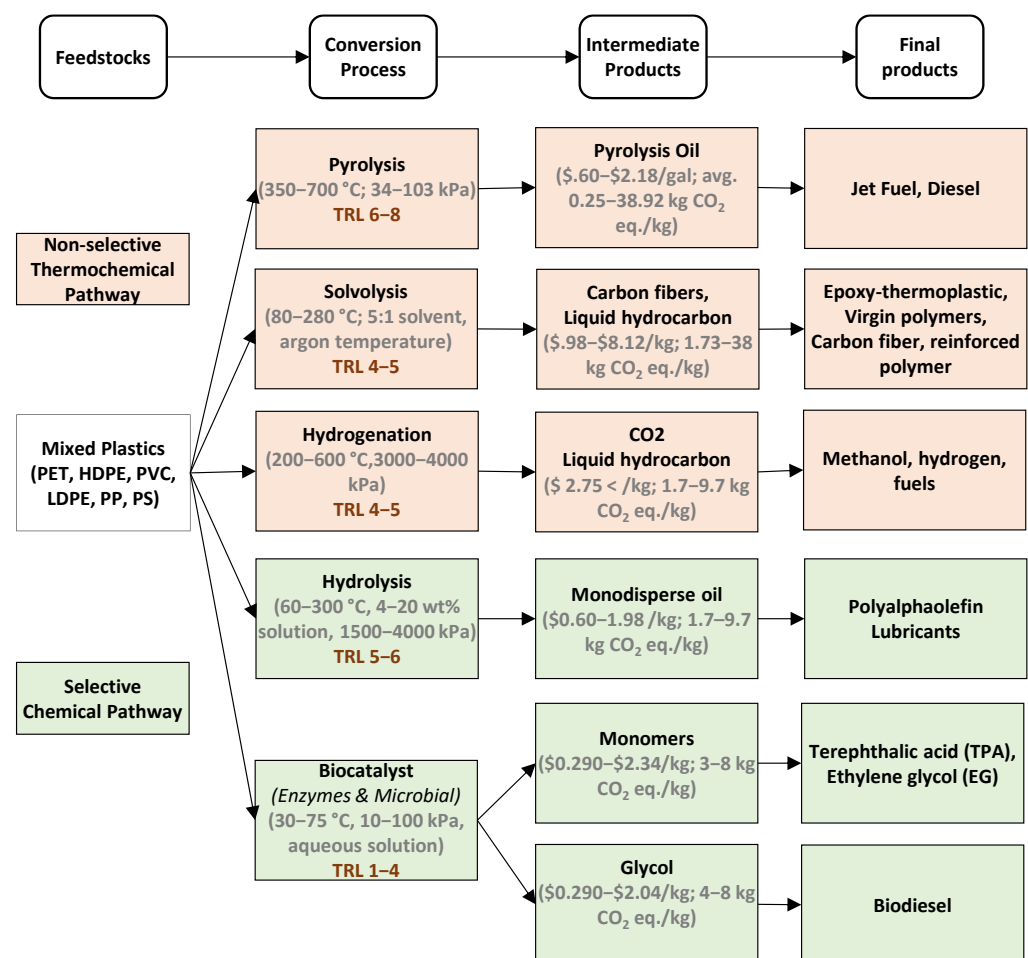


Figure 1. Fuel conversion pathways from plastic wastes.

Selective chemical pathways: chemical depolymerization is a process that depolymerizes plastic into intermediates that can be purified as virgin-like or other chemicals as raw materials, not limited to hydrogenolysis, hydrolysis, and microbial-enzymatic processes. Hackler et al. (2021) studied the production of HDPE plastic waste polyolefin lubricant by hydrogenolysis catalytic conversion. The results showed that hydrogenolysis could be economically feasible with a total production cost ranging between \$0.48–\$1.20/kg and it is environmentally friendly, producing 0.6–1.98 CO₂eq/kg of total emissions [10]. Other studies have conducted research on hydrolysis and biocatalyst depolymerization for producing other intermediates (e.g., terephthalic acid and ethylene glycol). The results have shown potential environmental benefits over incineration or landfill disposal by 3.7–5.6 CO₂eq/kg [11]. Singh et al. (2021) studied PET depolymerization by biocatalysts to produce monomers as intermediate products and terephthalic acid (TPA) as a final product. The results show potential for TPA production with a cost of \$1.93/kg and 3.7 kg CO₂eq/kg of total emissions, making enzyme catalyst a promising technology [12]. Billen et al. (2020) studied the biodegradation of polyethylene (PE) via macro-organisms to produce glycol as an intermediate and biodiesel as the final product. The results show a high cost of \$289.5 per ton and 4–8 ton CO₂eq/t, mainly due to the larvae making this process achievable but not equitable [13]. Eukert et al. (2022) studied the enzymatic hydrolysis of PET to produce TPA and ethylene. The results show a cost of \$2.04/kg and 1.88 kg CO₂eq/kg total emissions. Roux et al. (2021) studied the economic viability of upcycling PET into 5-furandicarboxylic acid as an intermediate product and producing polyethylene furanoate (PEF) and polytrimethylene terephthalate (PTT) as final products. Their techno-economic analysis results show that the production is approximately \$2.34/kg with a minimum selling price of \$3.13/kg, making it a feasible process [14].

Non-selective thermochemical pathways: thermochemical depolymerization includes but is not limited to pyrolysis, solvolysis, hydrogenation, and gasification. Pyrolysis is a process in the absence of oxygen at high temperatures, promoting the decomposition of large polymer molecules to convert them into a mixture of small intermediate chemical compounds. The mechanical pretreatment processes before pyrolysis involve sorting, metal separation, and shredding. After the pyrolysis conversion process, the hydrocarbon vapors are condensed to produce pyrolysis oil. The non-condensable gases (syngas) and pyrolysis char (biochar) can be either utilized for reheating the pyrolysis process or sold for other purposes, such as energy recovery or chemical production. Previous studies have identified recycling plants with a capacity of up to 5000 metric tons per year with a proposed oil yield of an average of 67% while only producing 38.9–250.4 kg CO₂eq of emissions. Total production cost was also reported to range from \$0.75–\$9.49/gallon of liquid oil, achieving the breakeven point within 4–6.2 years. In addition, biochar can be recovered as a byproduct utilized on different products (e.g., asphalt, concrete, insulation, and energy source cement). Recycling plastics via the pyrolysis process can mitigate approximately 100 kg CO₂eq/ton compared to emissions generated by landfill disposal [15–18].

The solvolysis process involves utilizing solvents to cleave the rigid chemical structure of polymers for recycling fibers. The primary agents are water and alcohol for the depolymerization reaction. The solvent concentration is an essential parameter in solvolysis. La Rosa et al. (2021) conducted a life cycle assessment of carbon fiber to reinforce thermoset composite via solvolysis. Their results indicated that solvolysis plastic recycling produces 0.58 kg CO₂eq/kg, making it affordable and environmentally friendly [19]. Other researchers exploring solvolysis closed loop have reported total emissions ranging from 1.7–16.2 kg CO₂eq/metric while a total cost ranging from \$0.98–1.4/kg of carbon-reinforced fiber recycled [20–22]. Hydrogenation is the cracking of hydrocarbon bonds by a catalyst and the addition of hydrogen to produce alkene and alkyne compounds. This process uses a platinum metal catalyst on a strontium titanate nano cuboid. Zhao et al. (2021) studied a consequential life cycle assessment of HDPE via hydrogenation for producing gasoline and diesel. Their results show total emission of 331.4 kg CO₂eq/ton and a total production cost of \$220.3 per ton [23].

Pyrolysis is categorized into two primary categories: fast and slow pyrolysis, which depends on operating conditions. The feedstock undergoes thermochemical decomposition between 300–500 °C for slow pyrolysis and 400–650 °C for fast pyrolysis, with a residence time of seconds for fast and anywhere from 10–90 min for slow [24]. The products derived from plastic pyrolysis are oil, char, and gas [25]. Plastic waste pyrolysis supports oil production with general yields of 37–75%, while 10–20% of the byproducts are composed of gaseous hydrocarbons and 15–25% char solids [26,27]. The slow pyrolysis process is an attractive technology for increasing the product yield of high-quality oil. As reported, a competitive advantage over other techniques includes long residence time, heat transfer control, and more effective control of inlet and outlet flow rates for better-quality products [28]. Regarding the pyrolysis products, char production is mainly favored at low temperatures between 300–450 °C, oil at intermediate temperatures ranging from 450–800 °C, while gas is dominant at high temperatures of about 800 °C. The yield of oil, char, and gas varies depending on the plastic type, particle size, temperature, heating rates, use of solvents, and pressure during the conversion. Plastic waste pyrolysis has proven challenging to commercialize as a recovery method due to waste collection and sorting and the lack of a clear pathway to analyze the value-added products from recycled plastics. A supply chain process for collection is essential to implement circular economy practices that can achieve economic feasibility for upscaling the recycling process. Recent studies have researched pyrolyzing various plastic wastes (e.g., PET, HDPE, PVC, LPDE, PP, and PS), which assessed the effects of different feedstocks at temperatures ranging between 300–500 °C. The various plastics contain different hydrogen/carbon (H/C) ratios, which is significant for oil conversion and economic feasibility [26,27]. This study focuses on oil and char production from PS wastes via the slow pyrolysis process. The oil produced from polystyrene consists mainly of styrene monomers, which can be used as raw materials to produce polystyrene for different industrial products [29,30].

1.3. Study Focus and Objectives

This study explores a fixed bed (batch) slow pyrolysis conversion process for converting plastic wastes to value-added products. The primary objectives and novelty of this study are to examine and improve the reactor design (e.g., height and capacity), conversion parameters (e.g., carrier gas pressure, reactor temperature, and residence time), and reaction kinetics (e.g., activation energy, heating rate, and chemical composition). The focus is determining the process yields and PS-derived oil composition at different temperatures. The pyrolysis reactor operates at temperatures between 450–575 °C for 30 min under 10–15 psi. The PS samples were pyrolyzed at heating rates of 5, 10, 15, 20, 25, 35, and 50 °C/min under nitrogen (30 mL/min) in temperatures ranging from 30 to 900 °C, using thermogravimetric analysis (TGA). TGA and differential scanning calorimetry (DSC) was also used to analyze thermal degradation characteristics.

2. Materials and Methods

2.1. Pretreatment Processes

The pyrolysis experiments were performed with PS as the feedstock obtained from disposable household and food plastic wastes, including beverage cups, food containers, and Styrofoam packing. A V-180 plastic grinder machine was used to produce different PS particle sizes (2–6 mm). After grinding, PS samples were dried in an oven at 90–100 °C for 12–24 h for size reduction. Table 1 presents the physical properties of the used PS samples in this study.

Table 1. Polystyrene characteristics.

Plastic Type	Particle Size (mm)	Density (g/cm ³)	Calorific Value (kJ/g)
PS	2–6	1.05	41.0 ± 1.0

2.2. Pyrolysis Conversion Process

The slow pyrolysis of PS was conducted with 60–80 g of PS samples in a stainless-steel batch reactor with temperatures between 475–575 °C and pressures between 10–15 psi with a residence time of 30 min (Figure 2). As the PS thermally degrades, pyrolysis products formed are condensable vapors, non-condensable products, and char. The batch reactor conditions are set with a programmable logic controller. Heating tape and a plate heater were used to supply heat to the batch reactor.

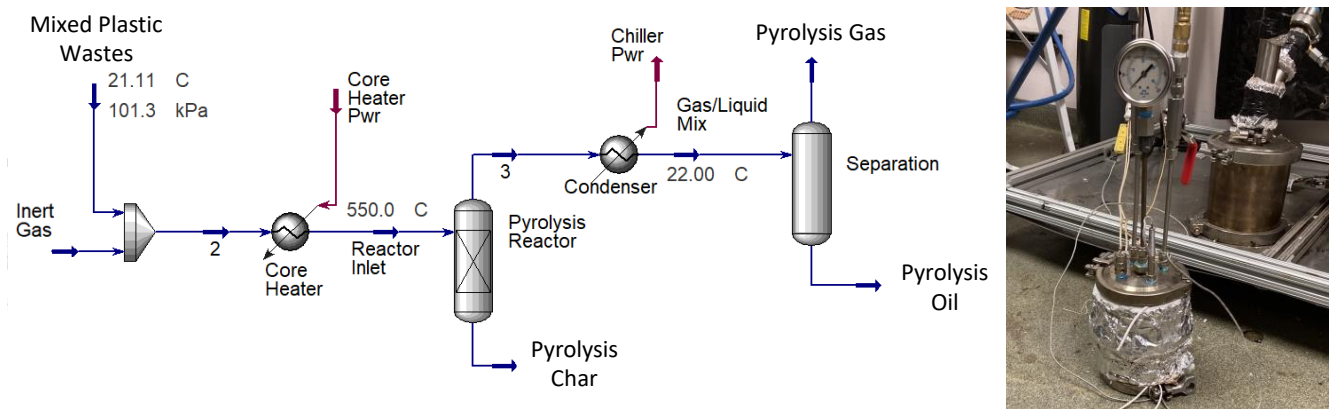


Figure 2. Fixed bed (batch) slow pyrolysis reactor for oil and char production from PS.

Table 2 presents the main parameters of the proposed batch slow pyrolysis reactor. The pyrolysis gases exit the reactor to a condenser column at 5 °C, are rapidly cooled, and the vapors condense in an oil trap succeeding the condenser. The oil produced was collected and stored in a refrigerator at 5 °C to prevent further chemical structure changes. The produced char was collected in the bottom of the reactor, weighed, and stored at room temperature. The mass difference estimated the yield of non-condensable gases byproduct. The experiment conditions were structured to analyze the temperature effects in the batch pyrolysis reactor. Experiments 1–3 were conducted to study the temperature of PS depolymerization at 475 °C. In experiments 4–6, the reactor temperature was increased to 525 °C. Finally, the batch reactor temperature was raised to 575 °C in experiments 7–9.

Table 2. Slow pyrolysis reactor configurations.

Parameters	Values
Reactor temperature (°C)	400–575
Reactor height (mm)	152
Reactor diameter (mm)	63.5
Condenser height (mm)	305
Condenser diameter (mm)	63.5
Reactor capacity (gram)	150

2.3. Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC)

TGA was performed on PS (5–6 mg), using a PerkinElmer TGA-7 instrument from 30 to 900 °C at heating rates (β) of 5, 10, 15, 20, 25, 35, and 50 °C/min under nitrogen (30 mL/min) to determine activation energy (E_a) and thermal degradation behavior. Isothermal TGA was also used to determine the mass yield of char during pyrolysis at a given temperature. The temperature was ramped from 30 °C at 200 °C/min to 475, 525, and 575 °C and then held for 30 min. The TGA data were analyzed using Pyris v11 software. Additionally, DSC was performed on the PS samples and char samples (8–9 mg) using a PerkinElmer DSC-7 instrument from 25 to 250 °C at a ramp rate of 10 °C/min under N₂ (20 mL/min) to determine glass transition temperature (T_g).

2.4. Pyrolysis Oil and Char Analysis

The oil samples, 2 mg in CH_2Cl_2 (1 mL), containing 1,2,4-trichlorobenzene (800 $\mu\text{g/mL}$) as an internal standard, were analyzed by gas chromatography–mass spectrometry (GC–MS) using Trace 1300-ISQ, ThermoScientific. Separation was achieved on the ZB-5 capillary column (30 m \times 0.25 mm \varnothing , 0.25 μm coating, Phenomenex, Torrance, CA, USA), using a temperature program of 40 $^{\circ}\text{C}$ (1 min) to 280 $^{\circ}\text{C}$ (10 min) at 5 $^{\circ}\text{C/min}$. The identity of the peaks was determined using authentic standards and matching spectra with the NIST 2017 library. Fourier-transform infrared (FTIR) spectra of PS and char samples were obtained using a Thermo-Nicolet iS5 spectrometer equipped with a ZnSe attenuated total reflection (iD5 ATR) accessory. FTIR spectra were baseline corrected using the Omnic v9.3 software (Thermo-Nicolet).

3. Results and Discussion

3.1. Thermal Analysis

TGA analyzed the thermal degradation and kinetic performance of PS. DSC and TGA are standard techniques that help measure thermal transition for identifying T_g and thermal degradation (T_d) for calculating activation energy under different conditions. The T_g of PS was 103.2 $^{\circ}\text{C}$. Figure 3 presents the TGA results of PS, indicating that the kinetics degradation encompasses a single stage with no water content at the beginning of the degradation process. The cleaving of polymer structure chains can explain the observed degradation. The equilibrium is achieved fast with an increase in temperature. Previous studies reported that the pyrolysis of PS occurs in three stages (i.e., initiation, transfer, and termination) of the radical chain process [31,32], which is crucial for designing and optimizing the pyrolysis conditions and vessels. Experiments were developed at three different temperatures (475, 500, and 575 $^{\circ}\text{C}$) to examine the effect of temperature on mass loss with respect to time.

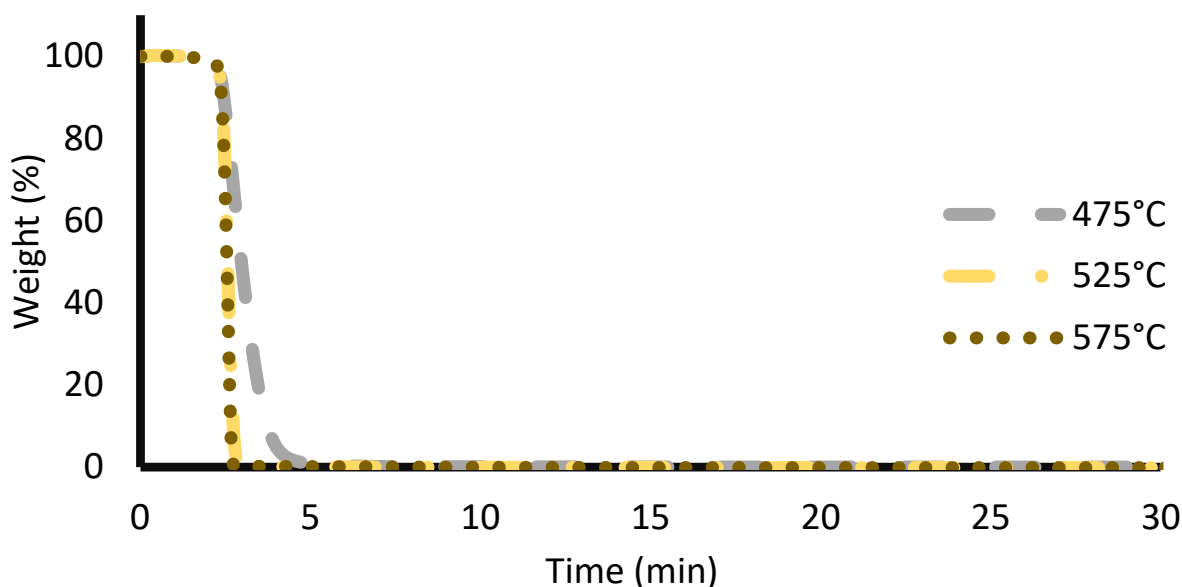


Figure 3. Isothermal TGA at 50 $^{\circ}\text{C}$ increments.

Additionally, the isothermal TGA indicates that the decomposition of PS plastic waste started within 2 min from all temperatures and the total decomposition point of 97% at 475 $^{\circ}\text{C}$ at approximately 5 min (Figure 3). By increasing the temperature from 475 $^{\circ}\text{C}$ to 575 $^{\circ}\text{C}$, the reaction reached maximum rates and showed a 50% time reduction for weight loss, while the complete decomposition was reached within 3 min. The TGA experiments indicate that PS waste degradation was achieved at a maximum point of 3 min and a temperature of 525 $^{\circ}\text{C}$ at the specified heating rates. Previous studies determined iso-conversional

methods are dependable for calculating the activation energy with the assumption of a first-order reaction model because maintaining a constant extent of conversion results in a reaction rate that is only a function of temperature [30,33].

This study used the Ozawa Flynn Wall (OFW) equation to analyze PS waste thermal degradation kinetic parameters. Figure 4 presents the iso-conversional effective activation energy dependencies of $\log \beta$ (K/T), which shows a linear regression of the OFW method in the conversion (α) range of 10–90%. The result indicates that iso-conversional lines have comparable kinetic parameters [33,34]. The analysis of E_a values shows that the degradation stage is constant at an average of 191 kJ/mol in $10\% \leq \alpha \leq 90\%$, with an almost linear relationship from $30\% \leq \alpha \leq 90\%$, and is led by a single reaction step (Table 3). The E_a analysis was compared with prior studies. For example, Nisar et al. (2019) reported activation energy ranging from 83.0 to 164 kJ/mol at heating rates of 5, 10, 15, and 20 °C/min [33]. While utilizing TGA of PS waste and virgin PS, previous studies observed an activation energy of 137 and 172 kJ/mol [35,36]. Aguado et al. (2003) reported 207–223 kJ/mol values at temperatures between 340–390 °C [37]. The activation energy of PS polymers can be heavily influenced by properties, such as molecular weight, density, and heating value. The results of this study are comparable with the findings reported by previous PS thermochemical decomposition reports.

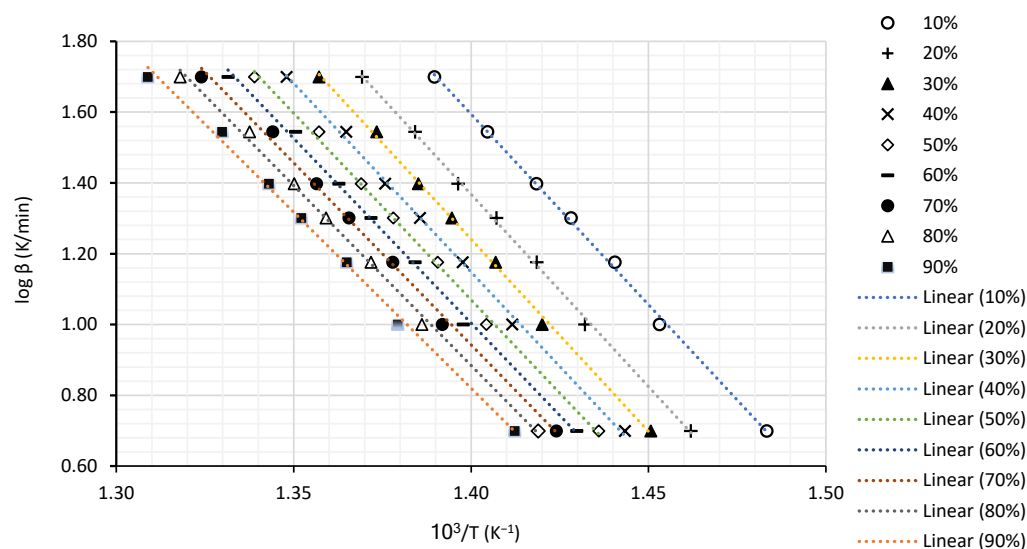


Figure 4. Apparent activation energy determination of PS.

Table 3. Activation energy of PS at different conversion factors.

Conversion Factors (α)	Slope	E_a (J/mol)
10%	10.76	196
20%	10.87	198
30%	10.86	198
40%	10.67	194
50%	10.54	192
60%	10.43	190
70%	10.28	187
80%	10.16	185
90%	9.95	181
Average		191

3.2. Product Yield

This study focuses on developing a slow pyrolysis setup to maximize the oil conversion yield from PS. The grinder and oven were utilized as pretreatment for size reduction. The

experiments were conducted at different temperatures (i.e., 475, 525, and 575 °C) to explore the temperature effects on the yield (Table 4) and quality (thermal stability) of the desired oil produced.

Table 4. PS pyrolysis products' yield in various temperatures.

Experiments	Temperature (°C)	Oil Yield (%)	Char Yield (%)
1	47.5	45.7	34.1
2	475	47.5	27.8
3	475	69.2	8.5
4	525	53.9	14.4
5	525	64.8	1.9
6	525	57.3	8.3
7	575	54.0	0.7
8	575	62.2	10.6
9	575	54.7	0.0

Exploring different temperatures at 30 min residence time allows for identifying the optimum temperature for slow pyrolysis of PS plastic waste while minimizing time and maximizing the oil yield. Miandad et al. (2016) determined that the decomposition started at 400 °C while reaching the optimal decomposition point of 91% at 450 °C, and while increasing the temperature to 650 °C resulted in 4–5% of weight loss, using TGA. Furthermore, when using a batch reactor at a residence time of 75 min, oil yield increased from 76% to 80.8% when increasing temperature from 400–450 °C while char decreased from 16% to 6.1% [38]. Prior studies utilizing batch reactors reported that maximizing oil yields from 69% to 91% at temperatures of 400–475 °C. Therefore, a controlled environmental condition (e.g., temperature and residence time) is a significant factor to consider while using small-scale reactors, maximizing oil yields, and minimizing char waste.

3.3. Product Characterization Results

The GC–MS analysis of PS condensed volatile products produced at 475–575 °C and were analyzed by GC–MS equipment (Trace 1300-ISQ, ThermoScientific) under various retention times, and trace mass in different types of aromatic hydrocarbon compounds were present in the analysis (Figure 5 and Table 5). Furthermore, the degradation of PS tends to favor depolymerization reaction due to the high stability of the benzylic radical intermediate, which leads to a high yield of aromatic compounds, such as styrene, toluene, and α -methyl styrene. The polyaromatic formation reactions of the radicals also lead to a noticeable concentration of polyaromatic hydrocarbons (i.e., 1,3-diphenyl-propane, 2,4-diphenyl-1-butene, and 2,4,6-triphenyl-1-hexene). Therefore, it can be concluded that the results of this GC–MS study align with previous studies [39]. Jaafar et al. (2022) reported that volatile products obtained from PS feedstock via pyrolysis were composed primarily of styrene, α -methylstyrene, and toluene [40]. Aguado et al. (2003) informed that ethyl benzene and toluene concentration increases at higher temperatures, while styrene compounds should decrease [37].

The pyrolysis chars were analyzed by DSC and FTIR spectroscopy. DSC was used on PS and char samples to investigate the transition temperature. The char samples 1, 2, 3, 4, 5, 6, and 8 were hard and glassy lumps in nature with T_g of 60, 65, 76, 60, 84, 82, and 87 °C, respectively. The chars have a lower T_g (between 16 and 43 °C lower) than PS, suggesting that the molar mass decreased. Solid char sample 7 was a powder and did not show a T_g . FTIR spectral analysis of PS pyrolysis char samples 1, 2, 3, 4, 5, and 6 were very similar to PS (Figures 6 and 7). DSC study shows that char sample characteristics are very similar to PS. Char samples 7 and 8 had bands associated with PS and char [41].

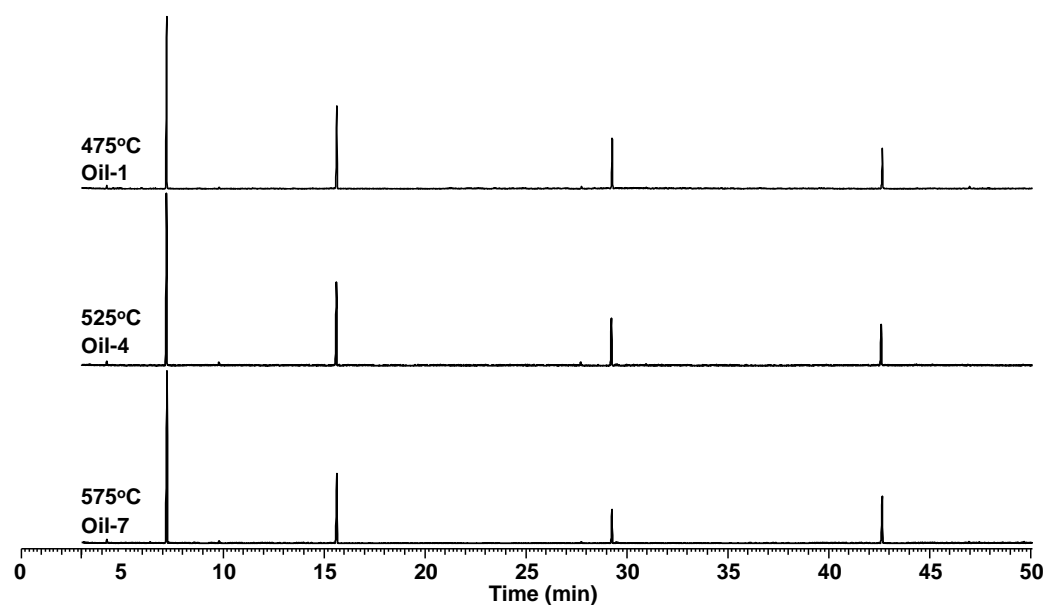


Figure 5. GC-MS chromatograms of PS pyrolysis oil-1, oil-4, and oil-5.

Table 5. PS pyrolysis oil composition.

Compound	M+ (<i>m/z</i>)	RT (min)	475 °C (mg/mg Oil)	525 °C (mg/mg Oil)	575 °C (mg/mg Oil)
toluene	92	4.23	0.008 ± 0.003	0.012 ± 0.001	0.011 ± 0.004
ethyl benzene	106	6.39	0.00	0.001 ± 0.002	0.003 ± 0.001
styrene	104	7.2	0.570 ± 0.016	0.565 ± 0.029	0.600 ± 0.021
a-methyl styrene	118	9.8	0.002 ± 0.003	0.010 ± 0.000	0.007 ± 0.001
1,3-diphenyl-propane	196	27.76	0.008 ± 0.001	0.009 ± 0.003	0.003 ± 0.002
2,4-diphenyl-1-butene	208	29.28	0.178 ± 0.009	0.147 ± 0.026	0.101 ± 0.010
2,4,6-triphenyl-1-hexene	312	42.66	0.145 ± 0.010	0.139 ± 0.009	0.158 ± 0.012
Total			0.913 ± 0.012	0.883 ± 0.006	0.883 ± 0.022

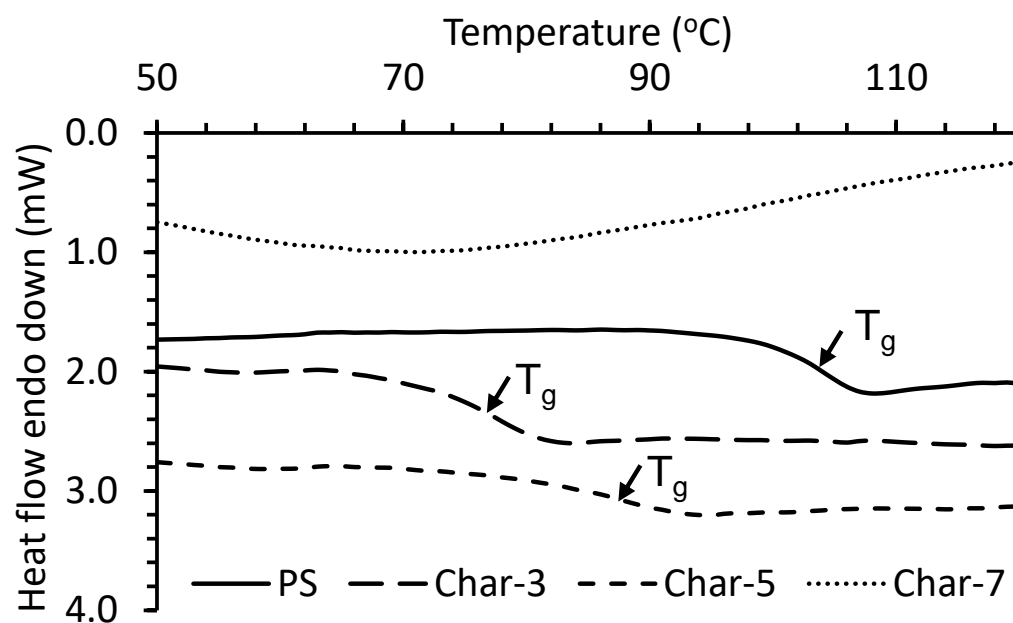


Figure 6. DSC thermograms of PS and char-3, char-5, and char-7.

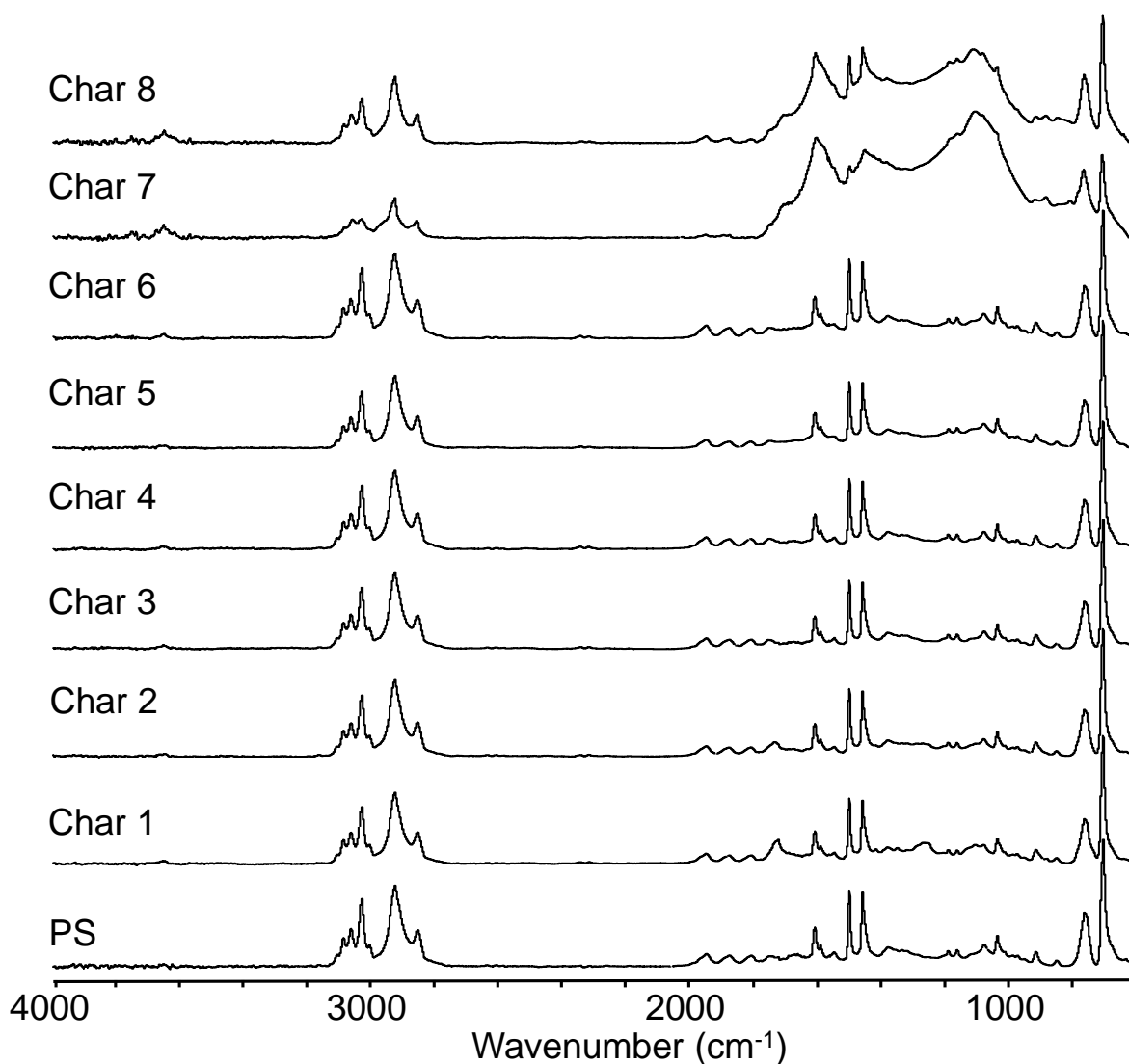


Figure 7. FTIR spectra of PS and char samples.

Plastic is a highly versatile consumer product due to its low weight, high strength, and durability advantages, making it an essential part of many industries, such as packaging, transportation, and agriculture. However, plastic-based products have rigid chemical structures, causing environmental degradation due to the lack of sustainable waste disposal methods. Pyrolysis is a thermochemical technology that operates in the absence of oxygen, degrading complex rigid molecule polymers into a short chain by heat and pressure application under inert conditions. The slow pyrolysis advantage is the duration leading to superior heat transfer and heat control flow rates of inlet and outlet with higher liquid yield making it a practical and sustainable waste management route for PS chemical recycling [28]. This study explored slow pyrolysis with 30 min of residence time to better understand the production of value-added products due to limited articles on the effects of reactor design and pyrolysis duration. In addition, the key parameters for producing high-quality intermediate products are feedstock type, conversion temperature, and residence time (Table 6). The intermediate products can be upgraded to value-added products, such as energy sources, fuel lubricants, and fuel additives (Figure 1). Currently, the technological readiness level (TRL) of plastic pyrolysis is between 6–8 (pre-commercial demonstration in expected conditions), which needs further studies, especially on reactor design for mixed plastics and scalability to reach TRL 9 (commercial operation in relevant environments).

Table 6. Recent studies on plastic waste recycling via the pyrolysis process.

Study	Research Focus	Feedstock Type	Temperature (°C)	Residence Time (min)	Process Yield (%)		
					Oil	Char	Gas
[42]	Process yield	PS	450–600	20	100.0	0.0	0.0
[43]	Oil quality	PP	500	60	84.9	10.5	4.6
[44]	Process yield	LDPE	420–510	–	87.0	8.4	4.4
[45]	Pyrolysis oil and gases	HDPE, red oak	525–675	54–68	57.6	14.0	36.7
[46]	Process yield	PS	400–500	60–120	78.5	8.9	12.6
[47]	Pyrolysis gases	PS	500	–	71.0	27.0	2.0
[48]	Process yield	PS, PE, PP, and PET	450	75	40.0	18.0	42.0
[49]	Techno-economic assessment	PE, PS, PP	530	–	87.2	8.7	4.1
[50]	Process yield	PP	500–650	–	88.0	7.0	5.0
[51]	Literature review	Various	300–900	20–150	84.0	3.0	13.0
[52]	Process yield	HDPE, LDPE, PP	300–900	30	67.5	17.3	15.3
[53]	Pyrolysis oil and gases	PE	200–800	15–75	83.7	5.0	11.3
[54]	Process yield	PP	400–460	70	84.3	5.9	9.7
This Study	Process yield and characteristics	PS	475–575	30	69.2	8.5	22.3

4. Conclusions

This study successfully converted waste polystyrene to oil and char products. PS pyrolysis conversion demonstrated a one-step process, using Ozawa Flynn Wall and isothermal methods. The PS char (solid) product contained partially reacted PS, and further pyrolysis is required for complete conversion. The PS slow pyrolysis oil contained predominantly styrene with the presence of dimers and trimers. Styrene can produce PS or vinyl-ester resins but needs to be refined and distilled to obtain a pure fraction. The results show that the conversion temperature remains the main parameter to achieve a high yield and quality for oil production from PS. It is concluded that pyrolysis can provide a sustainable pathway for PS waste recycling and conversion to value-added products, such as various chemical compounds. Future studies will (a) examine the use of the PS pyrolysis oil for use in polymers and (b) optimize the pyrolysis process for oil yield and styrene content.

Author Contributions: G.A.: Conceptualization, Methodology, Software, Formal Analysis, Investigation, Data Curation, Writing—Original Draft. A.M.: Writing, Methodology, Conceptualization, Reviewing, Editing, Resources, Supervision, Project Administration, Funding Acquisition. A.G.M.: Writing, Method Development, Conceptualization, Reviewing, Editing, Resources, Supervision, Funding Acquisition. E.S.: Writing, Editing, Data Curation, Software, Validation, Analysis, Investigation. F.S.: Writing, Data Curation, Software, Validation, Analysis, Investigation. All authors have read and agreed to the published version of the manuscript.

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