The Evolving Nature of Thermal Conversion Process

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The environment today is confronted by an unending cascade of global anthropogenic and ecosystem-based challenges. Biomass is considered to have the potential to be utilized as an alternative energy source. The conversion of the high carbon content of biomass through thermochemical treatment resulted in better fuel properties of biochar production. Understanding the underlying thermal conversion process principles alongside the associated/exhibited operational challenges that are specific to biomass types is crucial for beginners.

Keywords: thermal conversion process ; feedstock ; temperature ; pressure ; process reactors ; learners

1. Introduction

The environment today is confronted by an unending cascade of global anthropogenic and ecosystem-based challenges. Biomass is considered to have the potential to be utilized as an alternative energy source. The conversion of the high carbon content of biomass through thermochemical treatment resulted in better fuel properties of biochar production. Pyrolysis is the most researched thermochemical technique in the past decade among the few well-established methods for treating biomass and biogenic waste in order to produce high-quality and yield energy products such as biochar, bio-oil, and pyrolytic gas. The obvious aftermath of the industrial revolution brought about a steady geometric increase in population growth, which noticeably altered the balance of global carbon. The global population in 2013 was estimated at 7.2 billion and is estimated to increase by a billion in 2025; this makes the energy demand that is required for agricultural, industrial, and transportation development very crucial [1]. Global waste management, on the one hand, is among the United Nations' Millennium Development Goals (MDGs) from 2000, and particularly key here is its 7th Goal: To Ensure Environmental Sustainability, which subsequently progressed in the 2008 Waste Framework Directive [2], which aims to improve (waste) management strategies in accordance with the Sustainable Development Goals (SDG) [3]. On the other hand, waste disposal methods like, for example, composting should be effective in helping to reduce greenhouse gas emissions [4]. Moreover, the generated bio-waste materials would noticeably vary, especially in composition, largely due to some factors like the type of community and its consumers, industrialization, institutions, and commercial entities [2]. A great portion of bio-waste material, and how it transforms into biofuel, as well as other energy sources remains a major research focus, especially from the environmental standpoint [5]. Biomass, however, is increasingly considered to be the potential alternative renewable energy source. Pyrolysis, among the initial stage(s) in gasification, would help utilize biomass energy, alongside other thermochemical conversion procedures. In addition to the prevailing environmental issues, there are other pressing biomass-related challenges that involve many pyrolysis-based studies. Besides that, the context of thermal conversion technology (i.e., determination of operating parameters of pyrolysis-based) and reactor types have been based on the desired characteristics of the product (bio-oil, biochar, and pyrolytic gas), as well as on the field of biomass pyrolysis and upgrading. Feedstock properties, product characteristics, reactor type, and upgrading options are among the key areas demonstrated in the synthesized literature, providing relevant information. It is worth mentioning that some conducted reviews have looked at the systematic approaches for mapping biomass resources to conversion pathways, forming the basis for biomass valuation and informing when biomass pre-processing is needed in order to ensure feedstocks are ready for conversion [5]. Furthermore, bio-oil derived from pyrolysis biowaste would serve as chemicals/fuel products. The production and composition of pyrolysis oil are affected by the biomass composition and process operating parameters [6].

In recent decades, the research momentum about pyrolysis and related thermal conversion processes is on the rise, involving a wide range of biomass/feedstock targets. For emphasis, pyrolysis simply depicts the use of heat treatment to bring about an irreversible chemical change in the absence of oxygen, specifically [5][7][8]. Moreover, pyrolysis remains one of the most efficient techniques for thermochemical conversion without the involvement of oxygen. This process yields carbon-enriched hydrocarbons (bio-oils), biochar, and volatile gases containing molecules that are rich in oxygen and hydrogen [9]. Generally, the major pyrolysis products include biochar, bio-oil, pyrolytic gas, and tar, among others, which largely depends on the process type, whether it is slow, fast, or flash, considering their tightly linked technological/product yield components [10][11][12][13][14][15][16]. The harnessing of the associated biomass energy via thermochemical processes should be eco-friendly and should be completed with solid waste conversion technologies at high temperatures [17]. If the target product(s) is to be achieved, a thorough prior knowledge and understanding of different biomasses, as well as the conditions/situations of their pyrolysis is warranted [5]. For the temperature of pyrolysis to achieve a target level, the specific energy demand largely depends on biomass moisture and the process temperature and duration [18]. To reiterate, the pyrolysis type would directly connect with the reactor types [19][20][21][22][23]. To learn the pyrolysis operating process, the description of reactors alongside their peculiarities that make them well suited for one or more biomass feedstocks is also warranted, as this has a direct influence on the type of the anticipated product output.

In addition to the heating methods and their reactor types, biomass properties can affect the pyrolysis process [24][25][26], especially when considering the wide range of decomposition processes and realized products (of biomass) [27]. In addition to the different biomasses and their prevailing conditions, understanding the intentions of specialists/stakeholders to engage in pyrolysis/thermal conversion activities emanates from the quest to achieve a desirable end-product (of a given biomass/feedstock). Some major advantages of pyrolysis can include the following: (a) a high degree of efficiency and profitability, as well as the suitability to convert a wide range of solid waste into storage energy; (b) the minimal nature of greenhouse gases like HCl, NO_x, and SO_x; (c) the absence of corrupt organic matter in the pyrolyzed residue to prevent the extraction of metal substances via solvent; (d)pyrolysis is capable of processing garbage waste that is not suitable for landfill and incineration; and (e) the fixing of harmful components like heavy metals and sulfur that are present in the (raw material) waste. Some disadvantages, however, can include: (a) the waste processing, if not properly developed, could still pose environmental problems, and (b) to implement the process in a large-scale pyrolysis project will require a permit by the government, given the differences in the prevailing policies [28][29][30].

2. The Evolving Nature of Thermal Conversion Process

Previous findings involving the implementation of thermal conversion based-studies on conditions/situations and different biomasses, along with how these experimental aim(s)/objective(s) of the various studies were developed and the respective subsections captured are all present in **Table 1**. Additionally, the pyrolysis-based studies shown engaged with varying aims/objectives. More so, to carry out the experimental procedures developed on the basis of pyrolysis, strong considerations need to be given to the parameters involved, such as the materials, the characteristics of biomass samples, the sample preparation and pyrolysis, the economic analysis, as well as validation via the experimental procedures. Additionally, there could be various thermo-kinetics of the feedstock, which would associate with the thermal operating conditions, if high quality pyrolytic products like biochar, bio-oil, and pyrolytic gas were to be achieved. Tian and colleagues' experiments that were conducted on rice husks were carried out using two pyrolysis-coupled real-time volatile monitoring techniques (TGA–FTIR and Py-GC/TOF-MS). The findings demonstrated that in the temperature range of 200 to 330 °C, 330 to 390 °C, and 390 to 600 °C, respectively, rice husks showed three mass loss and gaseous product evolution stages. It was shown that 2,3-dihydro-benzofuran was the main hemicellulose product after speculating on the formation pathways of the 24 main volatile species. On the other hand, 2-methoxy-4-(1-propenyl)-phenol was a potentially key active intermediate and was highly unstable during the pyrolysis of the lignin constituent in RHs [31]. Besides the acquisition of knowledge regarding primary volatile compositions, the behavior of mass loss in a given feedstock, as well as the reaction kinetics properties [31][32] are important. For instance, seven partners participated in an international round-robin study, conducting TGA pyrolysis experiments on pure cellulose and beechwood at various heating rates. The activation energies of cellulose, hemicellulose, and conversions of up to 0.9 with beechwood showed deviations of about 20–30 kJ/mol in all experiments [33], feedstock preparation via the adoption of the biochar catalyst method upgrading options, hybrid pretreatment methods, and the comparisons of untreated and hydrochloric acid treatment of various biomass feedstock [34][35][36]; these are all examples of studies where feedstock was directly associated with the thermal operating conditions. In Téllez and colleagues' study, using lab-scale fast pyrolysis in a vacuum, rice husks (RHs) were converted into pyrolytic oils, enriched with levoglucosan (LG). They investigated how the pretreatment of the biomass and the pyrolysis temperature (300–700 °C) affected the yields of pyrolysis products and the selectivity for the LG formation. RHs pretreated with hydrochloric acid at 400 °C produced a maximum oil yield of 47 wt.%, which was 1.4 times more than the amount of oil produced at the same temperature from untreated RHs [36]. Also, activated carbon would help purify the bio-oil organic compounds, which could lead to environmental pollution [37]. Besides the thermal conversion operating parameters, like temperature [38] alongside the catalyst sorbent addition, there is the application of the Coats–Redfern method that could impact the end products' properties. Thus, understanding the influence of temperature on the evolution of the structures and the organic content of biochar [39][40][41][42][43] is key. The co-pyrolysis of rice straw (RS) and *Ulva prolifera* macroalgae (UPM) was investigated by Hoa et al., using a range of activated biochar catalysts supported by nickel-iron layered double oxides (NiFe-LDO). The bio-oil yield from co-pyrolysis was higher than that from individual pyrolysis. At 500 °C, the biomass mixture of RS/A-UPM produced the highest bio-oil yield (46.68 wt.%). However, the combination of RS and UPM without acid-treated UPM demonstrated a reduced bio-oil yield. Because of the coke formation during the catalytic pyrolysis up-gradation, the bio-oil was reduced. However, using the 5% Ga/NiFe-LDO/AC catalyst improved the bio-oil quality [39]. The correlations of pyrolysis characteristics with biomass types should be considered alongside the associated mechanisms [44]. A bio-fuel could be upgraded by various thermal conversion methods from the feedstock [45][46]. Furthermore, conventional thermogravimetric analysis could be applied to investigate the mechanism interaction of the co-pyrolysis process [47], which might offer fresh perspectives for eco-innovative circular economy solutions [48].

Table 1. A summary of various experimental procedures of pyrolysis specific to their aims/objectives and analytical methods.

Aims/Objective	Methods	Ref.
Nine holocelluloses (two forestry and seven agricultural wastes) were selected as the feedstock to investigate the impact on the compositions of bio-oils and to screen the best feedstock suitable for the production of long-chain ethers precursor, for the ensuing improvement of yield and selectivity	Preparation of native holocellulose, evaluation of the sample, experimental apparatus, and procedures	[49]
To offer details on the yields and features of char produced from ten types of wood that are common in Southern Europe, undergoing biomass carbonization technologies condition	Biomass feedstocks, experimental facility, experimental procedure, charcoal characterization, and overview of the experiments	[50]
To perform intricate experimental analysis as well as the numerical modeling of oat straw’s slow pyrolysis. The pyrolysis products are described using advanced methods of analysis, with tests focusing on the properties and yield of the solid, liquid, and gaseous species	Feedstock sample, ultimate and proximate analyses and employing semi-batch vertical reactor where simultaneous thermal, infrared spectroscopy, qualitative of tars were analyzed, and pyrolysis gas analyzation, and numerical computations	[51]
The wet torrefaction of corn stalk was studied, and the biomass pyrolysis polygeneration performance of the wet torrefied sample was examined. More so, the solid material, energy, carbon, and hydrogen yields, as well as the effectiveness of removing ash and oxygen were also compared between WT and dry torrefied (DT) of corn stalks	Materials, torrefaction technique, characterization of torrefied samples, and pyrolysis technique	[52]
The determination of the thermal degradation characteristics of heating residues of eucalyptus (EU) and corncob (CC) for gasification using TGA rates of 10 °C/min in a nitrogen environment. The study covers the impact of biomass composition and kinetic parameters on heating rate	Preparation of biomass samples and experimental procedures	[32]
This experimental study set out to characterize the bioenergy potential of DS pyrolysis, measure gas emissions and byproducts, estimate kinetic and thermodynamic parameters, and detect the joint optimization of multiple responses in response to changing biofeedstock, heating rate, and temperature, as well as significant interactions between operational conditions	Sample preparation, physical and chemical analysis, TG experiments beforehand, activation energy, pyrolytic characteristic parameters, Friedman and Starink methods, Py-GC/MS experiments, TGA–FTIR experiments, and joint optimizations	[53]
To provide a thorough understanding of primary volatile compositions, mass loss behavior, reaction kinetics, and formation pathway during fast RH pyrolysis	Materials, pyrolysis process and kinetic methods	[31]
The impact of feedstock particle size on the distribution of fast pyrolysis products and the kinetics of slow pyrolysis	Characterization of MWSD, thermogravimetric analysis, evaluation of apparent activation energy, the pyrolysis of MWSD and product characterization, different profiles of mass loss and the impact of particle size on mass loss	[54]
To look into the reproducibility of TGA biomass pyrolysis experiments and potential deviations when mass loss kinetics are calculated from the same sample using various TGA technologies	TGA experiments and kinetic analysis	[33]
To fill the knowledge gap in orange and potatoes peel pyrolysis kinetics that was discovered during the literature review	Materials, TGA, and kinetics	[55]
To accurately evaluate the HHV using lumped-parameter pyrolysis kinetic models, and to demonstrate a straightforward correlation that can be used to assess HHV without relying on three different biomass species	Experimental samples, experimental procedures, and experimental results	[56]
Examine the combustion kinetics and study the combustion properties of five different types of biomass fuel pellets that can be used as biomass fuel	Analysis of the thermal weight loss and the components of five different biomass fuel pellet types	[44]

Aims/Objective	Methods	Ref.
To investigate how the content of the biomass influences the kinetics, temporal evolution of the pyrolysis vapors, and production of the main bio-oil components during biomass pyrolysis	Materials, Py-FTIR analysis, isothermal mass loss of biomass, and using Py-GC/MS for the product analysis	[57]
To investigate the thermal decomposition of stalk and sour cherry flesh using thermogravimetric analysis, and to evaluate the activation energies using three kind of isoconversional approaches—Flynn–Wall–Ozawa, Friedman, or Kissinger–Akahira–Sunose. The findings reveal the pyrolysis kinetics and characteristics, as well as the ideal conditions for designing, optimizing, and simulating the pyrolysis process	Materials, physicochemical characterization, thermogravimetric analysis, and kinetic modeling	[58]
TGA/DTG investigation in an inert environment was performed to examine the thermal degrading and pyrolysis kinetics of biowastes.	Collection and preparation of biomass, proximate and ultimate investigation of samples as well as the calorific value, thermogravimetric/FTIR analysis	[59]
To carry out an extensive study that includes biochemical and physicochemical characterization, and the kinetic thermodynamic study of pyrolysis and thermal breakdown behavior of biomass from banana leaves	Sample preparation, banana leaves biomass pyrolysis reaction model determination using kinetic modeling, thermodynamic analysis, and thermogravimetric experiments	[60]
To clarify the pyrolytic behavior in terms of thermodynamic and kinetic characteristics, as well as the bioenergy potential of biological wastes resulting from the manufacturing of bio-products	The processing of bacterial biomass produced in a pilot-scale operation, sample characterization, FTIR spectroscopy, data processing using PCA, a TGA experiment, the characteristics of pyrolysis, thermo-kinetic studies pyrolysis, Py-GC/MS analysis, and the development of a model based on SVR	[61]
Pyrolyze three samples using thermogravimetric analysis and characterize them by determining how well various Phragmites Hirsuta components pyrolyze, thus this study offers theoretical direction for the formulation of the Phragmites preparation process, bioenergy is converted into Hirsuta by a thermochemical process	Material, characterization, Thermogravimetric analysis, kinetic modeling, reaction model determination, and thermodynamic analysis	[62]
To outline a straightforward method for analyzing the kinetic parameters (frequency factor, activation energy, and reaction model) of biomass with complicated thermal behavior. A multi-step mechanism for the biomass pyrolysis processes was employed to get the kinetic parameters using a deconvolution algorithm process coupled with isoconversional approaches.	Sample selection, preparation, and characterization, performed kinetics, and thermogravimetric analysis	[63]
In-depth research was conducted on the mechanisms causing the variations and the correlations between the pyrolysis characteristics and the various types of biomass. By improving our knowledge of the pyrolysis process in various biomass types, this work also serves as a reference for their thermal conversion methods	Materials, physicochemical of biomass, thermogravimetric, and kinetic analysis using the Coats–Redfern method TG and multi-peak fitting in the derivative thermogravimetric analysis.	[64]
Using a laboratory-scale (5 kg/h) AFP unit to accurately assess the impact of feedstock type on the characteristics of bio-oils produced from straw, miscanthus, and beech and poplar wood	Biomass that has been pyrolyzed, the pyrolysis process, the physicochemical characteristics of bio-oils, and a quantitative analysis of the chemical makeup of bio-oils	[6]
On the physical and chemical characteristics of biochar, particularly their effects on nitrogen (N) content and composition, the impact of feedstock type and temperature of pyrolysis were examined	Materials, preparation of biochar and sample preparation, and analytical methods	[65]
Studies involving feedstock, pyrolysis, and biochar, including policies on emission	Reviewing different concepts	[66]
The investigation of the effects of CaO addition sorbent and the temperature of pyrolysis on the chemical and the physical characteristics of obtained biochar and syngas	Material characteristics, experimental procedure, and methods	[38]
To look into how the structure of the resulting bio-char changed as the gaseous and liquid products evolved in relation to the pyrolysis temperature, and understanding how temperature affects the development of organics and the composition of biochar	Feedstock and chemicals, pyrolysis experiments, characterization of the products, and kinetic analysis	[43]

Aims/Objective	Methods	Ref.
To ascertain how the duration time and pyrolysis temperature affect the properties of hydrochars in comparison to biochars produced through direct slow pyrolysis. In order to do this, hydrochar produced by HTC of waste biomass was pyrolyzed at two different temperatures (350 and 500 °C) and three different times (1, 3 and 5 h), and the testing was conducted to establish a number of properties relevant to the use of chars as soil amendment, inexpensive adsorbent, or fuel, and growing media, including pH, electrical conductivity, electrochemical potential, porosity, phytotoxicity, and elemental composition	Selection of hydrochar, pyrolysis of hydrochar made from waste biomass, pyrolysis of waste biomass, and char characterization	[67]
To investigate the impact of the pyrolysis temperature using fluidized bed pyrolysis system, three reactions were carried out to convert solid waste into renewable aviation fuel in attempt to show the distributions of the liquid and gas products at different temperatures	Feedstock, equipment, experimental procedures, and product analysis	[26]
The reaction mechanism of the co-pyrolysis of biomass and coal in the TGA analyzer was investigated using both conventional TGA and a novel congruent-mass TGA analyses. Studies that compare how these two approaches differ in how they assess the likelihood of a coal–biomass interaction	Materials and TGA	[47]
To research the kinetics of the co-pyrolysis of the coal and pretreated watermelon rind (WMR) blends	Selection of the biomass, pretreatment, compositional analysis, determination of the (WMR) higher heating value, calculation of its exergy, preparation of sample blends, thermogravimetric analysis of the coal and pretreated (WMR), kinetic analysis, and estimation of the thermodynamic parameters	[68]
The following research goals were achieved: (a) performing a thorough thermogravimetric analysis (TGA) of the nut shells; (b) identifying the characteristic points in the nut shells' thermal decomposition process; (c) determining the temperature range at which hemicellulose, cellulose, and lignin decomposed in the examined nut shells; (d) estimating the fundamental kinetic parameters of the nut shells thermal decomposition; and (e) the physiochemical properties of the nut shells conversion rates as a function of the process temperature	Characteristics of the feedstock used in the research, thermogravimetric analysis, kinetic modelling, and model-fitting method: Coats–Redfern Method	[42]
TGA–FTIR (thermogravimetric analysis with FTIR analysis of evolved gases) pyrolysis experiment combined with advanced data analysis and modeling methods to assess the viability of developing an advanced methodology for the evaluation of biomass materials	Selection of the sample and testing on a suite of biomass materials	[41]
To assess the pyrolysis behavior of corks with various properties that might be used in scaling up the pyrolysis of cork-rich materials, in the strengthening of their value as well as their integration in thermochemical platforms	Materials, thermogravimetric analysis, kinetic analysis, estimation of chemical composition, wet chemical characterization, and FTIR analysis	[69]
The characteristics of green corn husks were described and analyzed in order to determine the thermokinetics conversion parameters through pyrolysis reactions that were kinetically studied using TGA and DTG, where the Flynn–Wall–Ozawa was used to compare the energetic efficiency from corn husk	Materials, biomass composition analysis, higher calorific value, non-isothermal thermogravimetric analyses, thermokinetics studies, master plots method, kinetic model proposed by Kissinger, kinetic model of Friedman, thermogravimetric analysis, and the mathematical simulation of the thermal decomposition kinetic of green corn husk biomass	[70]
To look into the technical and financial effects of different lignocellulosic elements on biomass pyrolysis, this work specifically investigates the basic mechanisms of cellulose, hemicellulose, and lignin transformation during pyrolysis	Characterization of biomass samples, sample preparation, pyrolysis, economic analysis, and validation via experimental values	[71]
To make available a theoretic framework for advancing the pyrolysis process and the efficient use of corn straw resources	Experimental materials, Instruments, and methods, analytical methods, and kinetics theory	[72]
Utilizing the pyrolysis poly-generation method to provide renewable energy and materials while overcoming the drawbacks of using rice husks	Materials, the preparation of an activated bio-char catalyst, a catalytic fast pyrolysis process, derived of amorphous SiO2 and porous carbon from bio-char, experiments on the adsorption of organic compounds, and physicochemical analysis	[34]

Aims/Objective	Methods	Ref.
To research, ascertain, and comprehend these solids' digestibility, as well as how the various hybrid method process parameters affected it	Feedstock and inoculum, pretreatment of wood chips, anaerobic digestion of pretreated solids and other analytical methods	[35]
In light of the fantastic outcomes produced in the chemical activation of rice husks (RHs), an assessment of bio-char made from RH pyrolysis was conducted to see if it could be used as a solid-phase extraction (SPE) to filter out harmful organic compounds from the biooil aqueous phase	Pyrolysis, chemical activation, characterization of activated carbon, SPE procedures, HPLC-DAD analysis, and method validation	[37]
Researchers have looked into the non-catalytic and catalytic co-pyrolysis of Ulva prolifera macroalgae (UPM) and straw (RS). To establish their ideal values, it has been investigated how temperature and mixing ratio affect the product's distribution	Feedstock characterization, experimental setup and procedures, catalysts preparation, catalyst characterization methods, and liquid products analysis methods	[39]
Studies of techno-economic performance of involving biorefinery concepts and steam pretreatment techniques	Feedstock composition/economic analysis	[73]
Based on the composition of the ash, the investigation's goal was to pinpoint the pertinent fractionation processes; the findings will later be applied to create a model for predicting slag composition and viscosity based on process parameters and fuel ash composition	Materials, feedstock preparation, and gasification process, and product char and gas analysis	[74]
To create the biofuel using a variety of techniques and examine the fuel's characteristics	Pyrolysis, extraction of pyrolysis oil, gasification, and procedure for producer gas generation, the analysis of the coconut shell using TGA, ultimate analysis, producer gas composition, and proximate analysis	[45]
A comparative investigation on the two-step pyrolysis (TSP) of lignocellulosic biomass was carried out on samples of walnut shell (WS), cotton stalk (CS), corncob (CC), and their acid-washed counterparts using TGA–FTIR and Py-GC/MS	Materials and preparation, samples characterizations, and TGA–FTIR and Py-GC/MS analysis	[40]
To assess how relations between lignin and cellulose, which occur during the co-pyrolysis of lignin and cellulose at temperatures between 100 and 350 °C, affect char structure changes	Sample preparation, fast pyrolysis experiments, and sample characterization	[75]
To examine the viability of spent coffee grounds (SCG) upcycling via pyrolysis for the production of biochar and energy, while also proposing a circular economy scenario for the effective use of SGC produced in the city of Larisa, Greece	Materials characteristics, pyrolysis and process protocol	[48]
To determine the levoglucosan percentage in the bio-oils prepared from fast pyrolysis of hydrochloric acid-treated and untreated rice husks (RHs) under vacuum conditions	Materials, characterization of RHs, pretreatment of RHs, Fast pyrolysis procedure, bio-oil characterization, and quantification of levoglucosan in bio-oils	[36]
To research the impact of total pressure, pyrolysis temperature, and CO2 concentration on biomass char gasification at various temperatures	Biomass samples, char preparation, and char reaction models	[76]
To research (a) the influence of biochar made from mesquite on the combined physical and hydraulic properties of various compacted soils, and (b) the interdependence of hydraulic properties of biochar-amended soil on the physical properties for possible use in bioengineered structures	Biochar, soils, physical properties, hydraulic properties, FTIR, FESEM, XRD, BET, and statistical analysis	[77]
To investigate levoglucosenone (LGO) production used levoglucosan (LGA) as feedstock. LGA dehydration has a lower activation energy and is chemically simpler than cellulose pyrolysis, enabling the reaction to occur at low temperatures	Materials, reaction, and product analysis	[11]
To look into how pressure affects the pyrolysis of biomass's thermal effects. Corn stalks, popular, switchgrass Trail-blazer, and switchgrass Alamo were the four energy crops chosen for experimental characterization	Materials, experimental techniques, and procedures	[78]
To assess the physicochemical potential of palm waste for pyrolysis processes that result in the production of biofuels	Preparation of biomass samples, and determination of physicochemical properties	[79]

Aims/Objective	Methods	Ref.
To clarify differences and similarities among the combustion of the original raw biowaste and the combustion of bio-oil and biochar in order to better understand how fly ash forms during these processes	**Biomass, biochar and bio-oil, fuel preparation prior to combustion experiments, combustion experiments, particle sampling system, operational procedure, and experimental plan, chemical analysis of the particulate matter, and multivariate data analysis are all covered in this study**	[80]
To look into the possibility of preventing agglomeration and enhancing sugar formation during the pyrolysis of herbaceous biomass by combining ferrous, magnesium, and ammonium cations with sulfate anions	**Methods for pretreatment, controlled pyrolysis duration-quench, continuous pyrolysis reactor system, assessment of sustainable throughput, quantification of sugar, ICP digestion, scanning, and electron microscopy analysis**	[81]
To research the energy potential of hydrochar made from straw, Virginia mallow, and wood (pine) biomass. The hydrochars' pyrolysis process was therefore investigated in order to determine how the gaseous byproducts changed with pyrolysis temperature	**Materials, hydrothermal carbonization process, and pyrolysis**	[82]
As an alternative technique for using waste biomass in the Polish context, a thorough study of slow solar pyrolysis of various waste biomass feedstock is presented. Although slow solar pyrolysis is the least expensive technology available due to the low heat input, it has the potential to produce highly porous solid fuels and provide a long-term solution for difficult waste disposal	**Feedstock characterization includes determining the amount of lignocellulose in the feedstock as well as its ultimate and proximate analyses.sample preparation, sample analysis for C, H, and N, and BET surface area measurement of porosity**	[83]
In order to comprehend pyrolysis behavior and potential interactions, investigations into the thermal decomposition of lignin and lignocellulosic biomass (watermelon rind) WMR were carried out at 325–625 °C to pyrolyze various lignin components in order to improve the pyrolytic products	**Materials, experimental set-up and procedures, and product analysis**	[84]

References

1. Tripathi, M.; Sahu, J.N.; Ganesan, P. Effect of Process Parameters on Production of Biochar from Biomass Waste through Pyrolysis: A Review. Renew. Sustain. Energy Rev. 2016, 55, 467–481.
2. Czajczyńska, D.; Anguilano, L.; Ghazal, H.; Krzyżyńska, R.; Reynolds, A.J.; Spencer, N.; Jouhara, H. Potential of Pyrolysis Processes in the Waste Management Sector. Therm. Sci. Eng. Prog. 2017, 3, 171–197.
3. Putra, P.H.M.; Rozali, S.; Patah, M.F.A.; Idris, A. A Review of Microwave Pyrolysis as a Sustainable Plastic Waste Management Technique. J. Environ. Manag. 2022, 303, 114240.
4. Kim, S.; Lee, Y.; Andrew Lin, K.Y.; Hong, E.; Kwon, E.E.; Lee, J. The Valorization of Food Waste via Pyrolysis. J. Clean. Prod. 2020, 259, 120816.
5. Rasaq, W.A.; Golonka, M.; Scholz, M.; Białowiec, A. Opportunities and Challenges of High-pressure Fast Pyrolysis of Biomass: A Review. Energies 2021, 14, 5426.
6. Auersvald, M.; Macek, T.; Schulzke, T.; Staš, M.; Šimáček, P. Influence of Biomass Type on the Composition of Bio-Oils from Ablative Fast Pyrolysis. J. Anal. Appl. Pyrolysis 2020, 150, 104838.
7. Basile, L.; Tugnoli, A.; Cozzani, V. The Role of Pressure in the Heat of Pyrolysis of a Lignocellulosic Biomass. Chem. Eng. Trans. 2015, 43, 451–456.
8. Kambo, H.S.; Dutta, A. A Comparative Review of Biochar and Hydrochar in Terms of Production, Physico-Chemical Properties and Applications. Renew. Sustain. Energy Rev. 2015, 45, 359–378.
9. Rangabhashiyam, S.; do Lins, P.V.S.; Oliveira, L.M.T.d.M.; Sepulveda, P.; Ighalo, J.O.; Rajapaksha, A.U.; Meili, L. Sewage Sludge-Derived Biochar for the Adsorptive Removal of Wastewater Pollutants: A Critical Review. Environ. Pollut. 2022, 293, 118581.
10. Nor, W.; Wan, R.; Hisham, M.W.M.; Ambar, M.; Hin, T.Y. A Review on Bio-Oil Production from Biomass by Using Pyrolysis Method. Renew. Sustain. Energy Rev. 2012, 16, 5910–5923.
11. Huang, X.; Kudo, S.; Shusaku Asano, J.H. Improvement of Levoglucosenone Selectivity in Liquid Phase Conversion of Cellulose-Derived Anhydrosugar over Solid Acid Catalysts. Fuel Process. Technol. 2021, 212, 106625.
12. Naik, D.K.; Monika, K.; Prabhakar, S.; Parthasarathy, R.; Satyavathi, B. Pyrolysis of Sorghum Bagasse Biomass into Bio-Char and Bio-Oil Products: A Thorough Physicochemical Characterization Pyrolysis of Sorghum Bagasse Biomass

into Bio-Char and Bio-Oil Products A Thorough Physicochemical Characterization. J. Therm. Anal. Calorim. 2017, 127, 1277–1289.

13. Michailof, C.M.; Kalogiannis, K.G.; Sfetsas, T.; Patiaka, D.T.; Lappas, A.A. Advanced Analytical Techniques for Bio-Oil Characterization. WIREs Energy Environ. 2016, 6, 614–639.
14. Pattiya, A. Bio-Oil Production via Fast Pyrolysis of Biomass Residues from Cassava Plants in a Fluidised-Bed Reactor. Bioresour. Technol. 2011, 102, 1959–1967.
15. Guizani, C.; Jeguirim, M.; Valin, S.; Limousy, L. Biomass Chars: The Effects of Pyrolysis Conditions on Their Morphology, Structure, Chemical Properties and Reactivity. Energies 2017, 10, 796.
16. Fu, P.; Hu, S.; Sun, L.; Xiang, J.; Yang, T.; Zhang, A.; Zhang, J. Structural Evolution of Maize Stalk/Char Particles during Pyrolysis. Bioresour. Technol. 2009, 100, 4877–4883.
17. Ighalo, J.O.; Eletta, O.A.A.; Adeniyi, A.G. Biomass Carbonisation in Retort Kilns: Process Techniques, Product Quality and Future Perspectives. Bioresour. Technol. Rep. 2022, 17, 100934.
18. Dupont, C.; Chiriac, R.; Gauthier, G.; Toche, F. Heat Capacity Measurements of Various Biomass Types and Pyrolysis Residues. Fuel 2014, 115, 644–651.
19. Elliott, D.C. Relation of Reaction Time and Temperature to Chemical Composition of Pyrolysis Oils; ACS Publications: Washington, DC, USA, 1988.
20. Mahinpey, N.; Murugan, P.; Mani, T.; Raina, R. Analysis of Bio-Oil, Biogas, and Biochar from Pressurized Pyrolysis of Wheat Straw Using a Tubular Reactor. Energy Fuels 2009, 23, 2736–2742.
21. Cetin, E.; Moghtaderi, B.; Gupta, R.; Wall, T.F. Influence of Pyrolysis Conditions on the Structure and Gasification Reactivity of Biomass Chars. Fuel 2004, 83, 2139–2150.
22. Uddin, M.N.; Techato, K.; Taweekun, J.; Rahman, M. An Overview of Recent Developments in Biomass Pyrolysis Technologies. Energies 2018, 11, 3115.
23. Qureshi, M.S.; Oasmaa, A.; Pihkola, H.; Deviatkin, I.; Tenhunen, A.; Mannila, J.; Minkkinen, H.; Pohjakallio, M.; Laine-ylijoki, J. Pyrolysis of Plastic Waste: Opportunities and Challenges. J. Anal. Appl. Pyrolysis 2020, 152, 104804.
24. Jahirul, M.I.; Rasul, M.G.; Chowdhury, A.A.; Ashwath, N. Biofuels Production through Biomass Pyrolysis—A Technological Review. Energies 2012, 5, 4959.
25. Chen, X.; Li, S.; Liu, Z.; Chen, Y.; Yang, H.; Wang, X.; Che, Q.; Chen, W.; Chen, H. Pyrolysis Characteristics of Lignocellulosic Biomass Components in the Presence of CaO. Bioresour. Technol. 2019, 287, 121493.
26. Chen, Y.K.; Lin, C.H.; Wang, W.C. The Conversion of Biomass into Renewable Jet Fuel. Energy 2020, 201, 117655.
27. Chowdhury, Z.Z.; Pal, K.; Yehye, W.; Suresh, S.; Detection, H. Pyrolysis: A Sustainable Way to Generate Energy from Waste; IntechOpen: London, UK, 2017; Volume 69036, pp. 1–36.
28. Dong, J.; Tang, Y.; Nzihou, A.; Chi, Y. Key Factors Influencing the Environmental Performance of Pyrolysis, Gasification and Incineration Waste-to-Energy Technologies. Energy Convers. Manag. 2019, 196, 497–512.
29. Lue, S. Principles and Advantages of Pyrolysis Moregreen. 2019, pp. 1–10. Available online: https://tomoregreen.com/principles-and-advantages-of-pyrolysis/ (accessed on 4 January 2024).
30. Henan Doing Environmental Protection Technology Co., Ltd. What Is the Advantage and Disadvantage of Using Pyrolysis Technology to Convert Plastic to Oil? Henan Doing Environmental Protection Technology Co., Ltd.: Zhengzhou, China, 2019; pp. 1–4.
31. Tian, B.; Xu, L.; Jing, M.; Liu, N.; Tian, Y. A Comprehensive Evaluation on Pyrolysis Behavior, Kinetics, and Primary Volatile Formation Pathways of Rice Husk for Application to Catalytic Valorization. Fuel Process. Technol. 2021, 214, 106715.
32. Kumar, P.; Subbarao, P.M.V.; Vijay, V.K. Assessment of Pyrolysis-Kinetics of Corncob and Eucalyptus Biomass Residue Using Thermo Gravimetric Analysis. Int. J. Sustain. Energy 2021, 40, 910–922.
33. Anca-Couce, A.; Tsekos, C.; Retschitzegger, S.; Zimbardi, F.; Funke, A.; Banks, S.; Kraia, T.; Marques, P.; Scharler, R.; de Jong, W.; et al. Biomass Pyrolysis TGA Assessment with an International Round Robin. Fuel 2020, 276, 118002.
34. Su, Y.; Liu, L.; Zhang, S.; Xu, D.; Du, H.; Cheng, Y.; Wang, Z.; Xiong, Y. A Green Route for Pyrolysis Poly-Generation of Typical High Ash Biomass, Rice Husk: Effects on Simultaneous Production of Carbonic Oxide-Rich Syngas, Phenol-Abundant Bio-Oil, High-Adsorption Porous Carbon and Amorphous Silicon Dioxide. Bioresour. Technol. 2020, 295, 122243.
35. Matsakas, L.; Sarkar, O.; Jansson, S.; Rova, U.; Christakopoulos, P. A Novel Hybrid Organosolv-Steam Explosion Pretreatment and Fractionation Method Delivers Solids with Superior Thermophilic Digestibility to Methane. Bioresour.

Technol. 2020, 316, 123973.

36. Téllez, J.F.; Silva, M.P.; Simister, R.; Gomez, L.D.; Fuertes, V.C.; De Paoli, J.M.; Moyano, E.L. Fast Pyrolysis of Rice Husk under Vacuum Conditions to Produce Levoglucosan. J. Anal. Appl. Pyrolysis 2021, 156, 105105.
37. Scapin, E.; Lazzari, E.; Benvenutti, E.V.; Falcade, T. Activated Carbon from Rice Husk Biochar with High Surface Area. Biointerface Res. Appl. Chem. 2021, 11, 10265–10277.
38. Sieradzka, M.; Gao, N.; Quan, C.; Mlonka-Mędrala, A.; Magdziarz, A. Biomass Thermochemical Conversion via Pyrolysis with Integrated CO2 Capture. Energies 2020, 13, 1050.
39. Hao, J.; Qi, B.; Li, D.; Zeng, F. Catalytic Co-Pyrolysis of Rice Straw and Ulva Prolifera Macroalgae: Effects of Process Parameter on Bio-Oil up-Gradation. Renew. Energy 2021, 164, 460–471.
40. Zhang, L.; Yang, Z.; Li, S.; Wang, X.; Lin, R. Comparative Study on the Two-Step Pyrolysis of Different Lignocellulosic Biomass: Effects of Components. J. Anal. Appl. Pyrolysis 2020, 152, 104966.
41. Serio, M.A.; Wójtowicz, M.A. Methodology for Identification and Classification of Biomass Pyrolysis Behavior; SAE Technical Paper; Advanced Fuel Research, Inc.: East Hartford, CT, USA, 2009.
42. Noszczyk, T.; Dyjakon, A.; Koziel, J.A. Kinetic Parameters of Nut Shells Pyrolysis. Energies 2021, 14, 682.
43. Zhang, C.; Chao, L.; Zhang, Z.; Zhang, L.; Li, Q.; Fan, H.; Zhang, S.; Liu, Q.; Qiao, Y.; Tian, Y.; et al. Pyrolysis of Cellulose: Evolution of Functionalities and Structure of Bio-Char versus Temperature. Renew. Sustain. Energy Rev. 2021, 135, 110416.
44. Jia, G. Combustion Characteristics and Kinetic Analysis of Biomass Pellet Fuel Using Thermogravimetric Analysis. Processes 2021, 9, 868.
45. Thamizhvel, R.; Suryavarman, K.; Velmurugan, V.; Sethuraman, N. Comparative Study of Gasification and Pyrolysis Derived from Coconut Shell on the Performance and Emission of CI Engine. Mater. Today Proc. 2021, 47, 978–983.
46. Swiechowski, K.; Koziel, J.A. The prediction of calorific value of carbonized solid fuel produced from refuse-derived fuel in the low-temperature pyrolysis in CO2. Materials 2020, 14, 49.
47. Mu, L.; Wang, R.; Zhai, Z.; Zhang, B.; Shang, Y.; Yin, H. Evaluation of Thermokinetics Methodology, Parameters, and Coke Characterization of Co-Pyrolysis of Bituminous Coal with Herbaceous and Agricultural Biomass. Biomass Convers. Biorefinery 2021, 13, 5957–5972.
48. Matrapazi, V.K.; Zabaniotou, A. Experimental and Feasibility Study of Spent Coffee Grounds Upscaling via Pyrolysis towards Proposing an Eco-Social Innovation Circular Economy Solution. Sci. Total Environ. 2020, 718, 137316.
49. Liu, Y.; Wu, S.; Zhang, H.; Xiao, R. Fast Pyrolysis of Holocellulose for the Preparation of Long-Chain Ether Fuel Precursors: Effect of Holocellulose Types. Bioresour. Technol. 2021, 338, 125519.
50. Charvet, F.; Silva, F.; Ruivo, L.; Tarelho, L.; Matos, A.; da Silva, J.F.; Neves, D. Pyrolysis Characteristics of Undervalued Wood Varieties in the Portuguese Charcoal Sector. Energies 2021, 14, 2537.
51. Mlonka-Mędrala, A.; Evangelopoulos, P.; Sieradzka, M.; Zajemska, M.; Magdziarz, A. Pyrolysis of Agricultural Waste Biomass towards Production of Gas Fuel and High-Quality Char: Experimental and Numerical Investigations. Fuel 2021, 296, 120611.
52. Wang, X.; Wu, J.; Chen, Y.; Pattiya, A.; Yang, H.; Chen, H. Comparative Study of Wet and Dry Torrefaction of Corn Stalk and the e Ff Ect on Biomass Pyrolysis Polygeneration. Bioresour. Technol. 2018, 258, 88–97.
53. Liu, H.; Liu, J.; Huang, H.; Evrendilek, F.; Wen, S.; Li, W. Optimizing Bioenergy and By-Product Outputs from Durian Shell Pyrolysis. Renew. Energy 2021, 164, 407–418.
54. Vinu, D.V.S.R. Effects of Biomass Particle Size on Slow Pyrolysis Kinetics and Fast Pyrolysis Product Distribution. Waste Biomass Valorization 2018, 9, 465–477.
55. Açıkalın, K. Evaluation of Orange and Potato Peels as an Energy Source: A Comprehensive Study on Their Pyrolysis Characteristics and Kinetics. Biomass Convers. Biorefinery 2021, 12, 501–514.
56. Moriyama, F.; Mizuno, S.; Tagami-Kanada, N.; Sawai, T. Evaluation of Energy Properties of Torrefied Biomass for a given Pyrolysis Condition by Isothermal Pyrolysis Kinetics. Mech. Eng. J. 2021, 8, 21-00069.
57. Ojha, D.K.; Viju, D.; Vinu, R. Fast Pyrolysis Kinetics of Lignocellulosic Biomass of Varying Compositions. Energy Convers. Manag. X 2021, 10, 100071.
58. Gözke, G.; Açıkalın, K. Pyrolysis Characteristics and Kinetics of Sour Cherry Stalk and Flesh via Thermogravimetric Analysis Using Isoconversional Methods. J. Therm. Anal. Calorim. 2020, 146, 893–910.
59. Mukherjee, A.; Okolie, J.A.; Tyagi, R.; Dalai, A.K.; Niu, C. Pyrolysis Kinetics and Activation Thermodynamic Parameters of Exhausted Coffee Residue and Coffee Husk Using Thermogravimetric Analysis. Can. J. Chem. Eng. 2021, 99,

1683–1695.

60. Singh, R.K.; Pandey, D.; Patil, T.; Sawarkar, A.N. Pyrolysis of Banana Leaves Biomass: Physico-Chemical Characterization, Thermal Decomposition Behavior, Kinetic and Thermodynamic Analyses. Bioresour. Technol. 2020, 310, 123464.
61. Shahbeig, H.; Nosrati, M. Pyrolysis of Biological Wastes for Bioenergy Production: Thermo-Kinetic Studies with Machine-Learning Method and Py-GC/MS Analysis. Fuel 2020, 269, 117238.
62. Liu, L.; Zhang, X.; Zhao, R.; Song, G.; Tian, L. Pyrolysis of Phragmites Hirsuta Study on Pyrolysis Characteristics, Kinetic and Thermodynamic Analyses. Int. J. Energy Res. 2021, 45, 15200–15216.
63. da Silva, J.C.G.; de Albuquerque, J.G.; de Araujo Galdino, W.V.; de Sena, R.F.; Andersen, S.L.F. Single-Step and Multi-Step Thermokinetic Study—Deconvolution Method as a Simple Pathway for Describe Properly the Biomass Pyrolysis for Energy Conversion. Energy Convers. Manag. 2020, 209, 112653.
64. Chen, H.; Liu, Z.; Chen, X.; Chen, Y.; Dong, Z.; Wang, X.; Yang, H. Comparative Pyrolysis Behaviors of Stalk, Wood and Shell Biomass: Correlation of Cellulose Crystallinity and Reaction Kinetics. Bioresour. Technol. 2020, 310, 123498.
65. Xu, S.; Chen, J.; Peng, H.; Leng, S.; Li, H.; Qu, W.; Hu, Y.; Li, H.; Jiang, S.; Zhou, W.; et al. Effect of Biomass Type and Pyrolysis Temperature on Nitrogen in Biochar, and the Comparison with Hydrochar. Fuel 2021, 291, 120128.
66. Rodriguez Franco, C.; Page-Dumroese, D.S.; Pierson, D.; Miller, M.; Miles, T. Policy and Regulations for Mobile Biochar Production in the United States of America. Forests 2024, 15, 192.
67. Bahcivanji, L.; Gascó, G.; Paz-Ferreiro, J.; Méndez, A. The Effect of Post-Pyrolysis Treatment on Waste Biomass Derived Hydrochar. Waste Manag. 2020, 106, 55–61.
68. Fakayode, O.A.; Wang, Z.; Wahia, H.; Mustapha, A.T.; Zhou, C.; Ma, H. Higher Heating Value, Exergy, Pyrolysis Kinetics and Thermodynamic Analysis of Ultrasound-Assisted Deep Eutectic Solvent Pretreated Watermelon Rind Biomass. Bioresour. Technol. 2021, 332, 125040.
69. Şen, U.; Pereira, H. Pyrolysis Behavior of Alternative Cork Species. J. Therm. Anal. Calorim. 2021, 147, 4017–4025.
70. Reinehr, T.O.; Ohara, M.A.; de Oliveira Santos, M.P.; Barros, J.L.M.; Bittencourt, P.R.S.; Baraldi, I.J.; da Silva, E.A.; Zanatta, E.R. Study of Pyrolysis Kinetic of Green Corn Husk. J. Therm. Anal. Calorim. 2021, 143, 3181–3192.
71. Pang, Y.X.; Yan, Y.; Foo, D.C.Y.; Sharmin, N.; Zhao, H.; Lester, E.; Wu, T.; Pang, C.H. The Influence of Lignocellulose on Biomass Pyrolysis Product Distribution and Economics via Steady State Process Simulation. J. Anal. Appl. Pyrolysis 2020, 158, 104968.
72. Chen, D.; Gao, D.; Huang, S.; Capareda, S.C.; Liu, X.; Wang, Y.; Zhang, T.; Liu, Y.; Niu, W. Influence of Acid-Washed Pretreatment on the Pyrolysis of Corn Straw: A Study on Characteristics, Kinetics and Bio-Oil Composition. J. Anal. Appl. Pyrolysis 2021, 155, 105027.
73. Yu, Y.; Wu, J.; Ren, X.; Lau, A.; Rezaei, H.; Takada, M.; Bi, X.; Sokhansanj, S. Steam explosion of lignocellulosic biomass for multiple advanced bioenergy processes: A review. Renew. Sustain. Energy Rev. 2022, 154, 111871.
74. Mielke, K.; Kolb, T.; Müller, M. Chemical Fractionation of Inorganic Constituents in Entrained Flow Gasification of Slurry from Straw Pyrolysis. Biomass Bioenergy 2020, 141, 105732.
75. Chua, Y.W.; Wu, H.; Yu, Y. Effect of Cellulose-Lignin Interactions on Char Structural Changes during Fast Pyrolysis at 100-350 °C. Proc. Combust. Inst. 2021, 38, 3977–3986.
76. Fermoso, J.; Stevanov, C.; Moghtaderi, B.; Arias, B.; Pevida, C.; Plaza, M.G.; Rubiera, F.; Pis, J.J. High-Pressure Gasification Reactivity of Biomass Chars Produced at Different Temperatures. J. Anal. Appl. Pyrolysis 2009, 85, 287–293.
77. Hussain, R.; Ghosh, K.K.; Ravi, K. Impact of Biochar Produced from Hardwood of Mesquite on the Hydraulic and Physical Properties of Compacted Soils for Potential Application in Engineered Structures. Geoderma 2021, 385, 114836.
78. Basile, L.; Tugnoli, A.; Stramigioli, C.; Cozzani, V. Influence of Pressure on the Heat of Biomass Pyrolysis. Fuel 2014, 137, 277–284.
79. Shrivastava, P.; Khongphakdi, P.; Palamanit, A.; Kumar, A.; Tekasakul, P. Investigation of Physicochemical Properties of Oil Palm Biomass for Evaluating Potential of Biofuels Production via Pyrolysis Processes. Biomass Convers. Biorefinery 2021, 11, 1987–2001.
80. Johansson, A.C.; Molinder, R.; Vikström, T.; Wiinikka, H. Particle Formation during Suspension Combustion of Different Biomass Powders and Their Fast Pyrolysis Bio-Oils and Biochars. Fuel Process. Technol. 2021, 218, 106868.
81. Rollag, S.A.; Lindstrom, J.K.; Brown, R.C. Pretreatments for the Continuous Production of Pyrolytic Sugar from Lignocellulosic Biomass. Chem. Eng. J. 2020, 385, 123889.

82. Magdziarz, A.; Wilk, M.; Wądrzyk, M. Pyrolysis of Hydrochar Derived from Biomass—Experimental Investigation. Fuel 2020, 267, 117246.

83. Sobek, S.; Werle, S. Solar Pyrolysis of Waste Biomass: A Comparative Study of Products Distribution, in Situ Heating Behavior, and Application of Model-Free Kinetic Predictions. Fuel 2021, 292, 120365.

84. Yu, J.; Wang, D.; Sun, L. The Pyrolysis of Lignin: Pathway and Interaction Studies. Fuel 2021, 290, 120078.