Enhancing Sustainable Waste Management: Hydrothermal Carbonization of Polyethylene Terephthalate and Polystyrene Plastics for Energy Recovery

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Abstract

Hydrothermal carbonization (HTC) of single plastic polymers such as polyethylene terephthalate (PET) and polystyrene (PS) has not yet been explored on a large scale, particularly their thermal behavior, chemical transformations under subcritical conditions, and the energy properties of the resultant hydrochar. This study investigated these aspects by employing techniques, such as thermogravimetric analysis (TGA), Fourier transformed infrared spectroscopy (FTIR), elemental and calorific analysis. The results show that PET hydrochar has a superior energy densification (1.37) and energy yield (89%) compared to PS hydrochar (1.13, 54%). Hydrothermal carbonization modifies the chemical structure of the polymers by increasing the number of carbonyl groups (C=O) in PET and forming new ones in PS, and by enhancing hydroxyl groups (O-H) in PET while retaining them in PS. Both materials preserve their aromatic and aliphatic structures, with the introduction of alkenes groups (C=C) in the PET hydrochar. PET hydrochar begins to decompose at lower temperatures (150-270°C) than PS hydrochar (242-283°C) but reaches higher peak temperatures (420-585°C vs. 390-470°C), with both types achieving similar burnout temperatures (650-800°C). PET hydrochar recorded a higher activation energy (121-126 kJ/mol) than PS hydrochar (67-74 kJ/mol) with the Mampel first-order reaction model as the best fit.

Keywords: Plastic waste management, Sustainability, Plastic hydrochar, Circular economy, Hydrothermal carbonization

1. Introduction

According to the United Nations Environmental Programme (UNEP), the global production of plastic exceeds 430 million tons every year, of which two-thirds is used in products with a brief lifespan which quickly become waste, ending up in oceans and the human food chain [1]. By 2060, the world may generate an estimated billion tons of plastic waste. UNEP highlights concern over chemicals linked to plastics, citing the Basel, Rotterdam, and Stockholm Conventions of the International Panel on Chemical Pollution [2]. It identifies over 13,000 chemicals in plastic production, with ten groups including flame retardants and phthalates posing health and environmental risks. Over 3,200 substances are hazardous, impacting health and raising concerns about endocrine disruption and cancer from leaching into food and water [2–4]. The presence of plastics, particularly in marine ecosystems, poses severe threats to biodiversity, contributes to soil and water contamination, and exacerbates aesthetic degradation of natural and urban spaces [5]. The production, decomposition and incineration of plastics contributes to greenhouse gas emissions, impacting global climate change [6] and releases harmful toxins into the air, degrading air quality and affecting respiratory health [7].

This wide-ranging impact necessitates a comprehensive approach in managing plastic waste [8], encompassing a reduction in usage, enhanced recycling, and increased public awareness [9–13]. Different policies have been adopted by different countries to reduce plastic usage and improve waste management strategies. Some policies adopted by South Korea include a ban on single-use plastics in various establishments and the introduction of the Volume-Based Waste Fee (VBWF) system utilizing RFID technology for waste disposal, along with the Extended Producer Responsibility (EPR) policy requiring producers to manage the waste from their products. The

Resource Circulation Act (RCA) and the Plastic Waste Control Plan (PWCP) are also aimed at promoting efficient resource use and reducing plastic waste [8, 14–16].

Despite these measures, the limitations of traditional waste management methods, such as landfill and incineration, highlight the urgent need for innovative solutions [6]. The pursuit of circularity in waste management has led to the innovation and adoption of several advanced technologies aimed at converting waste into valuable resources [17–19]. These technologies are designed to close the loop on waste, minimizing environmental impact while recovering energy and materials [19–24]. Gasification transforms carbon-based materials into syngas, through high-temperature reactions with controlled oxygen, useful for power generation and as a feedstock in the chemical industry [25–28]. Pyrolysis thermally decomposes materials in an inert atmosphere, altering their chemical composition to create products such as py-oils used for heating in boilers which can aid in waste reduction and energy recovery [29–42]. Hydrothermal processing employs hot, pressurized water to break down wastes into either hydrochar, gas or oil, which are value-added products, and is ideal in processing wet waste without pre-drying [43–49]. These technologies are integral to advancing sustainable waste management and embodying the circular economic principles [28, 29, 34].

This study aims to explore the viability of hydrothermal carbonization (HTC) technology in transforming plastic waste into a valuable resource, representing an innovative approach to waste management, offering circularity in plastic waste management and energy recovery [50]. HTC is a thermochemical conversion process that occurs at moderate temperatures and pressures, typically between 180-250°C and 10 to 40 bar [51]. It occurs in a closed system using water as the reaction medium [52], making HTC more energy-efficient and eco-friendly than similar processes such as hydrothermal liquefaction or gasification [50, 53]. The role of water as a solvent in hydrothermal processing is critically influenced by its dielectric constant [52], which is notably high at room temperature, enabling it to dissolve many ionic and polar substances effectively. However, as the temperature increases towards the critical point (374°C and 22.1 MPa), the dielectric constant decreases significantly. This reduction broadens the solvation capabilities of water, allowing it to dissolve non-polar substances that are typically insoluble under normal conditions [54]. At the critical point, water undergoes transformative physical and chemical changes, becoming a supercritical fluid that exhibits neither pure liquid nor pure gaseous properties [55], allowing it to adjust its solvency according to the needs of the molecular structures it encounters [56–58]. This state significantly diminishes the ability of water to stabilize charged particles [52], thereby enhancing its interaction with non-polar molecules [59]. Additionally, near this point, water maintains a high diffusivity like gases while its density increases, boosting its ability to penetrate and dissolve non-polar molecules [58]. The increased thermal motion at these higher temperatures helps overcome intermolecular forces in non-polar substances, facilitating their dissolution. While HTC operates under subcritical conditions, the elevated temperatures and high pressures ensure that water remains liquid, thus retaining its enhanced solvent properties [60]. The dielectric properties of water at 200°C resemble those of room-temperature methanol, while at 300°C they are like room-temperature acetone, and at 370°C they compare to methylene [59]. This capability is crucial for breaking down complex plastic materials, as it disrupts the hydrogen bonding within polymers, aiding in their decomposition into simpler molecules that eventually form hydrochar [60]. In HTC, water also acts as a weak acid catalyst, promoting the hydrolysis of polymers into simpler structures that undergo further chemical reactions like dehydration and decarboxylation, crucial for producing stable, carbon-rich hydrochar [61, 62].

Some studies have successfully reported the conversion of various types of feedstocks to evaluate their potential for sustainable energy recovery through HTC [50, 63]. For example, proximate analysis on several feedstocks before carbonization, including polyvinyl chloride (PVC), food waste, lignite, sub-bituminous and low-rank coal revealed that polyvinyl chloride (PVC) contained the highest volatile matter, within the range of 93 to 95%, and also the lowest levels of fixed carbon (4–6%) and ash content (0.44%)[50, 64]. By comparison, all coal varieties demonstrated significantly high fixed carbon contents and the lowest volatile matter percentages, spanning from 34 to 59%. These coal types also had higher ash content, ranging from 2 to 9.6%, which is similar with food waste (1.7–9.2%) [50, 64]. Ultimate analysis further emphasized the chemical structural changes during HTC, where the mixed hydrochar developed fuel characteristics closer to bituminous coal and high-quality fuel oil [64, 65]. Another study reported the heating values of most hydrochars to be significantly higher than those of the individual feedstocks, with mixed waste hydrochars approaching the energy content of coal [64]. In that study, PVC (20MJ/kg) was blended with corncob (19MJ/kg) and the resultant hydrochar had a higher heating value (32.8 MJ/kg) than their respective feedstocks. This suggests that HTC not only aids in energy densification but also enhances the energy recovery potential of waste polymers, making it a promising technology for sustainable waste management [64]. Similar findings were found in the study of Iniguez [66], where mixed plastic marine debris was decomposed and converted to hydrochar with slightly improved heating value from 36 to 39 MJ/kg at varying temperatures of 220 to 250^{o}C.

HTC provides several advantages over traditional pyrolysis and gasification, primarily due to its operation at lower temperatures (180°C to 250°C), which significantly reduces the required energy for heating [50, 67]. HTC efficiently processes a variety of feedstocks, including those with high moisture content, eliminating the need for pre-drying and thus reducing energy and operational costs. Additionally, HTC does not typically require catalysts, thus removing costs associated with catalyst handling and disposal [56]. Environmental benefits include reduced emissions of volatile organic compounds and greenhouse gases due to lower operating temperatures, alongside the carbon sequestration capabilities of the hydrochar produced, which can help reduce atmospheric CO_2 levels [51, 68, 69]. The technology operates in a water-rich environment, which helps minimize the release of harmful emissions and is particularly effective in handling plastic waste, converting it into usable hydrochar for energy recovery [50]. This contributes to a circular economy by transforming waste into valuable products, promoting resource efficiency, and facilitating compliance with strict environmental regulations due to lower emissions [51].

Hydrochar is used as a solid fuel in coal furnaces and cement rotary kilns, where its high carbon content and calorific value are particularly advantageous. Hydrochar also plays a role in environmental remediation [51], effectively removing heavy metals and halogens [70] like chlorine from environments due to its strong adsorptive properties. Its adsorptive properties also make hydrochar useful in water treatment processes [71], helping to adsorb contaminants and improve water quality [50, 54, 72–77]. In agriculture, hydrochar is valued for soil amendment by enhancing soil fertility and water retention while sequestering carbon, thus helping to reduce atmospheric CO_2 levels [70, 78, 79]. Additionally, the porous structure and high surface area (2300-3000m^2g^{-1}) of activated hydrochar makes it a suitable precursor for carbon-based materials such as supercapacitors, direct carbon fuel cell and catalysts in advanced materials technology, where high reactivity and conductivity are required [50]. Hydrochar enhances energy recovery from waste by improving biomethane yields through various mechanisms such as facilitating direct electron transfer, providing additional organic substrates, supporting microbial growth, and enhancing syntrophic microbial interactions [80, 81]. These contributions make hydrochar a valuable component in the optimization of anaerobic digestion processes for more efficient and higher yield biogas production [82]. Hydrochar significantly enhances volatile fatty acid production and recovery in anaerobic digestion, thereby improving methane yields. This is due to its ability to accelerate the solubilization and hydrolysis of organic matter, increase acidification, and interact beneficially with microbial biomass. Additionally, hydrochar mitigates the inhibitory effects of ammonia in anaerobic digestion processes, optimizing conditions for methanogenic bacteria [80, 83, 84]. These diverse applications of hydrochar not only demonstrate its versatility but also underline its contribution to sustainable waste management. By converting waste into valuable products like hydrochar, HTC promotes the recycling and reuse of materials, reduces reliance on landfills, minimizes environmental pollution, reduces the ecological footprint of human activities, and supports a circular economy [59, 60, 78, 79].

HTC has been studied extensively at the laboratory scale, with a major focus on biomass conversion [63, 72, 76, 78, 79, 85]. Several studies have been published as review articles which highlight the potential of hydrothermal carbonization [5, 50, 54, 60, 78] while a few others studied the cohydrothermal carbonization (coHTC) of biomass and PVC waste centered on the dechlorination of PVC [66, 86, 87]. Some researched mixed plastic waste conversion using HTC while some focused on coHTC of plastic waste and biomass [64, 88]. Among these studies, there is limited knowledge on the conversion of single polymer (plastic) waste into hydrochar. Also, there is limited knowledge on large-scale conversion. This study explores the possibility of converting single waste plastic to hydrochar by understanding the degree of conversion, yield, thermal behavior, chemical transformations, fuel quality, and chemical composition of the resultant plastic hydrochar. This study used a 200-L reactor to demonstrate the possible behavior in real-world waste management scenarios and establish the feasibility of large-scale conversions [89].

This study sets out to investigate the behavior of subcritical fluids on polar and non-polar polymers of similar structure, to see if it can decompose materials of different polarities. We chose to focus on polyethylene terephthalate (PET), a polar aromatic polymer due to the oxygen atoms within its terephthalic acid monomers, including carbonyl groups that significantly enhance its polarity, and on polystyrene (PS), a non-polar aromatic polymer with carbon and hydrogen atoms with phenyl rings that lack polar functional groups [14]. Annually, over 82 million metric tons of PET are manufactured worldwide [90]. In 2022, the worldwide production capacity for PS was 15.44 million metric tons. This figure is projected to increase modestly by 2026, reaching an expected production capacity of 16.75 million metric tons [91]. PET and PS possess distinct properties that make HTC particularly effective for their transformation [92]. PET, a polyester composed of ethylene glycol and terephthalic acid [93], features ester bonds that readily undergo hydrolysis under the high temperatures and pressures in HTC, leading to breakdown into smaller, water-soluble molecules that form hydrochar. PET is thermally stable [94], yet it decomposes efficiently in the presence of hot, pressurized water. In contrast, PS is built from styrene monomers, forming a simpler, more brittle structure with benzene rings [95] that, though less prone to hydrolysis [96, 97], may thermally decomposed in HTC conditions. This process modifies or removes benzene rings, producing simpler carbon structures that also form hydrochar. The hydrochar derived from both PET and PS boasts high carbon content and stability, with properties like increased porosity that make it valuable for energy production and soil amendment (if completely decomposed). This conversion process does not only manage plastic waste but also promotes environmental sustainability through carbon sequestration, highlighting the role of HTC in mitigating the ecological impacts of plastic waste [50].

Despite these properties, hydrothermal carbonization of single plastic polymers such as polyethylene terephthalate (PET) and polystyrene (PS) has not yet been studied on a large scale, particularly regarding their thermal behavior, chemical transformations under subcritical conditions, and energy properties of the resultant hydrochar. As such, this study employed a variety of analytical techniques to thoroughly evaluate the properties of hydrochar derived from PET and PS plastic wastes. These methods included proximate analysis to determine the moisture, volatile matter, fixed carbon, and ash content of the hydrochar, essential for understanding its overall composition and quality. Ultimate analysis is used to provide a detailed elemental breakdown (carbon, hydrogen, nitrogen, sulfur, and oxygen), crucial for assessing the environmental impact of hydrochar and its suitability for energy applications. Calorific analysis measures the energy content of the hydrochar, indicating its potential as an alternative energy source. Fourier Transform Infrared Spectroscopy (FTIR) is utilized to identify functional groups and analyze the chemical structure of the hydrochar, which aids in understanding its chemical stability and potential applications. Thermogravimetric/derivative thermogravimetric (TG/DTG methods are employed to quantitatively analyze the thermal stability and decomposition patterns of the plastic materials under study, providing data on the mass loss and rate of decomposition at various temperatures. This information is crucial in determining the optimal conditions for HTC and predicting the behavior of plastics under scaled-up conditions. The results from these techniques provide a comprehensive profile of hydrochar derived from PET and PS waste. High-quality hydrochar with favorable chemical and physical properties can be leveraged in various sustainable waste management and energy recovery initiatives. From an energy recovery perspective, its high calorific value and advantageous elemental composition make hydrochar a viable solid fuel alternative that could lessen reliance on non-renewable energy sources.

A follow-up study will further investigate wastewater (condensed steam), energy balance, optimization of process conditions, feasibility, techno-economic and life cycle analysis.

2. Materials and Methods

2.1. Reactor description

The HTC batch reactor is used for processing. The reactor is made of high pressure and acid-resistant alloy steel which ensures durability and safety. The pilot reactor has an inbuilt automated system with temperature and pressure sensors for high pressure regulation. There is one inlet for waste feeding (Fig. 1D) and one outlet for hydrochar discharge (Fig. 1E). To enhance proper distribution of heat across the waste material, the pilot plant has three independent heaters (coiled around the reactor and covered with light steel), where two are located at the different ends of the reactor and one at the center (Fig. 1D). The reactor has a total power or energy consumption of 125kWh (25kW for 5 hours) and is designed to withstand a pressure of 30 bar and a temperature of 280°C. Inside the reactor, shovels are used for agitation at a maximum speed of 100 rpm (Fig. 1J).

2.2 Sample preparation

This study is focused on polyethylene terephthalate (PET) bottle waste and polystyrene (PS) waste. The single plastic waste samples were sorted from waste bins in Sejong, South Korea. The mass of the plastic waste was measured, and the gross volume taken. Single (homogenous) plastic wastes were then fed into the reactor and one liter of tap water added. The waste was then subjected to hydrothermal carbonization (200-L pilot plant). The experiments were carried out separately for PET and PS.

Several preliminary test experiments were performed and basic conditions for complete decomposition were established. The maximum operating temperature in this study was 200°C and a pressure limit of 20 bar. At 200°C, the vapor pressure of water was about 15.5 bar which ensures water remains in its liquid phase throughout the process, which is crucial for hydrothermal carbonization. Maintaining water in a liquid state helps to facilitate the necessary chemical reactions for decomposing and transforming the plastic material. The liquid medium acts as a solvent and catalyst, enhancing the hydrolysis and subsequent reactions that lead to the formation of hydrochar.

The time to reach the desired maximum temperature was between 30 mins and the maximum pressure was around 50 mins. The agitation speed was maintained at 30 rpm and the reaction time was 30 minutes and 3 hours of processing time (Fig. 2).

During the HTC process, waste was constantly stirred by shovels to ensure even heat distribution and consistency. Once the waste was fully decomposed, the gas valve was opened to release steam into the condenser. After decomposition, the hydrochar was air dried, crushed, and sieved to obtain 500 μm particle size. The refined hydrochar was then ready for chemical and thermal analysis using FTIR and TGA. The feedstock samples were labeled PET plastic and PS plastic and the processed samples labelled PET hydrochar and PS hydrochar respectively.

2.3. Hydrochar yield

The hydrochar yield is a measure of the efficiency of the plastic waste conversion process. It is calculated based on the mass of the feedstock and the mass of the resulting hydrochar [98], see Eq. (1):

$$\text{Hydrochar Yield (\%)} = \frac{\text{mass of hydrochar}}{\text{mass of plastic waste}} \text{ x } 100 \qquad (1)$$

2.4. Fuel quality parameters

2.4.1. Proximate analysis

Proximate analysis was determined using modified ASTM D7582 standard method, where 99.999% N_2 of 3 L/min flow rate was used for moisture and volatile matter determination and 99.999% O_2 gas of 3.5 L/min for ash determination. Fixed carbon was then calculated by subtracting the total of moisture, ash, volatile matter from 100 [98]. The atomic ratios of H/C and O/C were calculated from elemental analysis results, see section 2.4.2, and the fuel ratio was calculated by dividing the percentage of fixed carbon with that of the volatile matter.

2.4.2. Ultimate analysis

Elemental analysis provided information of the elemental composition of the hydrochar which is useful for fuel applications. Carbon, hydrogen, oxygen, nitrogen, and sulphur were determined with the Thermo Scientific™ FlashSmart™ Elemental Analyzer from the research institute of standard analysis at Inha University, South Korea. The ultimate analysis is used to calculate the atomic ratios for hydrogen:carbon ratio (H/C) and oxygen:carbon ratio (O/C) which is used in the van Krevelen diagram.

2.4.3. Heating values

The heating values (MJ/kg) were determined using a bomb calorimeter. This was done by the Fiti testing institute, Daejeon, South Korea using the IKA C 2000 series model which measures the higher heating value (HHV) of fuels under precise operating conditions such as oxygen pressure (20-30 atm), ignition by an electric wire, and temperature measurement. Key parameters include the sample mass, the calorimeter water equivalent, the temperature rise post-combustion, and calibration against a standard like benzoic acid. These aspects ensure accurate energy content assessment in various fuels.

2.4.4. Energy densification

Energy densification refers to the increase in energy content per unit volume or mass through a process such as hydrothermal carbonization [98–100]. It is calculated with Eq. (2):

$$\text{Energy densification } = \frac{HHV of\ hydrochar}{HHV of\ feedstock} \tag{2}$$

2.4.5. Energy yield

Energy yield represents the percentage of energy from the original feedstock that is retained in the hydrochar after the conversion process [98]. It is calculated with Eq. (3):

$$\text{Energy Yield } = \text{Hydrochar yield x Energy densification} \tag{3}$$

2.5. Determination of Chemical Transformations with FTIR

FTIR provides essential information on the functional groups and chemical bonding in the raw plastics and the resulting hydrochar, aiding in understanding the chemical changes during the HTC process. The plastic waste was shredded into 2 mm thickness and the hydrochar was sieved into 500µm. The FTIR analysis was done with a Thermo Fisher Scientific^{TM}, Nicolet^{TM} IS.10, USA at the organic chemistry laboratory lab of Inha University research institute of standard analysis, South Korea. The functional groups on the surface of the solid samples were identified through FTIR analysis, employing KBr pellets. For each pellet, a mixture was created using 1 mg of the solid sample and 100 mg of KBr [98, 100]. This mixture was thoroughly combined and then compressed into a pellet at a pressure of 2 MPa for a duration of 8 minutes. The analysis conducted 16 scans across a spectrum ranging from 400 to 4000 cm^{-1}. The results were displayed using the OPUS TOUCH FT-IR spectroscopy software.

2.6. Thermal analysis with thermogravimetric analyzer (TGA)

TGA assesses the thermal stability and degradation of the samples under high temperatures, crucial for evaluating the quality of hydrochar and potential applications. The combustion temperatures, indices and activation energies provide useful information on the recyclability of the HTC technology.

TGA was performed using the TGA801 thermogravimetric analyzer with cornerstone Brand software version 3.1.x, part Number 200-795,02/2023 containing 20 carousel locations. Samples were analyzed using a modified ASTMD7582 method and three different heating rates of 5°C/min, 10°C/min, and 19°C/min were employed and nitrogen gas was used as the heating atmosphere with operating pressure of 35 psi and a flow rate 3 L/min. The maximum furnace temperature was 800°C. The drying temperature was set at 105°C, starting at room temperature (~ 25°C), with a hold time of 10 minutes and the heating temperature was set from 105 to 800°C with a heating rate of 10°/min and no hold time. The TGA curve was obtained by plotting the100- mass change % column versus temperature (°C) obtained from the TGA data. The DTG curve is plotted as the first derivative mass against temperature.

2.7. Combustion properties

In thermogravimetric analysis (TGA), various temperatures such as onset temperature (Ti), peak temperature (T_{max}), and burnout temperature (T_b) are critical in understanding the thermal behavior of a material. The onset temperature is the temperature at which a specific thermal event begins. For instance, in a TGA curve, it could be the start of a mass loss due to decomposition. On a TGA curve, it is identified as the point where the baseline starts to deviate. The peak temperature refers to the temperature at which the rate of a thermal event (like decomposition or reaction) is at its maximum. It is the apex of a peak on a DTG curve, corresponding to the peak point where the rate of weight loss is the highest. The burnout temperature is the temperature at which the combustion or decomposition process is essentially complete. On a TGA curve, it is identified as the point where the mass loss curve levels off and returns to a baseline, indicating the end of significant mass loss.

2.8. Kinetic analysis

2.8.1. Model free (non-isothermal conversions) kinetic analysis

The Flynn-Wall-Ozawa (FWO), The KAS (Kissinger-Akahira-Sunose) and the Starink method are among the several non-isothermal conversion methods used in determining the activation energy without necessarily knowing the intercept or other constants. The equations assume that the rate of reaction at a constant degree of conversion (α) is only a function of temperature and not heating rate. These approaches are advantageous because they do not require the assumption of a specific reaction model. For each heating rate, temperature data points corresponding to the degree of conversions (α) were selected. The conversion degree of 0.1 to 0.9 was determined using Eq. (4):

$$\alpha = \frac{m_0 - m_f}{m_0 - m_t} \tag{4}$$

where m_o is the initial mass before the reaction, m_t is the mass at a particular time t and m_f represents the remaining mass after complete decomposition.

The FWO equation is shown in Eq. (5):

$$\ln(\beta) = \ln\left(\frac{AE_a}{\mathrm{Rg}(\alpha)}\right) - 5.3305 - 1.052\frac{E_a}{\mathrm{RT}} \tag{5}$$

At each selected conversion rate, ln(β) was plotted against 1/T and a linear regression performed.

The KAS equation is given in Eq. (6):

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{A}{E_a \mathrm{g}(\alpha)}\right) - \frac{E_a}{RT} \tag{6}$$

A plot of $\ln\left(\frac{\beta}{T^2}\right)$ versus 1/T for each level of conversion degree is made to obtain the activation energy.

Compared to other non-isothermal conversional methods, the Starink method is known for providing more accurate estimates of activation energy, particularly at lower levels of conversion. The Starink method is beneficial for materials or compounds where the reaction mechanisms are not well understood, see Eq. (7):

$$\ln\left(\frac{\beta}{T^{1.92}}\right) = -1.008\frac{E_a}{RT} + Constant \qquad (7)$$

The slope of the linear regression line (m) is calculated from the plot of $\ln\left(\frac{\beta}{T^{1.92}}\right)$ vs 1/T for each conversion level.

These plots are crucial for understanding the kinetic behavior of these materials at a significant point in their thermal decomposition process. From linear regression the slope (m) was obtained, and the activation energy was calculated using Eq. (8):

$$E_a = -\mathrm{m}\cdot\mathrm{R} \qquad (8)$$

Plots of activation energy with conversion rates are produced to visualize the energy barrier or energy requirement at each stage of the decomposition process.

In the above equations, β is the heating rate, T is the absolute temperature at the specific conversion level, A is the pre-exponential factor, E_a is the activation energy, g(α) is the integral function and R is the gas constant. The slope of this plot is used to calculate the activation energy for that specific conversion level. By repeating the analysis for different levels of conversion, a range of activation energies for the process can be obtained. The values for the activation energies using the three-model free iso conversion methods (FWO, KAS, and Starink) for different materials were obtained from the plots of the left side of the Eqs. (5) to (7) vs 1000/T (Fig. S1-S3).

2.8.2. Model fitting kinetic analysis

In accordance with the International Confederation for Thermal Analysis and Calorimetry (ICTAC) Kinetics Committee's recommendations [101] for performing kinetic analysis in thermal analysis, Eq. (9) is used to calculate the function $G(\alpha)$ which is involved in the analysis of non-isothermal kinetic data,

$$[\ln(\mathrm{G}(\alpha)] = \ln\left(\frac{\mathrm{A}E_a}{\mathrm{R}\beta}\right) - 2.315 - 0.4567\frac{E_a}{\mathrm{RT}} \qquad (9)$$

Where $G(\alpha)$ is the integral function related to the specific reaction mechanism, see Table 1, and the extent of conversion α.

Plotting ln [G(α)] versus 1000/T will give a slope relevant for activation energy (E_a) determination across the three heating rates [102]. The R^2 values are calculated and will be used to select the best model that fits our TGA data. When the R^2 values are either identical or closely resembling each other, or when the presence of noise leads to potential overfitting or underfitting, the average activation energies generated by the model across three different heating rates are utilized as a reference point for comparison with the chosen model-free iso-conversion techniques. The model with the smallest difference or deviation is chosen as the best model for that sample.

3. Results and Discussion

3.1. Hydrochar yield

The hydrochar process is efficient in converting both PET and PS plastics, with high yields and significant volume reductions. PET hydrochar has a higher yield (65.1%) than PS hydrochar (47.9%), see Table 2. This might be due to variations in the chemical structure and properties of the plastics. Both hydrochars showed notable volume reduction, especially for PS hydrochar, which volume reduced by 98.6%. This is a substantial compaction of the material, which is beneficial for reducing the space required for waste storage and disposal.

3.2. Fuel quality evaluation

PET hydrochar has a higher moisture content (1.39%) compared to PS hydrochar (0.39%), as shown in Table 3. While both values are relatively low and indicate that minimal energy will be lost to moisture evaporation during combustion, PS hydrochar is slightly more advantageous in this regard. Both hydrochars have high volatile matter content, with PET hydrochar at 85.2% and PS hydrochar at 87.9%. This suggests that both hydrochars will easily ignite and combust, which is beneficial for energy recovery processes. However, this can become a problem if the volatile matter composes harmful gases such as NO_x and SO_x [103]. The absence of sulfur (not detected) in the ultimate analysis is particularly beneficial for the environment, as it suggests that burning these hydrochars would not produce significant sulfur dioxide emissions, which are harmful pollutants. PET hydrochar has a lower ash content (1.98%) compared to PS hydrochar (5.13%). A lower ash content is preferred for combustion applications as it means less residual material after burning and reduces the risk of slagging and fouling in boilers and furnaces. The fixed carbon for PET plastic and PS plastic are 12.9 and 0% respectively, in line with findings of Lei Dai et al., [104] who reported 13.2 and 0% respectively. The higher fixed carbon in PET hydrochar (11.4%) compared to PS hydrochar (6.55%) suggests that PET hydrochar might have a slightly higher energy content available for combustion, although this is contradicted by the higher heating value of PS hydrochar. The ultimate analysis of the plastic samples, especially PET, agree with the findings of [105].

PS hydrochar has a higher HHV (55.2 MJ/kg) compared to PET hydrochar (30.7 MJ/kg). This implies that PS hydrochar can release more energy upon complete combustion and, therefore, may be a more efficient fuel in terms of energy output yielding more energy per unit mass [106].These results agree with several reports cited in Bardhan et al. [107], where most hydrochar have a higher heating value compared to their feedstock, where PET hydrochar records a 37% increase and PS hydrochar a 13% increase. The heating value is a critical indicator of the potential energy content of a fuel [108].

The H/C and O/C atomic ratios are considered when evaluating the quality of fuel for combustion processes. The assessment of the molar ratios of hydrogen to carbon (H/C) and oxygen to carbon (O/C) are key factors in identifying the deoxygenation level and aromatic nature of hydrochar. A higher H/C ratio signifies a lower aromatic content, while a higher O/C ratio indicates reduced hydrophobicity and increased polarity in the hydrochar [107, 109].

The PS hydrochar has a slightly higher H/C ratio (0.12) than the PET hydrochar (0.09), which would typically suggest a lower degree of carbonization [68] and potentially less energy content. However, the higher HHV of the PS hydrochar indicates that it may contain other structural features that enhance its energy content. The O/C ratios of the PET hydrochar at 0.53 and the PS hydrochar at 0.10 indicates that they both have a low degree of oxidation, which is beneficial for a higher energy yield [110, 111]. This is evident in the higher heating values of PS hydrochar compared to PET hydrochar. Assuming there is complete decomposition with no microplastic, the PS hydrochar would be much more stable in soils due to its lower O/C ratio compared to the PET hydrochar [68]. Fig. 3 shows the van Krevelen diagram, where the PS hydrochar is closer to the anthracite region [112], indicating the possibility of performing well in coal kilns. The position of PS hydrochar on the van Krevelen diagram suggests it is carbon-rich and somewhat hydrogenated, but with minimal oxygen content. The upward/right movement (indicating an increase in both H/C and O/C ratios) can be interpreted as a mild incorporation of both hydrogen and oxygen relative to carbon. This could be due to a combination of hydrogenation and slight oxidation processes during the formation of the hydrochar [113]. The hydrochar becomes slightly more oxidized than its feedstock but retains a high level of carbon, which is beneficial for energy yield. The PET hydrochar has a moderate O/C ratio and a lower H/C ratio. The position on the van Krevelen diagram indicates a higher level of oxygenation compared to the PS hydrochar. The upward/left movement (increasing H/C ratio and decreasing O/C ratio) suggests an increase in hydrogenation or a reduction in the oxygen content of the material leading to an increase in energy yield due to the higher proportion of combustible hydrogen [113].

3.3. Fuel ratio

PET hydrochar had a higher fuel ratio (0.15) compared to the PS hydrochar (0.07). The results show that PS hydrochar has a higher ignition behavior than PET hydrochar. It also implies that PET hydrochar can maintain a better stable combustion process than PS hydrochar, although the values are still below the stable combustion range of 0.9 to 1.5 [69].

3.4. Energy densification ratio

3.4.1. Energy densification and energy yield

A higher energy densification value indicates a more efficient conversion of the feedstock into a high-energy-density fuel [114, 115]. The energy densification value for PET hydrochar is 1.37 (Table 3), which suggests that the hydrothermal carbonization process has significantly increased the energy density of the original PET material. The PS hydrochar also improved the energy density of the original PS material, with an energy densification value of 1.13, although this was not as much as for the PET hydrochar. The results suggest that, in terms of energy densification, PET hydrochar has a superior performance compared to PS hydrochar. This could be due to the conditions under which hydrothermal carbonization was conducted, or the presence of catalytic agents that might favor the reaction for PET.

Energy yield represents the percentage of energy from the original feedstock that is retained in the hydrochar after the conversion process [116, 117]. An energy yield of 89.1% indicates that a high proportion of the energy content of the original PET material is preserved in the hydrochar form, which is excellent for energy recovery purposes. An energy yield of 54.3% for PS is lower than that of PET hydrochar, suggesting that a significant portion of the original energy content of PS was lost during the conversion process. The high energy yield of PET hydrochar implies that the process used to convert PET into hydrochar is highly efficient, retaining most of the energy content from the original material. This is a desirable feature in energy applications because it means less raw material is needed to produce the same amount of energy, which can improve the sustainability and economic viability of the process. For PS hydrochar, the energy yield is over 50%, which is still significant, but it indicates that the process is less efficient compared to PET. This might make PS hydrochar less attractive from an economic standpoint in which the costs of processing may not justify the energy content of the product.

3.4.2. Implications for energy applications and environmental impact

When considering the use of hydrochar in energy applications, both values for densification and yield are important. PET hydrochar is more likely to be the preferred choice for applications where a high energy content is required from a relatively small volume or mass of fuel. However, PS hydrochar might still be considered for energy applications, particularly if the lower yield is offset by other factors, such as availability, lower feedstock costs, or if the process results in other beneficial properties such as improved handling characteristics or reduced emissions. The process of converting waste plastics into hydrochar can be considered as a form of waste-to-energy, which carries a significant potential to reduce the environmental impact of plastic waste.

The high energy yield of PET hydrochar suggests that the process is more efficient compared to PS hydrochar and could contribute to waste reduction efforts. PET hydrochar shows superior energy densification and yield, making it an excellent candidate for energy recovery.

3.4.3. Hypothetical waste conversion scenario

Energy densification refers to the process of increasing the energy content per unit volume or mass. The energy densification value for PET hydrochar is 1.37, i.e., the energy content per unit mass compared to the original plastic waste increased by 1.37. The PS hydrochar showed an energy densification of 1.13. Practically, if 5,000 tons of plastic waste is processed, the total energy content of the PET hydrochar produced would be equivalent to 5,000 tons of PET plastic waste multiplied by the energy densification factor (5,000 * 1.37), assuming a linear scale-up.

Energy yield is a measure of the percentage of the original energy content of the feedstock that is retained in the final product after the HTC process. It reflects the efficiency of the process in terms of energy conservation. The energy yield values indicate that 89.1% of the original energy content in the PET waste is retained in the PET hydrochar and 54.3% of the original energy content in PS plastic waste is retained in the PS hydrochar. This implies that the HTC process is more efficient for PET plastic, as a higher percentage of the original energy content is conserved. If an HTC facility processes 5,000 tons of plastic waste daily, it can be hypothesized that the facility would generate PET hydrochar with an energy content 36.9% higher than the original plastic mass, and 89.1% of the original energy would be retained while the facility would produce PS hydrochar with an energy content 13.3% higher than the original plastic, but only 54.3% of the original energy would be conserved.

3.5. Chemical transformations

3.5.1. PET plastic and its hydrochar

O-H stretch (alcohols/phenols)

Table 4 shows the peaks and their transmittance expressing the chemical composition of the plastics and their hydrochar. PET hydrochar exhibits multiple O-H stretch peaks (3433, 3551, 3541, 3593, 3339, 3302, and 3233 cm^{-1}) with transmittances between 0.36 and 0.28 (Fig 4.a), indicative of hydroxyl groups or moisture [118, 119]. In contrast, PET plastic shows a significant reduction in the O-H stretch peak at 3451 cm^{-1} (transmittance: 0.14) (Fig. 4b). PET plastic is composed of long chains of ethylene glycol and terephthalic acid linked by ester bonds and during polymerization, these components react to form ester linkages, which consume hydroxyl groups from ethylene glycol, integrating them into the structure and releasing water as a byproduct. This results in a dense, stable polymer structure with minimal free hydroxyl groups, as most potential reactive sites are used up in forming the ester bonds. Hydrochar, in contrast, is produced through hydrothermal carbonization of PET, a process that involves heating PET in water under elevated temperatures and pressures. This environment leads to partial hydrolysis of the ester bonds, breaking them down into alcohol and acid components and generating new hydroxyl groups. Additionally, the interaction of water with the fragmented polymer chains at high temperatures facilitates the further incorporation of hydroxyl groups into the carbon framework of the hydrochar. Thus, while PET plastic has few hydroxyl groups due to its stable and dense ester-linked structure, PET hydrochar is enriched with hydroxyl groups, owing to the breaking and reforming of chemical bonds during hydrothermal carbonization.

C=O stretch (carbonyls/esters)

PET plastic displays increased transmittance in 1717 and 1690 cm-1 (0.45 and 0.38, respectively), implying a decrease in carbonyl content, [120]. In PET hydrochar, C=O stretch peaks appear at 1726, 1740, 1691, and 1711 cm^{-1} with around 0.27 transmittance, characteristic of the ester functional groups [120] in the PET backbone [121, 122]. Through hydrothermal carbonization, the breakdown and rearrangement of chemical bonds can lead to an altered configuration that exposes or generates more functional groups, including carbonyls. The hydrothermal process likely facilitates the hydrolysis and partial oxidation of ester bonds, leading to an increased carbonyl content in the resulting hydrochar.

C=C stretch (alkenes)

In PET hydrochar double carbon bond (C=C) stretches occurred in the region of 1632, 1616, 1641, and 1582 cm^{-1}, also with transmittances around 0.27 to 0.28, which are indicative of the alkenes present in the terephthalate units [123]. However, it is absent in PET plastic. PET is a stable polyester composed of terephthalic acid and ethylene glycol linked by ester bonds, featuring aromatic rings that do not typically exhibit C=C stretches due to their saturation within the ester linkage structure. However, under the conditions of HTC, the ester bonds in PET partially break down, leading to depolymerization that liberates parts of the molecule. This depolymerization, along with subsequent decarboxylation and dehydration reactions, removes oxygen groups and can lead to the formation of unsaturated compounds through elimination processes. Additionally, the thermal conditions and dehydration facilitate aromatization and cyclization, which can further result in the formation of new aromatic rings and unsaturated structures, including alkenes. This is evidenced by the detection of C=C stretches at 1632, 1616, 1641, and 1582 cm^{-1} in PET hydrochar, indicating not only the presence of new olefin groups but also suggesting a restructuring or increased exposure of unsaturated groups originally embedded within more complex systems in the PET.

C≡N stretch (nitriles)

A specific peak at 2257 cm^{-1} was identified in PET hydrochar suggesting the presence of nitriles. This peak did not appear in PET plastic, indicating possible modification or addition of nitrile groups during HTC. Under hydrothermal conditions, the presence of nitrogen in the system (either originating from additives, contaminants, or residual catalysts involved in original polymerization of the original PET) can interact with decomposed or rearranged carbon structures to form nitrile groups. It can also be influenced by environmental factors within the reactor, such as pH and the availability of nitrogen sources, which facilitate the integration of nitrogen into the carbon matrix, resulting in the creation of new functional groups in the hydrochar.

C-H stretch (alkanes)

In PET plastic the C-H stretch peaks in the alkane region at 2924, 2964, 2851, and 2880 cm^{-1} have much lower transmittance values (0.14 to 0.12) compared to PET hydrochar with peaks around 2808, 2893, and 2961 cm^{-1} with higher transmittance values around 0.26 to 0.32 due to the methylene groups in the ethylene part of PET. The increased transmittance (and thus decreased absorbance) in the hydrochar suggests a looser structural arrangement or an increased exposure of the methylene groups. This change is likely a result of the hydrothermal carbonization process, which breaks down the original PET structure, leading to partial degradation or rearrangement of the polymer chains. This process makes certain functional groups like the methylene chains more accessible and detectable by infrared spectroscopy, whereas this higher absorbance in PET plastic suggests that the methylene groups within the polymer matrix are more densely packed or less accessible to infrared radiation, typical of a more tightly bound and intact macromolecular structure.

C=C stretch (aromatic rings) and C-H stretch (aldehydes)

PET plastic, characterized by its aromatic nature due to the presence of stable terephthalic acid benzene rings, undergoes significant changes during hydrothermal carbonization to become PET hydrochar. Initially, in PET, aromatic compounds are linked with ethylene glycol through ester bonds, creating a polymer with a strong aromatic backbone. However, HTC induces several chemical alterations, impacting the dynamics of functional groups and the aliphatic content. In PET hydrochar, the emergence of unique spectral peaks, such as the C=C stretch at 1526 cm^{-1} and the C-H stretch at 2762 cm^{-1}, signifies notable modifications. The 1526 cm^{-1} peak indicates the alteration or formation of new aromatic bonds possibly through the breakdown and reorganization of original ester linkages. Meanwhile, the 2762 cm^{-1} peak, typically linked to aldehyde groups, suggests the formation of new carbonyl functionalities due to decarboxylation and dehydration reactions during HTC, highlighting the transformation from the original structure to a new structure (hydrochar) [123, 124].

3.5.2. PS plastic and its hydrochar

O-H stretch (alcohols/phenols)

PS plastic shows a slightly lower transmittance of 0.06 at a lower wavenumber of 3435 cm^{-1}. PS hydrochar shows a slightly higher transmittance of 0.07 at 3437 cm^{-1}. This indicates that HTC causes a minor shift. However, the hydroxyl groups are retained [125].

C=O stretch (carbonyls/esters/ketones)

PS hydrochar has a peak at 1732 cm^{-1} with a transmittance of 0.05. During the hydrothermal carbonization process of polystyrene (PS), the formation of a new carbonyl group at 1732 cm^{-1}

could be indicative of oxidative reactions affecting the aromatic rings and side chains of the styrene units [126], [127]. Furthermore, the hydrothermal conditions foster the formation of new functional groups such as carbonyls, potentially through the action of hydroxyl radicals or oxygen attacking the aromatic structures, leading to the creation of ketonic groups.

C=C stretch (alkenes)

In PS plastic, the peaks observed at 1686, 1647, 1637, and 1603 cm^{-1} with varying transmittances (0.06, 0.03, 0.03, 0.02) are characteristic of the aromatic C=C stretches within the benzene rings of the styrene units. These peaks indicate the presence of stable aromatic structures that are typical of untreated PS. In contrast, PS hydrochar shows C=C stretch peaks at slightly different positions: 1601, 1583, and 1639 cm^{-1}, with transmittances of 0.07, 0.03, and 0.03, respectively. During HTC, the high temperatures and pressurized water environment can lead to a structural rearrangement within the PS, potentially altering the locations of double bonds within the aromatic rings. This rearrangement also contributes to the formation of new aromatic compounds, thereby altering the original absorption characteristics. Also, the thermal and chemical stress from the HTC conditions can induce breaks in the polymer chains resulting in the formation of new double bonds and modifications to the aromatic rings [122].

C-H stretch (alkanes)

PS plastic shows wavenumbers of 2920 and 2851 cm^{-1} with transmittance of 0.03 and 0.02, respectively, while PS hydrochar shows wavenumbers at 2922 and 2851 cm^{-1} with transmittance of 0.08 and 0.07, respectively. This shows the C-H stretches were maintained during the conversion with a decrease in absorption.

Aromatic ring stretch (C=C)

PS plastic shows transmittance values (0.01-0.02) at 1576, 1560, 1543 and 2721 (0.01) cm^{-1}, which likely correspond to specific aromatic vibrations within the styrene polymer units. PS hydrochar shows transmittance values (0.01) at 1541 and 2725 cm^{-1}. This observation indicates that although HTC modifies the PS polymer structure, the core aromatic and characteristics are still detectable, implying that the process may primarily alter the polymer superficially [127] [125].

Aldehyde C-H stretch (aldehydes)

This peak (2721cm $^{-1}$) appears only in the PS plastic with a transmittance of 0.01.

C≡N stretch (nitriles)

There is a strong peak in PS hydrochar at 2255 cm^{-1}. This peak is absent in the PS plastic, suggesting that any nitrile groups present in the hydrochar were introduced by the HTC process.

3.6. Degradation temperatures

The curves at different heating rates provide information on the kinetics of degradation. In this study the degradation temperatures increase with heating rates, see Fig. 5. Higher heating rates lead to higher degradation temperatures due to the delay in heat transfer. PET plastic has a higher onset temperature range (353-410°C) compared to PS plastic (300-352°C), see Table 5. This indicates that PET plastic starts to decompose at a higher temperature, suggesting greater thermal stability. This could be due to the chemical structure of PET, which is known for its higher resistance to heat. In line with other studies, onset temperatures for PET plastic have been reported to increase with heating rates and Das et al. [128] reported onset temperatures within the range of 385°C to 427°C from 10 to 50°C /min for PET plastics, which are comparable to our findings.

In our study the peak temperatures, as observed in the DTG curve in Fig. 5, increase with heating rates which match the findings of Das et al. [128]. The peak temperatures of PET plastic (451-520°C) are higher than those of PS plastic (425-500°C). This suggests that the maximum rate of combustion occurs at a higher temperature for PET, which is consistent with its higher thermal stability. These results were in line with the results in Heikkinen et al. [105], where the peak temperatures for PET and PS plastic were reported as 444°C and 437°C respectively. Some studies have generally reported PET plastics to have degradation temperatures of between 400 and 700°C. PET plastic has a higher burnout temperature range (660-800°C) compared to PS plastic (554-650°C). Burnout temperature is the point at which combustion is complete, and the higher range for PET indicates its ability to withstand higher temperatures.

Both PET and PS plastics exhibit higher thermal stability with higher onset, peak, and burnout temperatures compared to their respective hydrochars. This suggests that the process of converting these plastics to hydrochars reduces their thermal stability, making the hydrochars more prone to earlier decomposition and combustion. This could be due to their altered chemical structure and increased porosity [129]. Plastics generally reach higher peak and burnout temperatures compared to hydrochars. This might be due to a more extensive and complete combustion process in the plastic materials. The lower onset temperatures for hydrochar implies that these hydrochars are thermally less stable than plastics and the higher peak and burnout temperatures in plastics might indicate more efficient combustion, which is relevant for energy recovery and recycling processes. Understanding the differences in the combustion temperatures is crucial for waste management and environmental impact assessments, as it helps in determining the preferable treatment or recycling method for different materials.

PET hydrochar has a lower onset temperature range (150-270°C), compared to PS hydrochar (242-283°C). This indicates that PET hydrochar begins to decompose at a lower temperature. PET hydrochar has a higher peak temperature range (420-585°C) than PS hydrochar (390-470°C), suggesting that at its peak combustion, PET hydrochar can withstand higher temperatures. Both hydrochars reach similar burnout temperatures (650-800°C), but PET hydrochar has a wider range at lower initial temperatures, indicating variability in its combustion behavior.

PET plastics demonstrate higher thermal stability compared to PS plastics, likely due to their molecular structure and resistance to heat. When comparing each plastic with its hydrochar, the plastics are more stable than their hydrochars, likely due to changes in chemical composition during the conversion to hydrochar. PET hydrochar begins to decompose at lower temperatures but reaches higher peak temperatures compared to PS hydrochar, indicating a distinct difference in their thermal degradation and combustion behaviors.

The DTG analysis highlights distinct differences between PET and PS plastics in terms of thermal degradation. The higher rate of PET plastic degradation at Tmax across various heating rates indicates a swift breakdown mechanism post threshold temperature, despite its inherently higher thermal stability as suggested by its higher onset temperatures. This rapid degradation could compromise the applicability of PET in environments subjected to high thermal stress, despite its initial resistance (Fig. 5 d, e, f). In comparison, PS plastic exhibits a less intense degradation rate, indicating a more gradual thermal decomposition. This characteristic suggests that PS plastic may be more suitable for applications where gradual heat exposure occurs, as it does not degrade as abruptly as PET plastic.

Transitioning to hydrochars, the reduction in degradation rate at Tmax for both PET and PS derivatives signifies the impact of the hydrothermal carbonization process on material stability.

However, the persistently higher rate of degradation for PET hydrochar compared to PS hydrochar, albeit lower than their respective plastics, reflects intrinsic material vulnerabilities remaining even after the conversion process. The slower degradation rates of hydrochars compared to their original plastics highlight a critical transformation, providing a buffer against immediate thermal breakdown. This aspect can be particularly beneficial in applications where controlled degradation or enhanced thermal stability is required.

The distinct degradation behaviors between the plastics and hydrochars, particularly at Tmax, illuminate the thermal stability and degradation kinetics of a material. PET plastic, despite higher initial thermal resistance, demonstrates rapid breakdown past critical temperatures, impacting their application in high-temperature environments. Conversely, the conversion into hydrochars, while reducing overall thermal stability, lessens the degradation intensity, offering a potentially more controlled thermal response. This analysis not only highlights the fundamental differences between PET and PS materials in terms of thermal degradation but also accentuates the effectiveness of hydrothermal carbonization process in altering material properties for enhanced thermal management. These insights are pivotal for developing efficient recycling and waste management strategies, emphasizing the importance of assessing the thermal behaviors of materials for optimal application and environmental sustainability.

3.7. Activation energy from model free iso-conversion methods

The values for the activation energies using the three-model free iso conversion methods (FWO, KAS, and Starink) for different materials are presented in Table 6. For PET plastic, the FWO method showed activation energies ranging from 84 to 120 kJ/mol, the KAS model ranged from 75 to 115 kJ/mol, and the Starink method from 75 to 114 kJ/mol, see Table 6. The activation energies reported in our study for PET plastics appear to be lower than those reported by Das et al., [128] which were from 200 to 350 kJ/mol. PET hydrochar displayed higher activation energies, with the FWO method ranging from 105 to 172 kJ/mol, the KAS method from 98.8 kJ/mol to 168 kJ/mol, and the Starink method from 99 to 167 kJ/mol. In the case of PS Plastic, the FWO method showed activation energies from 103 kJ/mol to 115 kJ/mol, the KAS method from 98 to 109 kJ/mol, and the Starink method from 97 to 108 kJ/mol. Lastly, PS hydrochar exhibited lower activation energies compared to its plastic counterpart, with the FWO model ranging from 65 to 107 kJ/mol, the KAS model from 57 to 100 kJ/mol, and the Starink method from 57 to 99 kJ/mol. Each polymer sample exhibits a unique profile of activation energy as a function of the conversion rate. This is in line with the findings of Liu et al. [127], where activation energy for PVC hydrochar is lower than the PVC plastic counterpart. These results indicate significant variations in activation energies across different materials, highlighting the complexities in recycling, plastic waste management, and waste-to-energy applications.

For PET plastic, the activation energies exhibit varying trends across different model free iso-conversion methods. The FWO method shows a high starting point at 120 kJ/mol, followed by a decrease to 84 kJ/mol, and then fluctuating across the conversion degrees. The KAS method begins at 115 kJ/mol, drops to 75 kJ/mol and displays a similar pattern of fluctuation. The Starink method starts at 114 kJ/mol, dips to 75 kJ/mol, and follows a fluctuating trajectory. In the case of PET hydrochar, the FWO method begins at 108 kJ/mol and shows a significant peak at 172 kJ/mol. The KAS model starts at 102 kJ/mol, climbing to a high of 168 kJ/mol. Similarly, the Starink method opens at 102 kJ/mol and peaks at 167 kJ/mol, illustrating a notable increase in activation energy as the conversion degree progresses. For PS plastic, the FWO method reveals a general upward trend, starting from 103 and peaking at 115 kJ/mol. The KAS method begins at a lower point of 97 kJ/mol, reaching its highest at 109 kJ/mol. The Starink method, starting at 97 kJ/mol, also shows an increasing trend and peaks at 108 kJ/mol. PS hydrochar in the FWO method starts at a lower activation energy of 65 kJ/mol, increases to a peak of 107 kJ/mol, and then shows a decrease. The KAS method begins at 57 kJ/mol, rises to its highest point at 100v, and subsequently decreases. The Starink method exhibits a similar pattern, starting at 58 kJ/mol, peaking at 99 kJ/mol, and then declining. These trends in activation energies reflect the complex thermal behavior of these materials, highlighting important considerations for optimizing recycling and waste-to-energy conversion processes. The analysis of the activation energies for PET plastic, PET hydrochar, PS plastic, and PS hydrochar across different iso conversion models (FWO, KAS, and Starink) reveals significant insights into their thermal decomposition behavior, which is crucial for applications in recycling and waste-to-energy conversion.

The activation energies across all methods for PET plastic start high and then exhibit fluctuating trends. This indicates that the initial stages of thermal decomposition require more energy, but as the process progresses, the energy requirement varies. Such behavior could imply that different stages of PET plastic degradation might be energy efficient, impacting its recycling and energy recovery processes. For PET hydrochar, all methods show a trend where the activation energy starts at a moderate level, peaks significantly, and then sustains at a higher level. This suggests that as the conversion process progresses, more energy is required to break down the material, potentially due to its more complex or stable structure compared to its plastic counterpart. This characteristic is important for waste-to-energy applications, where higher energy inputs might be needed for efficient conversion. The activation energies for PS plastic generally show an increasing trend across all methods. This pattern suggests that as the degradation process progresses, the energy requirement gradually increases. This may result from the initial breakage of weaker single C-C bonds, followed by the breakdown of double bonds and aromatic structures.

Understanding this behavior is vital for optimizing the recycling process and energy recovery from PS plastics. PS hydrochar displays a unique trend where the activation energy starts relatively low, peaks, and then increases progressively. This indicates that initially, it is relatively easier to initiate the conversion process, but as it reaches a certain point, the energy requirement increases sharply. This behavior could be attributed to the composition and structure of the hydrochar, which might initially facilitate degradation but then requires more energy as more stable compounds are reached. These trends in activation energies reflect the inherent complexities of thermal decomposition in different materials. Understanding these patterns is essential for developing efficient and sustainable recycling strategies and waste-to-energy systems. Each material's behavior under thermal processing informs the design of processes for effective material recovery or energy generation, highlighting the need for tailored approaches based on the specific thermal properties of each material.

The thermal behavior of PET and PS hydrochar, altered through HTC, reveals distinct responses due to their functional group modifications. PET hydrochar, enriched with oxygenated groups like carbonyls and hydroxyls, exhibits lower onset temperatures (see Table 5) for decomposition, indicating increased reactivity and a decrease in thermal stability. This leads to easier initiation of breakdown processes such as hydrolysis or oxidation, yet it also demands higher activation energies (see Table 6) for complete decomposition due to the complexity added by new aromatic and olefin (C=C) bonds (see Table 4). In contrast, PS hydrochar undergoes milder chemical changes, retaining hydroxyl groups and aromatic structures that contribute to higher onset temperatures, suggesting greater material stability. Additionally, the simpler modifications in PS hydrochar, alongside retained structures like alkenes and alkanes, necessitate lower activation energies for decomposition, indicating a less complex and energetically demanding breakdown compared to PET hydrochar.

3.8. Activation energy determination from model fitting

Activation energy from the reaction models (power law, 1-D Avrami, contracting cylinders, and 1-D diffusion) are obtained from the slopes of the different Ln [G(α)] vs 1000/T (Fig.S4-S7). The R^2 values show the best model that fits our TGA data, see Table 7 and their activation energies presented on Table 8.

For PET plastic, the reaction model of contracting cylinders showed the highest coefficient of determination (R^2) across all the heating rates (0.731 to 0.976) (Table 7.b), while for PET hydrochar the highest R^2 were recorded with the 1-D Avrami-Erofeev (Mampel first order) model ranging from 0.909 to 0.951 (Table 7.b). PS plastic (Table 7.c) and PS hydrochar (Table 7.d) follow the 1-D Avrami-Erofeev (Mampel first order).

3.9. Policy implications, environmental impact, and recommendations

This study emphasizes the role of energy densification and yield in shaping the operations and strategies of waste-to-energy facilities, highlighting the benefits of processing various plastic types to maximize energy recovery. The hydrothermal carbonization process, by converting plastics like PET into hydrochar, emerges as a significant energy resource with the potential to augment electricity grids and support high-energy-demand industrial activities. This conversion, rooted in circular economy principles, not only facilitates waste management but also reduces the environmental impact of plastic disposal through substantial energy retention.

The research advocates for the development and enforcement of incentive-based regulations to boost waste-to-energy conversions, which would aid industry expansion and promote sustainable management of plastic waste. It underscores the necessity of setting quality and emissions standards for hydrochar, especially as a solid fuel, to ensure its environmentally friendly application.

Investment in research and development is identified as vital for advancing hydrochar technology, enhancing energy recovery efficiency, and uncovering new uses. By replacing traditional fossil fuels with hydrochars, significant reductions in greenhouse gas emissions can be achieved, contributing to climate change mitigation, and offering a cleaner energy alternative. This shift also highlights the potential health and environmental benefits from decreased air pollutants.

Utilizing waste plastics for energy recovery aligns with sustainable development objectives by decreasing reliance on finite resources, thus lessening the environmental footprint of energy production. The widespread adoption of hydrochar technology is seen as beneficial for biodiversity and ecosystem health, improving air, water, and soil quality, and promoting healthier habitats.

The findings urge further optimization of the HTC process, exploration of technological scalability, and comprehensive environmental impact assessments through lifecycle analyses. Policymakers are encouraged to integrate HTC into waste management frameworks to tackle the mounting issues of plastic waste and meet energy recovery objectives, aligning with global efforts to reduce landfill use, curb plastic pollution, conserve natural resources, and mitigate greenhouse gas emissions.

4. Conclusion

PET hydrochar demonstrates superior energy characteristics, with an energy densification of 1.37 and an impressive yield of 89%, significantly outperforming PS hydrochar, which has a densification of 1.13 and a yield of 54%. Despite the lower high heating value (HHV) of PET hydrochar at 30 MJ/kg compared to the 55 MJ/kg of PS hydrochar, it features a higher fuel ratio of 0.13, indicative of a greater proportion of fixed carbon that supports a longer and more stable burn. PET hydrochar also decomposes at lower temperatures, ranging from 150-270°C, which is beneficial for applications requiring lower operational temperatures. However, it necessitates higher activation energy (121-126 kJ/mol) for initiating reactions, in contrast to the lower activation energies (67-74 kJ/mol) of PS hydrochar, which allow for easier ignition and might be preferred for applications needing rapid and higher heat release. Hydrothermal carbonization (HTC) significantly alters the chemical and physical properties of both PET and PS, enhancing their applications in sustainable waste management and energy recovery. This process infuses both types of hydrochar with enriched oxygenated functional groups, such as increased hydroxyl and carbonyl groups, boosting their chemical reactivity and utility across various uses. Specifically, PET hydrochar, with its low ash content and high carbon levels, not only improves its energy density but also its environmental performance through newly introduced functional groups, which promote cleaner burning by minimizing residues. These chemical transformations grant both polymers improved circularity properties by transforming waste into valuable hydrochar tailored for specific industrial needs, thereby closing the loop in resource utilization.

List of symbols, abbreviations and acronyms

A	pre-exponential factor
α	conversion degree
β	heating rate (^{o}C/min)
DTG	differential thermogravimetry (first derivative mass curve)
E_a	activation energy (kJ/mol)
EPR	extended producer responsibility
FTIR	Fourier transformed infrared spectroscopy
FWO	Flyn-Wall-Ozawa
$g(\alpha)$, $G(\alpha)$	function of the degree of conversion (α)
GNP	gross national product
HHV	high heating value (MJ/kg)
HTC	hydrothermal carbonization
ICTAC	International Confederation for Thermal Analysis and Calorimetry
KAS	Kissinger-Akahira-Sunose
m_0	initial sample mass (g)
m_f	mass after complete decomposition (g)
m_t	sample mass at time t (g)
m	slope
PET	polyethylene terephthalate
PS	polystyrene
PWCP	Plastic Waste Control Plan
R	universal gas constant (8.314 J/mol K)

RCA	Resource Circulation Act
RFID	radio-frequency identification
T	temperature (K)
T_b	burnout temperature (K)
T_i	onset temperature (K)
T_{max}	maximum degradation temperature
TGA	thermogravimetric analysis
UNEP	United Nations Environment Program
VBWF	volume-based waste fee

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