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GABRIELA FONTES MAYRINCK CUPERTINO

Co-pyrolysis of biomass and polyethylene terephthalate (PET) is an alternative to produce chemical and energy products

JERÔNIMO MONTEIRO – ES
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Dissertation presented to the Graduate Program in Forest Sciences of the Center for Agricultural Sciences and Engineering of the Federal University of Espírito Santo as part of the requirements for obtaining the Master's Degree in Forest Sciences in the Forest Sciences Concentration Area.
Advisor: Prof. PhD Ananias Francisco Dias Júnior.
Co-advisors: Prof. PhD Michel Picanço Oliveira and Prof. PhD Daniel Saloni.

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DEDICATION

To my grandparents Antônio Francisco (in memoriam) and Janir Ferreira (in memoriam), my biggest supporters in life and, today, my stars in the sky.
"De todo o amor que eu tenho, metade foi vocês que me deram".

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GENERAL ABSTRACT

CUPERTINO, Gabriela Fontes Mayrinck. **Co-pyrolysis of biomass and polyethylene terephthalate (PET) is an alternative to produce chemical and energy products.** 2022. Dissertation (Master’s degree in Forest Sciences) – Federal University of Espírito Santo, Jerônimo Monteiro, ES. Advisor: Prof. PhD Ananias Francisco Dias Júnior. Co-advisors: Prof. PhD Michel Picanço Oliveira and Prof. PhD Daniel Saloni.

Polyethylene terephthalate (PET) plastics are valuable materials for packaging and various consumer items, but poorly managed PET waste constitutes a serious environmental issue. In order to solve this problem, the process of co-pyrolysis of PET and biomass has been an alternative for reuse of this material and generation of solid and liquid products of industrial interest. Therefore, the main objective of this study was to evaluate the effect of different heating rates (1, 3 and 5 ºC.min^{-1}) and the addition of PET in different proportions (0, 15 and 25%, weight basis) on the co-pyrolytic charcoal and wood vinegar from the co-pyrolysis of biomass and PET. Subsequently, the co-pyrolysis products (co-pyrolytic charcoal, pyroligneous liquid and non-condensable gases) were calculated. Co-pyrolytic charcoal was evaluated for its physical (bulk density, apparent density, and moisture), chemical (Fourier-transform infrared spectroscopy) and energy (higher, lower, and net heating values) properties. For purification of the pyroligneous liquid, double-distillation was carried out at 100 °C to eliminate the toxic fraction of the material and obtain the fraction of interest, called wood vinegar. Purification yields were calculated. Subsequently, the pH, density and viscosity of wood vinegar were analyzed. The chemical evaluation of wood vinegar was performed using GC-MS analysis. The addition of PET reduced by 7% the yield of co-pyrolytic charcoal and by 20% the yield of pyroligneous liquid, products of the co-pyrolysis. Higher PET additions (25%) associated with lower heating rates (1 ºC.min^{-1}) were responsible for a maximum energy density of 4.7 Gcal.m^{-3} of the co-pyrolytic charcoal. Regarding wood vinegar, lower heating rates (1 ºC.min^{-1}) favored the formation of more chemical compounds (ketones, hydrocarbons, furans and pyrans). However, ketones were still the major compounds. In short, the co-pyrolysis of biomass and PET can be a sustainable and innovative strategy for generating solid and liquid products of commercial value.

Keywords: reuse of PET; circular economy; heating rate; sustainability, chromatography.

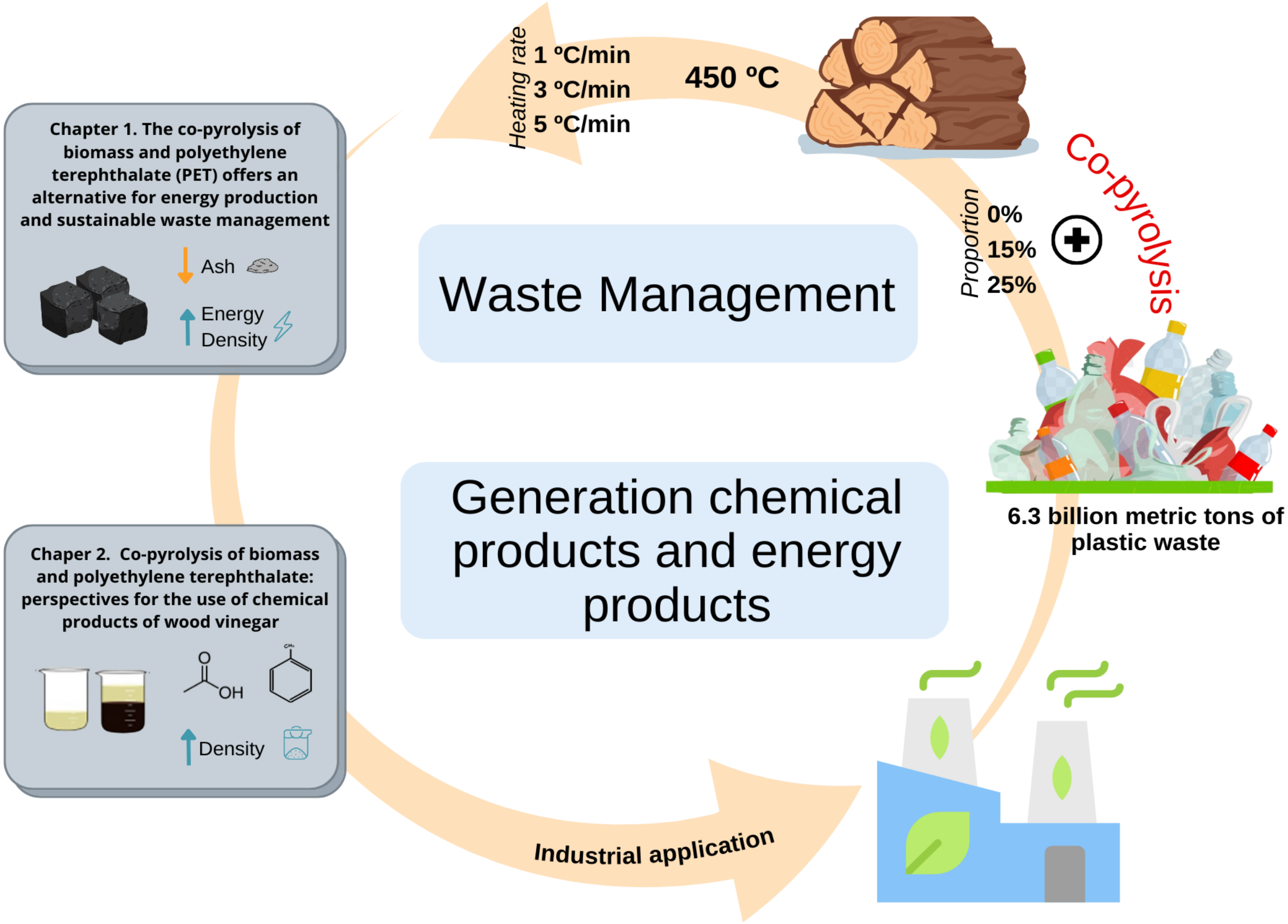
RESUMO GERAL

CUPERTINO, Gabriela Fontes Mayrinck. **Co-pirólise de biomassa e tereftalato de polietileno (PET) é uma alternativa para a produção de produtos químicos e energéticos**. 2022. Dissertação (Mestrado em Ciências Florestais) – Universidade Federal do Espírito Santo, Jerônimo Monteiro, ES. Orientador: Prof. Ananias Francisco Dias Júnior. Coorientadores: Prof. Dr. Michel Picanço Oliveira e Prof. Dr. Daniel Saloni.

Os plásticos de polietileno tereftalato (PET) são materiais excepcionalmente úteis para embalagens e diversos itens de consumo, mas os resíduos de PET mal gerenciados constituem sérios problemas ambientais. A fim de solucionar essa problemática, o processo de co-pirólise de PET e biomassa tem sido uma alternativa para reaproveitamento desse material e geração de produtos sólidos e líquidos de interesse industrial. Diante disso, este estudo teve como principal objetivo avaliar o efeito de diferentes taxas de aquecimento (1, 3 e 5 ºC.min^{-1}) e adição de PET em diferentes proporções (0, 15 e 25%, em relação ao peso) no carvão co-pirólitico e vinagre da madeira proveniente da co-pirólise de biomassa e PET. Posteriormente os produtos da co-pirólise (carvão co-pirolítico, líquido pirolenhoso e gases não condensáveis) foram calculados. O carvão co-pirólitico foi avaliado frente às suas propriedades físicas (densidade a granel, densidade aparente e umidade), químicas (espectroscopia no infravermelho por transformada de Fourier) e energéticas (poder calorífico superior, inferior e útil). Para a purificação do líquido pirolenhoso, foi realizada a bidestilação à 100 °C para eliminação da fração tóxica do material e obtenção da fração de interesse denominada vinagre da madeira. Os rendimentos da purificação foram calculados. Posteriormente, foram analisados o pH, a densidade e a viscosidade dos vinagres da madeira. A avaliação química do vinagre da madeira foi realizada por meio da GC-MS análise. A adição de PET reduziu em 7% os rendimentos de carvão co-pirólitico e em 20% de líquido pirolenhoso, produtos da co-pirólise. Maiores adições de PET (25%) atreladas a menores taxas de aquecimento (1 ºC.min^{-1}) foram responsáveis por uma densidade energética máxima de 4,7 Gcal.m^{-3} do carvão co-pirólitico. Em relação ao vinagre da madeira, nota-se que menores taxas de aquecimento (1 ºC.min^{-1}) favoreceram a formação de mais compostos químicos (cetonas, hidrocarbonetos, furanos e piranos), contudo, as cetonas ainda foram os compostos majoritários. Em suma, a co-pirólise de biomassa e PET pode ser uma estratégia sustentável e inovadora para a geração de produtos sólidos e líquidos de valor comercial.

Palavras-chave: reaproveitamento de PET; economia circular; taxa de aquecimento; sustentabilidade, cromatografia.

GRAPHICAL ABSTRACT



Chapter 1. The co-pyrolysis of biomass and polyethylene terephthalate (PET) offers an alternative for energy production and sustainable waste management

Chaper 2. Co-pyrolysis of biomass and polyethylene terephthalate: perspectives for the use of chemical products of wood vinegar

Waste Management

Generation chemical products and energy products

SUMMARY

1. GENARAL INTRODUCTION

Municipal solid waste (MSW) is considered one of today's primary environmental pollutants, with a faster generation than greenhouse gases. According to the World Bank report, around 2 billion metric tons of MSW are produced annually worldwide. World estimates indicate that approximately 40% of MSW is not adequately managed (ADEKOLA et al., 2021; KAZA et al., 2018). Being considered an acute problem in emerging cities, the management of this waste represents one of the highest costs in municipal budgets in towns around the world. Typically receiving more than 10,000 tons of waste per day, landfills such as Leogang in Shanghai, China, Sudokwon in Seoul, Jardim Gramacho in Rio de Janeiro, Brazil, and Bordo Poniente in Mexico City, are vying for the title of world's largest (HOORNWEG; BHADA-TATA; KENNEDY, 2013). The global view is worrying. Studies indicate that in the middle of this century, the world population will produce 4 billion tons of MSW a year (KAZA et al., 2018). The planet is already suffering from the impacts of current waste. We are on our way to doubling the amounts. How can the current situation be improved? The first step is to see waste as an opportunity and not as garbage, to obtain environmentally viable alternatives. In this perspective, plastics, one of the main constituents of the world's MSW, should be considered.

Plastic materials, erroneously called the “contemporary symbol of modernity,” have taken over everyday human life and have uniquely transformed the modern world. This fact justifies their exorbitant annual production. About 367 million metric tons of plastic were produced in 2020 (WILLIAMS; RANGEL-BUITRAGO, 2022). This high volume of production raises concerns about these materials. This is because most plastics used in everyday life are single-use, being discarded immediately. In the United States, for example, every hour, 3 million PET water bottles are used and immediately discarded (WILLIAMS; RANGEL-BUITRAGO, 2022). The numbers are staggering. PET represents 30% of the global demand for plastics, with an estimated production of 488 billion tons. This material can be an excellent raw material in production systems (CHU et al., 2022; WANG et al., 2021; VOLANTI et al., 2019). Considered a typical example of “material that does not disappear,” due to the long decomposition time in nature, PET is a danger to humans, a threat to rivers, coasts, and ocean life, in addition to being an aesthetic problem (HU et al., 2020; SUCHITHRA et al., 2022). The situation is worrying. Studies claim that by 2050 there will be more single-use plastic such as PET than fish in our ocean (AGYEMAN et al., 2019; LOKESHWARI et al., 2019; SUCHITHRA et al., 2022). Strategies for managing and reusing plastic materials are extremely urgent.

In order to improve the inappropriate disposal of these materials, the interest of the scientific and industrial community in co-pyrolytic techniques has increased considerably in recent years. This co-pyrolysis process can act as a promising and efficient waste management technology, capable of significantly reducing the volume of PET waste as more waste is consumed as raw material, reducing the landfill required and lowering costs for waste treatment. In addition to solving several environmental problems. Co-pyrolysis consists of the thermal degradation of two or more different materials in partial or total absence of oxygen. As in the pyrolysis process, it generates solid (charcoal), liquid (pyroligneous liquid), and gaseous (non-condensable gases) products (ABNISA; WAN DAUD, 2014; ZHOU et al., 2006). Co-pyrolysis is a promising technique to simultaneously process biomass and plastic and produce high value-added liquid products. In addition to being an environmentally viable technique, several studies claim that this process has been used to improve the characteristics of the products generated (FANG et al., 2016; HONG et al., 2017; WANG et al., 2018; ZHANG et al., 2018; ZHANG et al. al., 2015a). It is reported that the pyroligneous liquid product derived directly from biomass generally has a nature of high oxygen content, acidity, instability, viscosity, and corrosion that significantly restricted its applications (ABNISA; WAN DAUD, 2014; CZERNIK; BRIDGWATER, 2004).

When PET is added to the process, a material with a high hydrogen content and a high effective ratio of hydrogen to carbon, the donation of hydrogen atoms can occur to intensify the thermal decomposition of the biomass and reduce the polycondensation of the intermediate products (ZHANG et al., 2015b). In this way, the oxygenated compounds originating from the biomass during the co-pyrolysis process can promote chain scission and plastic cracking, significantly improving the quality of the liquid product (ZHANG et al., 2013). However, most of these studies use a large percentage of plastic in co-pyrolysis. Thus, the behavior of the liquid when biomass is the majority raw material in the process is not known. In addition, studies on co-pyrolysis of biomass and plastics focus on crude pyroligneous liquid, not evaluating the potential of the purified fraction, called wood vinegar. In general, the co-pyrolysis of biomass and plastics is a well-established process in the literature regarding the benefits of the pyroligneous liquid. However, the co-pyrolytic charcoal produced has not received much attention. Some studies have evaluated the potential of charcoal from the co-pyrolysis of PET and biomass as a raw material for the manufacture of activated carbon, carbon nanotubes, as an adsorbent and soil amender (AKANCHA, KUMARI, and SINGH, 2019; JAMRADLOEDLUK and LERTSATITTHANAKORN, 2014; VANAPALLI et al., 2021). However, many discoveries still need to be made regarding its energy potential. The study by Samal et al. (2021b) was the only one that verified the energy properties of co-pyrolytic charcoal from biomass and plastic materials, emphasizing that it has potential for the sector since plastic favored the energy characteristics of the material. Thus, it is evident that discoveries need to be made to optimize the application of co-pyrolytic charcoal in the industry.

It can be said that co-pyrolysis is an alternative PET waste management method and an efficient strategy for the generation of solid and liquid products with high added value. (DORADO; MULLEN; BOATENG, 2015). The proportion of raw material used in the process contributes immensely to the synergistic effects of co-pyrolysis. The amount of biomass and PET used in the process can be a differential for improving the quality and quantity of the resulting products (ZHANG et al., 2016). In addition to the proportion of raw materials, the heating rate can play an essential role in co-pyrolysis since the raw materials in question have different degradation temperatures (UZOEJINWA et al., 2018). It should be emphasized that there are still no reports on the influence of the heating rate on the products of the co-pyrolysis of biomass and PET. It is noted that the mixtures of raw materials and heating rate are factors that directly contribute to the synergistic effect and, therefore, should be further investigated (QUAN; GAO, 2016). Most studies evaluate the kinetics involved in the process parameters or the characteristics of the products obtained (BURRA; GUPTA, 2018; OYEDUN et al., 2014; VAN NGUYEN et al., 2019; VO et al., 2022; ZHAO et al., 2022; ZHAO et al., 2018). Studying the impact of process parameters on the characteristics of co-pyrolytic charcoal and wood vinegar would contribute to the possible use of the materials as a product, in addition to helping to further refine the process.

There are no reports of studies that aim to apply co-pyrolysis of biomass and PET as an alternative to obtain liquid and solid products simultaneously. The main objective of this study was to investigate the effect of heating rate and PET addition on co-pyrolytic charcoal and wood vinegar from the co-pyrolysis of biomass and PET. We present insights into the possibilities of using these materials, promoting sustainability, waste management, and technological innovation through the results.

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3. CHAPTER 1. The co-pyrolysis of biomass and polyethylene terephthalate (PET) is an alternative for energy production and sustainable waste management

Highlights

- Biomass and PET co-pyrolysis can be used to repurpose plastic.
- The addition of PET in pyrolysis increased the heating rate of charcoal.
- The ash content of co-pyrolytic charcoal was reduced with the addition of PET.
- Co-pyrolytic charcoal can be considered a material for power generation.

Graphic Abstract

Abstract

Disposal of waste plastics is an environmental problem that has gained attention over the years. Co-pyrolysis is a promising alternative for transforming this material into new products. This study evaluated how heating rates and PET proportions influence the properties of charcoal obtained by co-pyrolysis. We evaluated the process using *Eucalyptus* spp biomass, three PET proportions (0, 15, and 25%), and three heating rates (1, 3, and 5 °C min^{-1}). We conducted co-pyrolysis in a low oxygen atmosphere without gas entry, a final temperature of 450 °C, and a final residence time of 15 min, and investigated the physical (bulk density, moisture content), chemical (proximate analysis and Fourier-transform infrared spectroscopy), energetic (higher, lower, and net heating values), and thermal (thermogravimetric analysis) properties of the produced material. We assessed the morphology of co-pyrolytic charcoal via scanning electron microscopy (SEM). The average yield of co-pyrolytic charcoal decreased by 5% compared to the biomass-only pyrolytic material. In addition to yield differences, the percentage of ash decreased by about 7% in charcoal with PET. The produced material had a maximum heating value of 7,684 kcal kg^{-1} and maximum energy density of 4.7 Gcal m^{-3}. SEM images showed the surface coverage and pore impregnation of liquefied PET, indicating the synergistic effect of raw materials. The co-pyrolysis of biomass and polyethylene terephthalate is a promising strategy for generating energy products and ensuring the reuse of plastic materials.

Keywords: circular economy; reuse of polymers, recycling of plastic materials.

Resumo

O plástico, material utilizado por diversas indústrias, é um problema ambiental que vem ganhando atenção ao longo dos anos. A co-pirólise é uma alternativa promissora para transformar esse material em novos produtos. Este estudo avaliou como as taxas de aquecimento e as proporções de PET influenciam nas propriedades do carvão obtido por co-pirólise. Avaliamos o processo utilizando biomassa de *Eucalyptu*s spp com a adição de três proporções de PET (0, 15 e 25%) e três taxas de aquecimento (1, 3 e 5 °C min^{-1}). Realizamos a co-pirólise em uma atmosfera de baixo oxigênio sem entrada de gás, temperatura final de 450 °C e tempo de residência final de 15 min. Investigamos os aspectos físicos (densidade aparente, umidade), químicos (análise próxima e infravermelho com transformada de Fourier espectroscopia), propriedades energéticas (valores de aquecimento superior, inferior e líquido) e térmicas (análise termogravimétrica) do material produzido. Além disso, avaliamos a morfologia do carbono co-pirolítico por meio de microscopia eletrônica de varredura (MEV). O rendimento médio do carvão co-pirolítico diminuiu 5% em comparação com o carvão oriundo apenas de biomassa. Além das diferenças de rendimento, a porcentagem de cinzas diminuiu cerca de 7% no carvão com PET. O material produzido apresentou um poder calorífico superior máximo de 7684 kcal kg^{-1} e uma densidade energética máxima de 4,7 Gcal m^{-3}. As imagens MEV mostraram a cobertura da superfície e a impregnação dos poros por PET liquefeito, evidenciando o efeito sinérgico das matérias-primas. A co-pirólise de biomassa e polietileno tereftalato consiste em uma estratégia promissora para geração de produtos energéticos e garantia do reaproveitamento de materiais plásticos.

Palavras-chave: economia circular; reutilização de polímeros, reciclagem de materiais plásticos.

1. INTRODUCTION

Can we imagine a world without plastics? It is difficult to think of something people use or interact with whose composition fails to include one or more types of plastic. Indeed, plastics are the third most used material worldwide, with annual global production of about 350 million metric tons (GILENO and TURCI, 2021; TAMBURINI et al., 2021). Moreover, studies indicate that this production should double by 2040 (MATTHEWS; MORAN; JAISWAL, 2021; VURAL GURSEL et al., 2021). The massive production of plastic has contributed to produce about 6.3 billion tons of plastic waste in the last 60 years, of which only 25% was recycled (GEYER, JAMBECK, and LAW, 2017; LIU et al., 2021). This situation is worrying. The planet is already suffering from the impacts of plastic wastes, and the outlook is for a twofold increase. How can we alleviate the current situation? Thinking about alternatives, one can apply Lavoisier's concept that "nothing is wasted in nature," and use the generated waste in environmentally friendly innovative ways based on technology and efficiency. The first step to obtaining environmentally viable alternatives is to view plastic waste as an opportunity rather than as garbage, a perspective that particularly applies to polyethylene terephthalate (PET). PET accounts for 30% of the global demand for plastic, and with estimated yearly production of 488 billion tons, it can be an excellent raw material in production systems (CHU et al., 2022; WANG et al., 2021; VOLANTI et al., 2021; VOLANTI et al., 2019).

To achieve sustainability, the interest of the scientific and industrial communities in co-pyrolytic techniques involving PET materials and biomass has increased considerably in recent years. These pyrolyzed materials improve pyrolysis yields. Studies have considered the co-pyrolysis of these materials in processes with limited oxygen as an environmentally friendly technique due to its reduced risk of emitting toxins into the air (AL-SALEM et al., 2017; VANAPALLI et al., 2021a). Many researchers have found co-pyrolysis of PET and biomass to be an important technique to convert these materials into valuable raw materials, enhancing benefits such as reducing waste volume and generating new products. This process dramatically influences the yield, chemical structure and physical properties of co-pyrolytic charcoal (AKANCHA; KUMARI; SINGH, 2019; CHATTOPADHYAY et al., 2016). Studies point to the occurrence of hydrodeoxygenation reactions during co-pyrolysis, favoring the yield and quality of the generated liquid due to the synergistic interactions between materials, favoring their applicability in various sectors, such as chemicals and biofuels (DEWANGAN; PRADHAN; SINGH, 2016; SURIAPPARAO et al., 2018; ZHANG et al., 2014).

Charcoal, a co-pyrolysis product with a carbon-rich structure, has received little attention from the literature. Some studies have evaluated the potential of charcoal produced by the co-pyrolysis of PET and biomass as a raw material to manufacture activated charcoal and carbon nanotubes, for use as adsorbents and soil rectifiers (AKANCHA; KUMARI; SINGH, 2019; JAMRADLOEDLUK; LERTSATITTHANAKORN, 2014; SAMAL et al., 2021; VANAPALLI et al., 2021a, 2021b). However, few studies have reported the use of large quantities of co-pyrolytic charcoal to generate energy, for example. Many discoveries are yet to be made on its thermal properties and applicability for energy generation. Although some studies have reported the thermal characteristics of charcoal from the co-pyrolysis of biomass and plastic materials (CHATTOPADHYAY et al., 2016; SAMAL et al., 2021), the literature still lacks an extensive thermal characterization of charcoal produced from biomass and PET under different process variables, including assessment of how the synergistic effect between biomass and PET influences the properties of the produced charcoal and evaluation of the effect of different co-pyrolytic parameters. Increasing the heating rates of biomass pyrolysis reduces charcoal yield, influences its properties, and produces a more porous material (SOMERVILLE; DEEV, 2020). However, studies are still lacking on how heating rates influence the charcoal produced by the co-pyrolysis of biomass and PET. Moreover, co-pyrolysis optimization requires the investigation of the best PET and biomass proportions.

Analysis of the properties and structure of co-pyrolytic charcoal for use in energy generation is relevant to fill some of the gaps in the scientific and lay literature. Furthermore, studying how pyrolytic parameters impact the possible energy applicability of charcoal will help further refine the variables involved in its production. The information obtained in this study can help to model, design, and operate thermochemical conversion processes with emphasis on co-pyrolytic biomass and plastic mixtures. Thus, we evaluated how heating rates and PET proportions influence the properties of co-pyrolytic charcoal to determine the parameters which best assess the energy use of this material.

2. MATERIAL AND METHODS

2.1.Materials and pyrolysis

Eucalyptus spp. biomass from an experimental plantation had the following chemical constitution: 30.41% total lignin, 0.95% extractives, and 68.64% holocellulose. For co-pyrolysis, the plastic source came from post-consumer polyethylene terephthalate-based materials (PET), such as bottles containing of water, juice, soda and other beverages obtained from a waste collection facility. Both materials were characterized (Table S1 and

Figures S1 and S2, supplementary material) to assess how their composition influenced the charcoal produced. Raw materials were fragmented into 5 x 5 cm samples. Then, PET and biomass were mixed and dried in an oven (103 ± 2 °C), following addition of 0, 15, and 25% of PET by weight. Co-pyrolytic charcoal was produced with varying parameters (heating rate and proportion of raw material fed into the reactor), thus labeled: 0, 15, and 25% added PET with a 1 ºC min^{-1} heating rate as P0T1, P15T1, and P25T1, respectively; 0, 15, and 25% added PET at a 3 ºC min^{-1} heating rate as P0T3, P15T3, and P25T3, respectively; and 0, 15, and 25% added PET at a 5 ºC min^{-1} heating rate as P0T5, P15T5, and P25T5, respectively.

Pyrolysis and co-pyrolysis were carried out in a fixed-bed reactor. For each test, 300 g of raw material (following the mixture proportions described above) was inserted into a closed metallic reactor inside a muffle furnace. Our experiments were carried out in a low oxygen atmosphere without gas entry, at a 450 °C final oven temperature, which was maintained for 15 min. Condensable products were recovered by attaching a gas condenser cooled with water and ice to the reactor. The gravimetric yields of solid, liquid, and gaseous products were quantified (Equations S1, S2). Non-condensable gases were estimated by subtracting the yields of liquid and solid products from the total yield.

2.2.Charcoal characterization

Apparent density was estimated by dividing the mass of the sample of co-pyrolytic charcoal by its volume (D = mass of co-pyrolytic charcoal/volume, in g cm^{-3}). Bulk density was assessed according to the standard test method for screening apparent specific gravity and bulk density of waste, D5057-17 (ASTM, 2017). Wet basis moisture was determined via the standard test method for chemical analysis of wood charcoal, D1762-84 (ASTM, 2021). Ash, volatile material, and fixed carbon content, were measured by the standard test method for chemical analysis of wood charcoal, D1762-84 (ASTM, 2021). Higher heating values of the produced charcoal were obtained by an IKA C200 calorimetric pump, following the European standard EN14918 (DIN, 2010). Lower heating values were estimated by the hydrogen percentage (6%) of the material (Equation 1), whereas the net heating values were determined by the material’s moisture (Equation S3). Both energy and bulk densities were estimated by multiplying the applicable heating values.

$$LHV = HHV - \left(600\,\frac{9H}{100}\right) \text{ (Equation 1)}$$

Where: LHV = lower heating value (kcal kg^{-1}); HHV = higher heating value (kcal kg^{-1}); and H = hydrogen content (%).

2.3.Thermogravimetric analysis (TGA)

This analysis was performed with Setaram Labsys Evo analyzer with approximately 4 mg of co-pyrolytic charcoal with 60-mesh granulometry at a 5 ºC min^{-1} heating rate. Thermogravimetric curves were produced from room temperature (25 °C) in an inert atmosphere (N2) with a 1.8L flow rate.

2.4.Fourier-transform infrared spectroscopy (FTIR)

Composite FTIR spectra were obtained by attenuated total reflectance within the 4000-600 cm^{-1} range with 4 cm^{-1} resolution and the aid of a Bruker Tensor 27 spectrometer. All told, 32 FTIR spectra were collected.

2.5.Visual analysis of charcoal microstructures (SEM)

Samples were ground, homogenized by passage through a 60-mesh sieve (0.250 mm). Samples retained in sieve were fixed on a metallic support with carbon tape and metalized with gold in a Balzers Union SCD 030 system. A JSM-IT200 scanning electron microscope (Tokyo, Japan) was operated at 10 Kv to obtain 500x magnified SEM images via proprietary JEOL software, which also identified pores and measured their diameter.

2.6.Data analysis

Data were subjected to tests of normality (Shapiro–Wilk) and homoscedasticity (Bartlett). Analysis of variance (ANOVA) was performed with a completely randomized design with nine response variables comprising three PET proportions (0%, 15%, and 25%) and three heating rates (1, 3, and 5 °C min^{-1}), with five repetitions for each investigated variable. Regression models were adjusted if response variables were significantly affected by independent ones, and contour plots were drawn for models with two independent variables. Tests were performed at 95% probability. Standard deviation was measured to better assess the confidence intervals of each studied variable. The Pearson correlation coefficient (95% probability) was calculated to assess the relation between energy properties and the other studied variables.

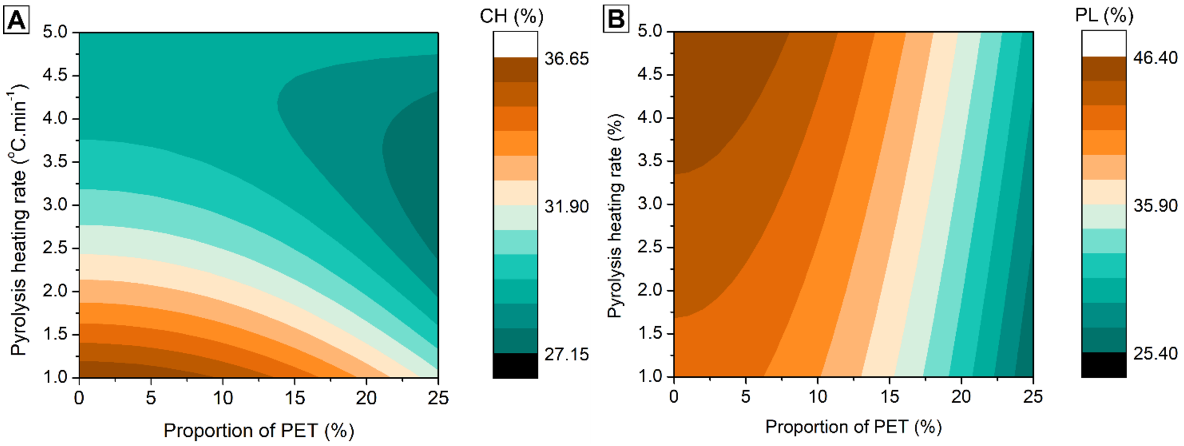
Subsequently, our dataset was standardized for multivariate analyses, with 0 mean and a standard deviation of 1. Multivariate principal component analysis (PCA), designed with a reduced number of dimensions and preserving as much information as possible, was used to simplify the observed variations. Hierarchical agglomerative clustering was used to identify similarities between treatments. The Manhattan distance was adopted as a measure of proximity and the unweighted pair group method using arithmetic averages (UPGMA) was used to treat similar groupings. The quality of the dendrogram obtained was evaluated by the cophenetic correlation coefficient, which measures the correlation between the distances recovered from the dendrogram and the original distance matrix. Thus, dendrograms with a cophenetic correlation coefficient greater than 0.7 were considered as containing low distortion (ROHLF, 1970). The R program (R Core Team) was used for all analyses.

3. RESULTS AND DISCUSSION

3.1.Influence of process parameters on products

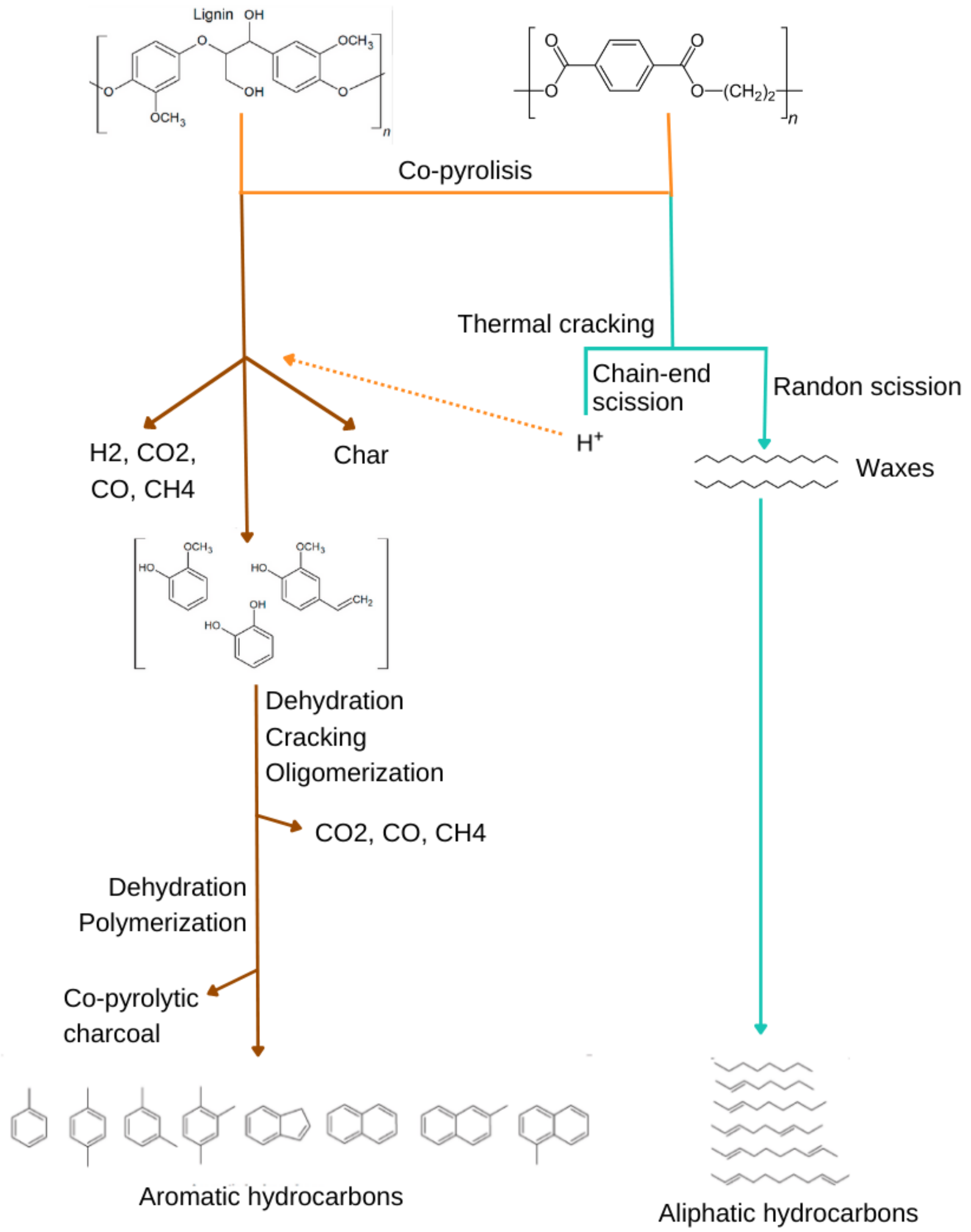
Figure 1 shows that pyrolytic and co-pyrolytic parameters, heating rate, and biomass/PET proportions significantly influenced the generated products.

Figure 1. Variation of charcoal and pyroligneous liquid yield according to heating rates and raw material proportions, where: A = charcoal yield (%) and B = pyroligneous liquid yield (%).



We found a relation between solid product (charcoal) and process parameters. The fastest heating rate (5 °C min^{-1}) and largest PET percentage (25%) decreased material yield by about 7% (Figure 1 and Figure S3). To explain this behavior, we should mention that the final temperature (450 °C) was close to the degradation temperature of PET (500 °C), whereas for biomass, degradation started between 220 and 315 °C as hemicellulose began to decompose (GRAUSE et al., 2011; ÖZSIN; PÜTÜN, 2017). The different thermal degradation temperatures of the materials in this study directly influenced the co-pyrolytic reactions. In the first step of the process, biomass components begin to form lignin-free radicals, enabling scission with the PET chain and stabilizing the thermal degradation of the biomass due to reactions transferring hydrogen from the polymer chain to lignin-free radicals (Figure 2) (KUMAGAI et al., 2016; SAMAL et al., 2021; ZHOU et al., 2006), resulting in greater mass losses and lower charcoal yields, as we observed.

Figure 2. Scheme of suggested interactions between PET and lignin. (Source: KUMAGI et al., 2016; ESSO, et al., 2022. adapted)

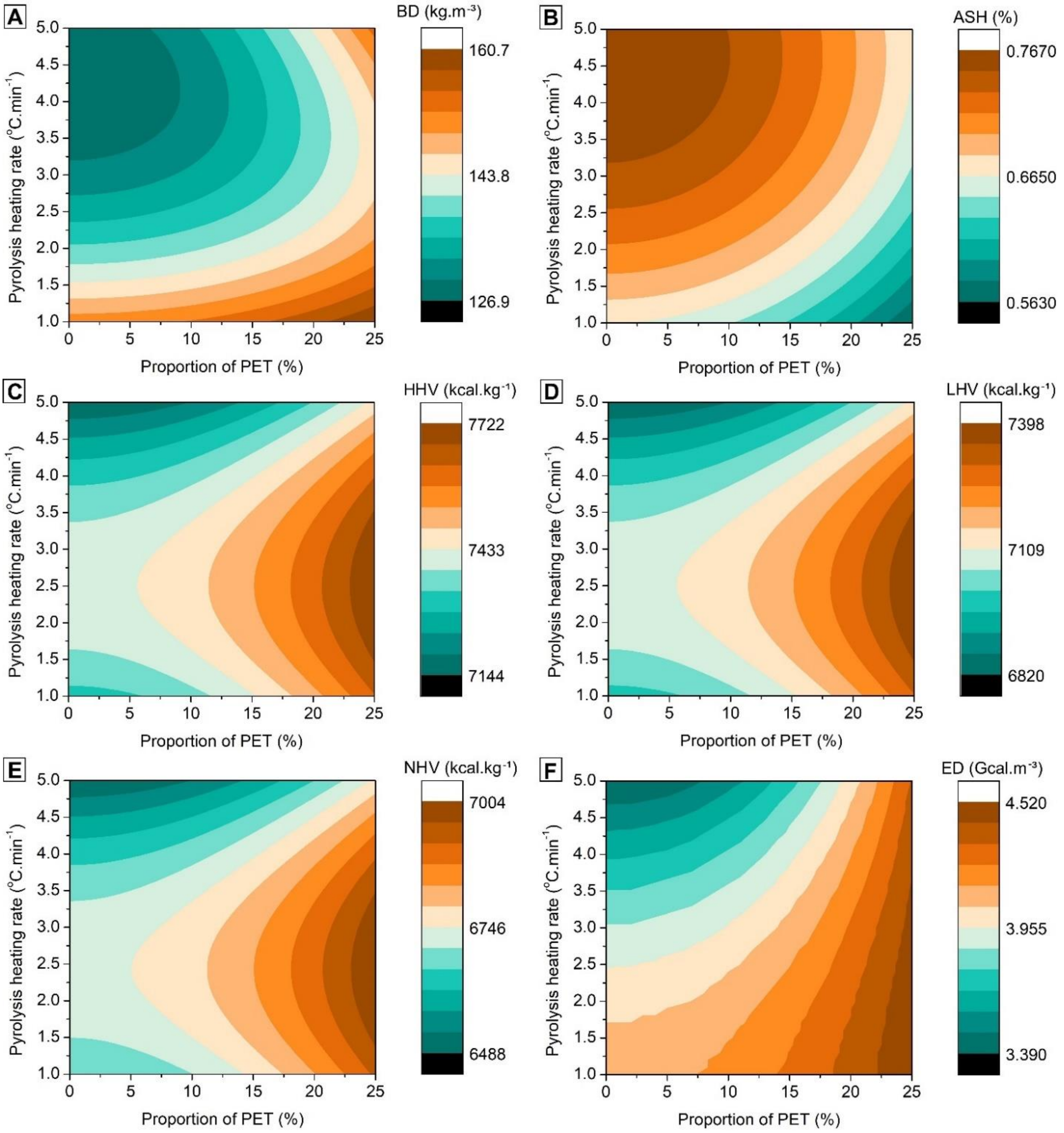


Pyroligneous liquid yield tended to decrease by up to 20% (P0T3 – P25T3) as the PET amount increased and heating rates decreased (Figure 1). Non-condensable gases had the opposite behavior, i.e., a higher yield, higher added PET and lower heating rates (Figure S4). Other researchers have explained this behavior by claiming that the inhibitory and synergistic influences of plastic on the degradation of biomass can also induce significant variations in co-production yields via the shielding effect and the radicals in the raw materials that interact during the process (DOMINGUES et al., 2017; SAMAL et al., 2021). In general, researchers considers lower yields as a negative factor when aiming to allocate charcoal to specific commercial sectors or evaluate its possible industrial viability, since among other factors, large-scale applications prioritize the highest possible production with the lowest possible energy costs. However, we note that the characteristics of charcoal can also be a differential, enabling its designation as a viable energy product or not. Moreover, using an abundant waste material (such as PET) in the process favors the reduction of production costs.

3.2.Effects of process parameters on co-pyrolytic charcoal properties

Varying heating rates, biomass and PET proportions influenced the charcoal's properties. Only heating rates influenced apparent density (the rate at which charcoal occupies the internal pores of the product) (Figure S5). Increasing heating rates significantly decreased (15%) apparent density (Figure S3 and Figure S5), from 0.221 to 0.162 g cm^{-3} (P0T1 – P0T5). Studies have attributed this behavior to the volatilization of organic compounds, which provides optimized void spaces (pores) in the material, and thus reduces the mass (DIAS JUNIOR et al., 2020; SAMAL et al., 2021). The lowest heating rate (1 ºC min^{-}1) and highest PET proportion (25%) increased bulk density to about 20 kg m^{-3} (Figure S3), a behavior similar to that reported by Samal et al. (2021), which can be explained by the filling of pores by the PET, increasing total mass. Moreover, adding PET may be a strategy to achieve larger masses, especially contributing to material transport and energy applicability.

Figure 3. Variation of charcoal (A) BD = bulk density (kg m^{-3}), (B) ASH = ash content (%), (B) HHV = higher heating value (kcal kg^{-1}), (B) LHV = lower heating value (kcal kg^{-1}), (E) NHV = net heating value (kcal kg^{-1}), and (F) ED = energy density (Gcal m^{-3}) according to heating rates and biomass and PET proportions



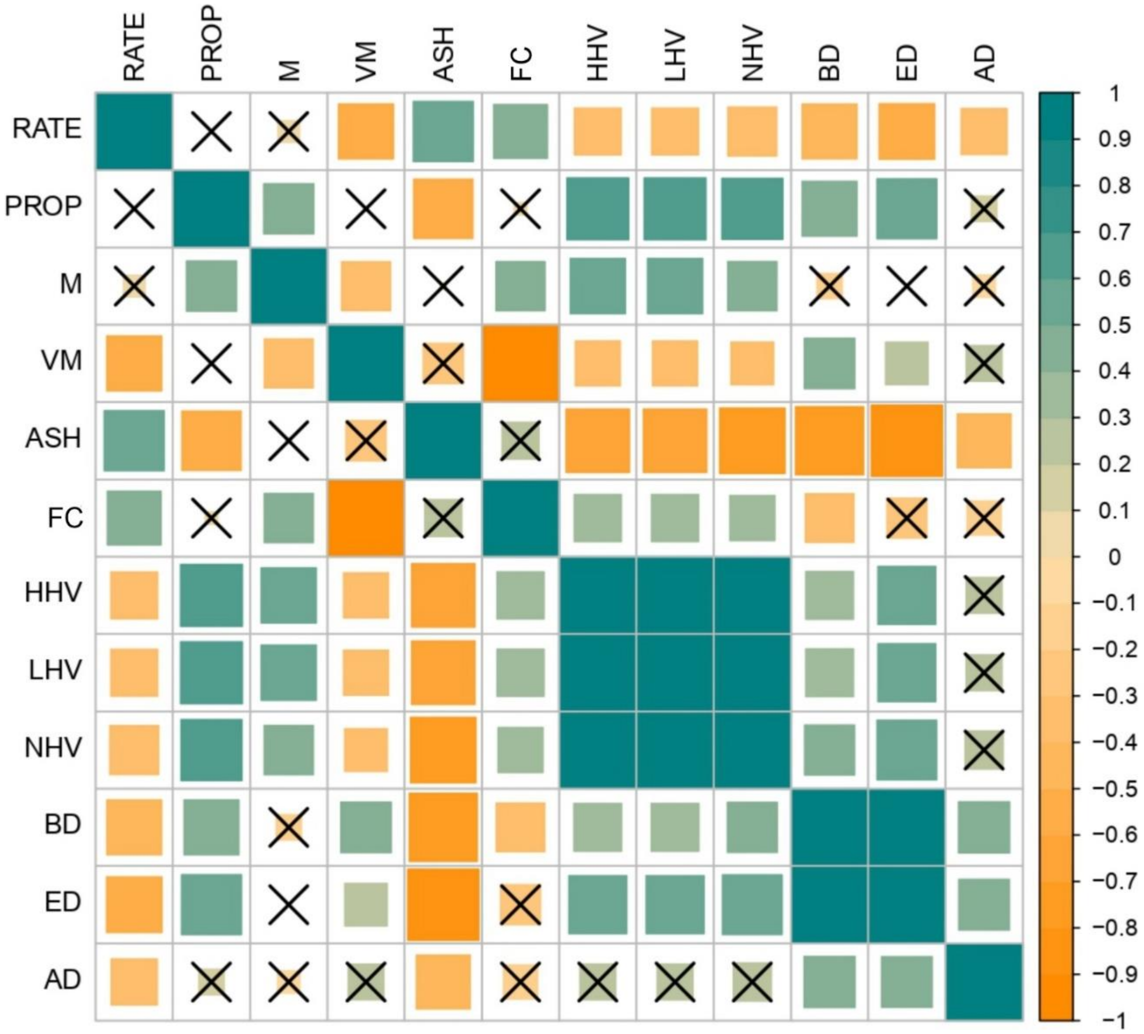
Moisture content is another important property to evaluate charcoal aimed at energy production. PET addition was the only parameter that influenced the moisture of the charcoal. Moisture content increased as PET addition did (Figure S6). This behavior can be related to the high content of volatile materials in the polymer, favoring increased moisture

(SAMAL et al., 2021). The chemical evaluation of co-pyrolytic charcoal found that PET addition and lower heating rates reduced its ash content (Figure 3). Thus, co-pyrolytic charcoal may be an attractive alternative for energy production, since ash is an inorganic constituent that resists degradation during combustion and negatively impacts the calorific value of the material.

Note that adding PET can be an innovative strategy to produce charcoal with a lower inorganic content, since in general PET has less ash than biomass (Table S1). Our results showed a more significant reduction of volatile compounds in charcoal produced at 3 ºC min^{-1}. Despite modest growth as the heating rate increased to 5 ºC min^{-1}, these compounds still decreased compared to charcoal obtained at a 1 ºC min^{-1} rate (Figure S7). Faster heating rate was the main parameter that significantly decreased volatile material content, offset by steep increases in fixed carbon fraction (Figure S7), a behavior resembling that reported by other researchers (RAFIQ et al., 2016; WU et al., 2012). The thermal decomposition of raw materials into condensable and non-condensable synthesis gases of atomically light short chains explains this loss of volatile content at higher heating rates (SAMAL et al., 2021).

Figure 3 shows that the co-pyrolytic charcoal heating values (higher, lower, and net) were greater for all studied heating rates as we added PET. Adding PET to charcoal increased its C/H ratio, which is directly linked to the high aromaticity of the material, thus containing a more significant amount of C=C bonds, which have a high binding energy (518 kJ mol^{-1}). The breaking of these bonds releases more energy, increasing heating values (LIU et al., 2013; SOARES et al., 2014). In addition to higher heating values, adding PET increased the energy density of the material to about 0.516 Gcal m^{-3} (P0T1-P25T1), 0.619 Gcal m^{-3}(P0T3-P25T3), and 0 993 Gcal.m^{-3} (P0T5-P25T5), indicating that it improves combustion efficiency (Figure 3 and Figure S3). In addition to evaluating these properties, we also assessed the influence of the properties of charcoal on its energetic performance to assess its suitability for energy generation (Figure 4).

Figure 4. Correlation matrix between heating rates, PET proportions, and co-pyrolytic charcoal properties, where: RATE = heating rate; PROP = PET proportion; M = moisture content; VM = volatile materials; ASH = ash; FC = fixed carbon; HHV = higher heating value; LHV = lower heating value; NHV = net heating value; BD = bulk density; ED = energy density; AD = apparent density; X = non-significant correlation.



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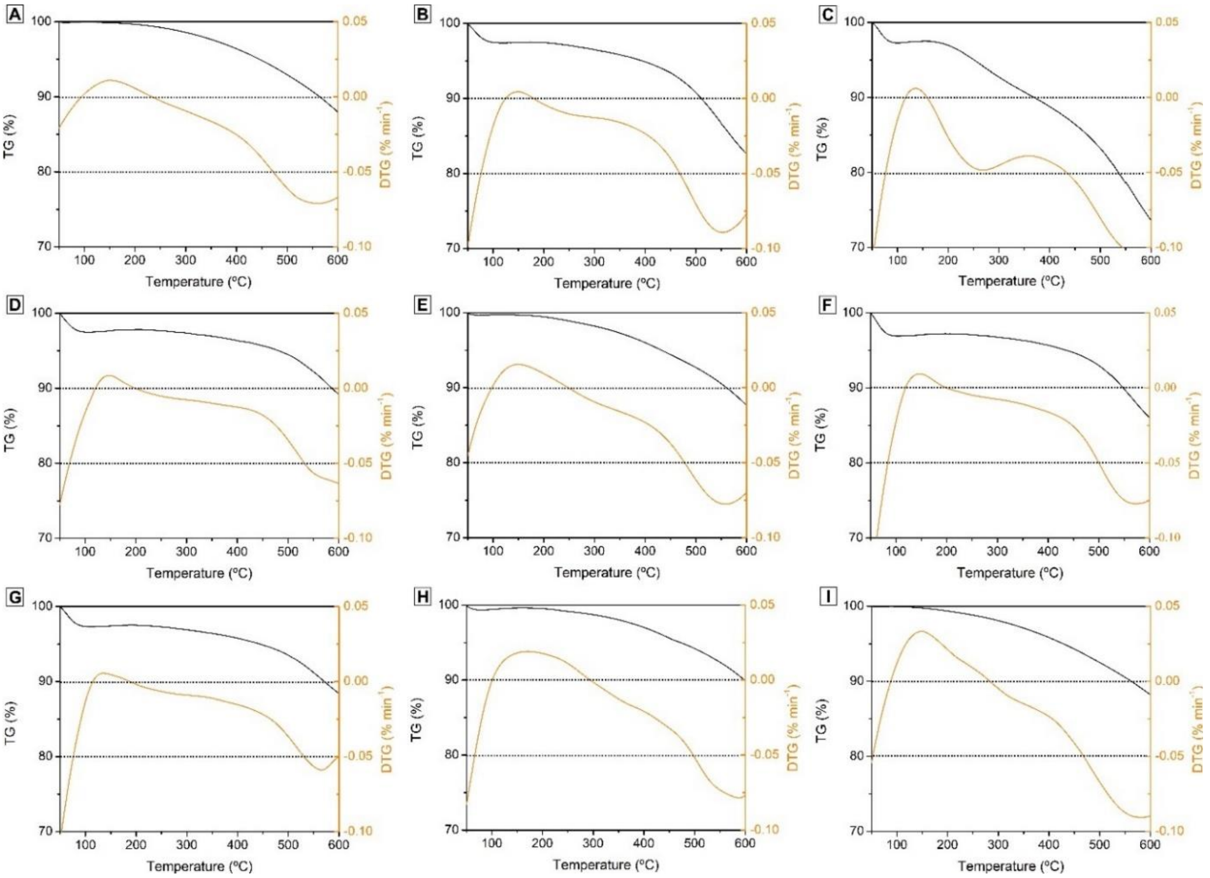
We found that PET proportions had a positive correlation (R^2=0.62) with the heating values of co-pyrolytic charcoal. At the same time, volatile material content had a negative correlation (R^2=0.32) with heating values (Figure 4). The increase in higher, lower, and net heating values due to PET coating can help to improve charcoal combustion efficiency, which especially results from higher heating rates after the spontaneous combustion of the plastic layer on the surface of the material. Its internal skeleton structure showed a higher concentration of fixed carbon than of volatile materials, indicating better fuel behavior due to greater efficiency during combustion (SAMAL et al., 2021; SHARMA; SARMAH; DUBEY, 2020). For energy applicability, charcoal with more volatile materials tends to release gases with low combustion efficiency when burned (XUE et al., 2015). Good-quality fuel, whether for cooking or combustion, has high fixed carbon values and low volatile and ash contents, as reported by Michalak et al. (2019). In practical terms, the charcoal produced by biomass and PET co-pyrolysis can behave better as fuel, with a broader temperature range, longer combustion duration, and lower environmental impact. Results in the literature indicate that using pulverized co-pyrolytic charcoal for blast furnace tuyere injection is potentially advantageous. Other studies have reported the use of plastic waste as a reducing agent for pig iron production, however indicating some problems, such as incrustation of blast furnace walls (WANG, et al., 2020). This study shows that co-pyrolysis adds PET properties to the biomass forming co-pyrolytic charcoal, which can be a positive strategy in the steel industry. Our results can serve as insights to design efficient and sustainable large-scale technology for the steel industry.

To evaluate the thermogravimetric behavior of charcoal produced under different pyrolysis and co-pyrolysis parameters (heating rates and PET proportions), Figure 5 shows the thermogravimetric (TG) and derivative thermogravimetric (DTG) curves.

Figure 5. TGA and DTG curves of charcoal from biomass pyrolysis and biomass and PET co-pyrolysis, where: A = P0T1; B = P15T1; C = P25T1; D = P0T3; E = P15T3; F = P25T3; G = P0T5; H = P15T5; and I = P25T5.

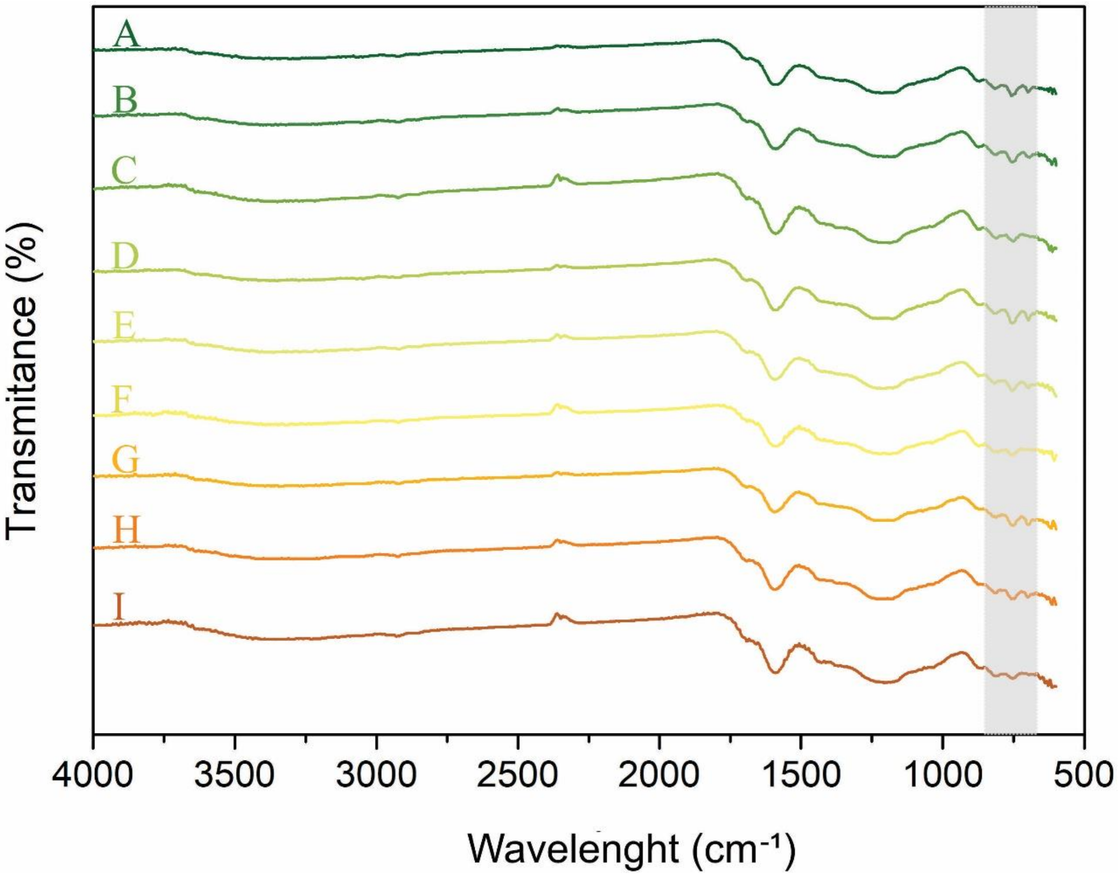


By evaluating charcoal from the pyrolysis of biomass (P0T1, P0T3, and P0T5), we noted that the lowest heating rate (1 ºC min^{-1}) resulted in more uniform mass losses and decomposition at lower temperatures (Figure 4. A). Our results show that the reactions which formed charcoal occur at lower temperatures and heating rates, a result in line with pyrolysis yields. When evaluating how PET addition affected charcoal via thermogravimetric analysis (Figure 4. B, C, E, F, H, and I), the curves showed a similar behavior. We found a significant interaction between biomass and plastic during the co-pyrolytic reaction, which gradually decreased mass loss with the increase of plastic content. The degradation of the materials involved in co-pyrolysis occurred at different temperature ranges. However, the highest biomass temperature range (250-400 ºC) was within the PET degradation range, favoring a synergistic effect (VO et al., 2021). The main degradation range of co-pyrolytic charcoal was between 150 and 350 ºC, as was the biomass range.

When we assessed the behavior of the PET material (Figure S1) and the charcoal from the co-pyrolysis of PET and biomass, we found a slight change in their peak decomposition temperatures, which can be attributed to the thermal stability of plastic due to the presence of biomass (ABOULKAS et al., 2008). Notably, the charcoal produced at a lower heating rate and higher PET proportion (P25T1) showed a particular behavior, with two DTG peaks, one in the 100-250 ºC range (generally related to moisture loss) and the other in the 350-400 ºC range (associated with the thermal hemicellulose depolymerization, presence of pectin, and cleavage of cellulose glycosidic bonds). In addition to the degradation of the PET polymer matrix (DAS et al., 2021) (Figure 5. C), higher thermal stability indicates charcoal which can withstand higher combustion temperatures without significant deterioration, an attractive factor for energy use (SELVARAJOO et al., 2022). Thus, the charcoal produced can be used in co-combustion processes in cement kilns and mono-incineration plants to reduce the amount of fossil fuel used.

The FTIR spectra of co-pyrolytic charcoal showed a profile (Figure 6) resembling that of pyrolytic charcoal (Figure S2). However, some slight modifications indicated the effect of PET addition in the composition of the material.

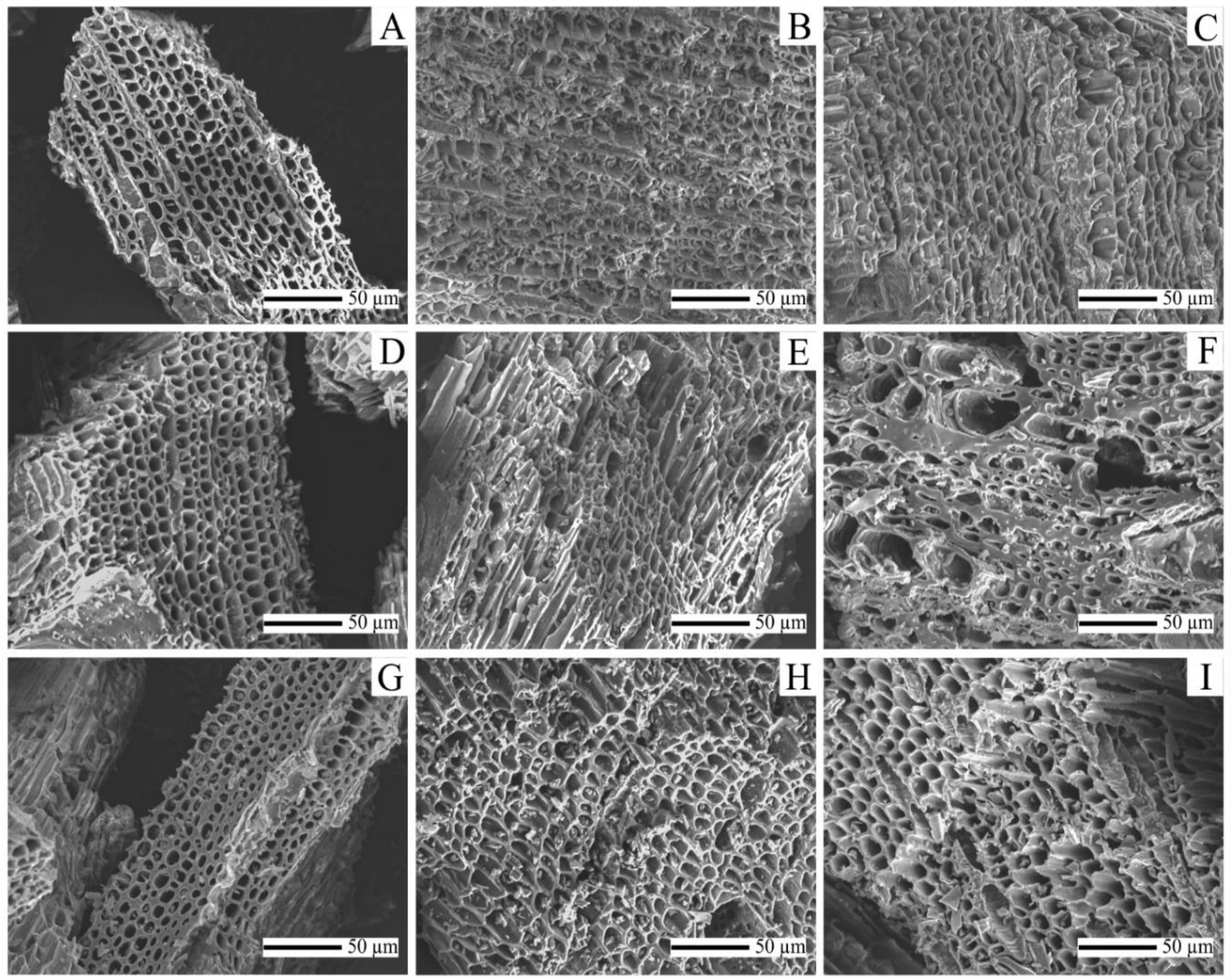
Figure 6. FTIR spectra of biomass and PET co-pyrolysis charcoal, where: A = P25T5; B = P15T5; C = P0T5; D = P25T3; E = P15T3; F = P0T3; G = P25T1; H = P15T1; and I = P0T1.



The main spectral differences were located between 800 and 700 cm^{-1}, the range related to the C=C and C-H bonds in the aromatic carbonic structure of charcoal. The 750 cm^{-1} absorption band in the FTIR spectrum of charcoal without PET addition underwent slight shifts to higher wavelengths as PET proportions increased, as observed in the spectra of co-pyrolytic charcoal (Figure 6). We found the same band shifting toward higher energies at 689 cm^{-1} in the FTIR spectrum of charcoal compared to the final spectra of the material. This spectral behavior indicates the synergistic effect of the pyrolytic combination of our two starting materials. During heat treatment, pyrolytic charcoal probably captures volatile products from the PET carbonization, contributing to increase its carbonic structure, which can increase its heating values (KO; RAWAL; SAHAJWALLA, 2014). FTIR analyses showed that co-pyrolytic heating rates failed to chemically modify the composite.

SEM images (Figure 7) showed the surface morphology of co-pyrolytic charcoal produced with different heating rates and biomass/PET ratios. In general, all treatments produced an irregular surface texture. The surface of co-pyrolytic charcoal was covered by small particles, some of which were even impregnated in the pores of the material (Figure 7).

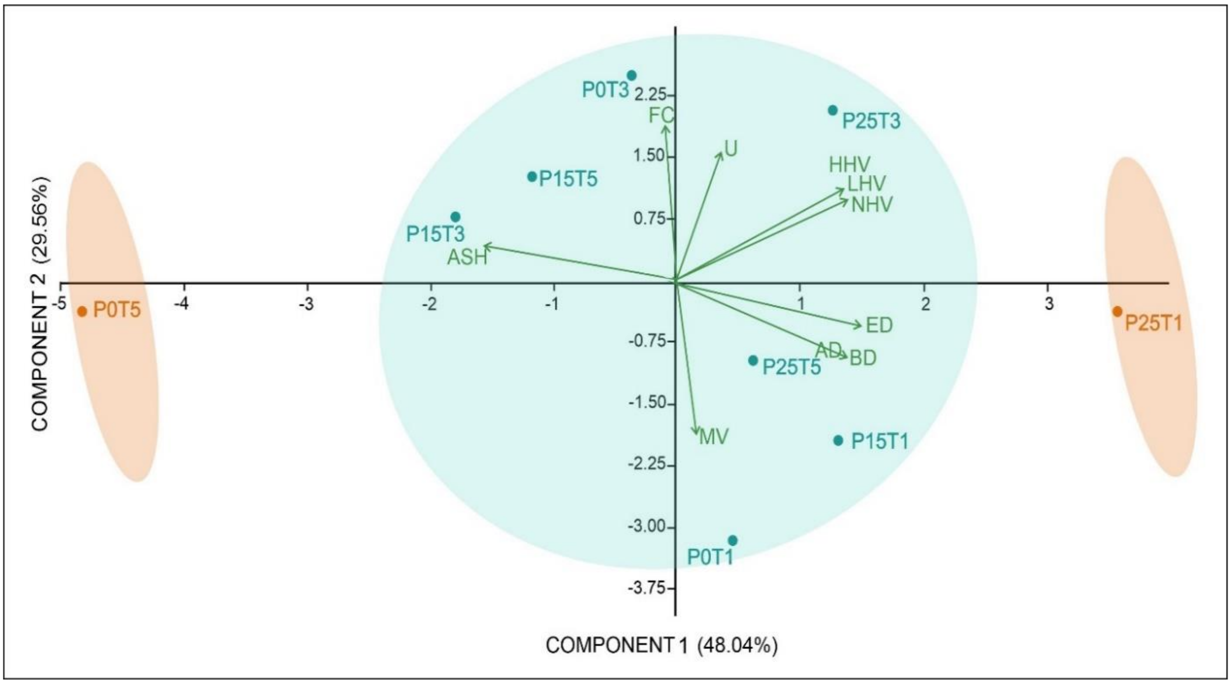
Figure 7. Scanning electron microscope (SEM) images of charcoal produced at different biomass/PET ratios and heating rates, where: A = P0T1; B = P15T1; C = P25T1; D = P0T3; E = P15T3; F = P25T3; G = P0T5; H = P15T5; and I = P25T5.



The influence of heating rates on pyrolytic charcoal was revealed by the development of porous structures (Figure 5. A, D, and G). The charcoal produced at 5 ºC min^{-1} (Figure 5. G) was porous, with about 2-10 µm-thick micro and mesopores. According to Kim et al. (2020), higher heating rates favor the formation of porous structures in charcoal since heat promotes more effective and intense removal of volatile components from the material. More porous charcoals tend to have lower density due to their higher percentage of voids (pores), so increasing heating rates (1 to 5 ºC min^{-1}) can be a disadvantageous factor for energy production. Adding PET to the co-pyrolysis of biomass produced charcoal with more significant changes in its structural arrangement (Figure 5. B, C, E, F, H, and I), with small particles covering the surface, some of which were even embedded in the pores. Charcoal produced from biomass failed to show this phenomenon (Figure 5. A, D, and G). The tiny particulate matter likely consisted of long-chain hydrocarbons derived from the PET. The polymer melts at around 200 °C but is unable to volatilize until it reaches higher temperatures (⩾450 °C) (XUE et al., 2015). This behavior results in the coating of biomass particles, whose degradation begins at lower temperatures (Figure S1). Due to their low volatility and short reaction time inside the reactor, long-chain hydrocarbons remain on the surface of the biomass after co-pyrolysis. These particles can increase the carbon and hydrogen contents in charcoal and therefore increase its HHV, culminating in satisfactory energy performance

Figure 8 shows diagrams ordering variables as a function of our first two main components. Of the eight components found, we selected the two which most represented an essential percentage (77% of all observed variation) in other studies with this purpose (DIAS JÚNIOR et al., 2021). Thus, the studied variables formed three groups (Figure 8).

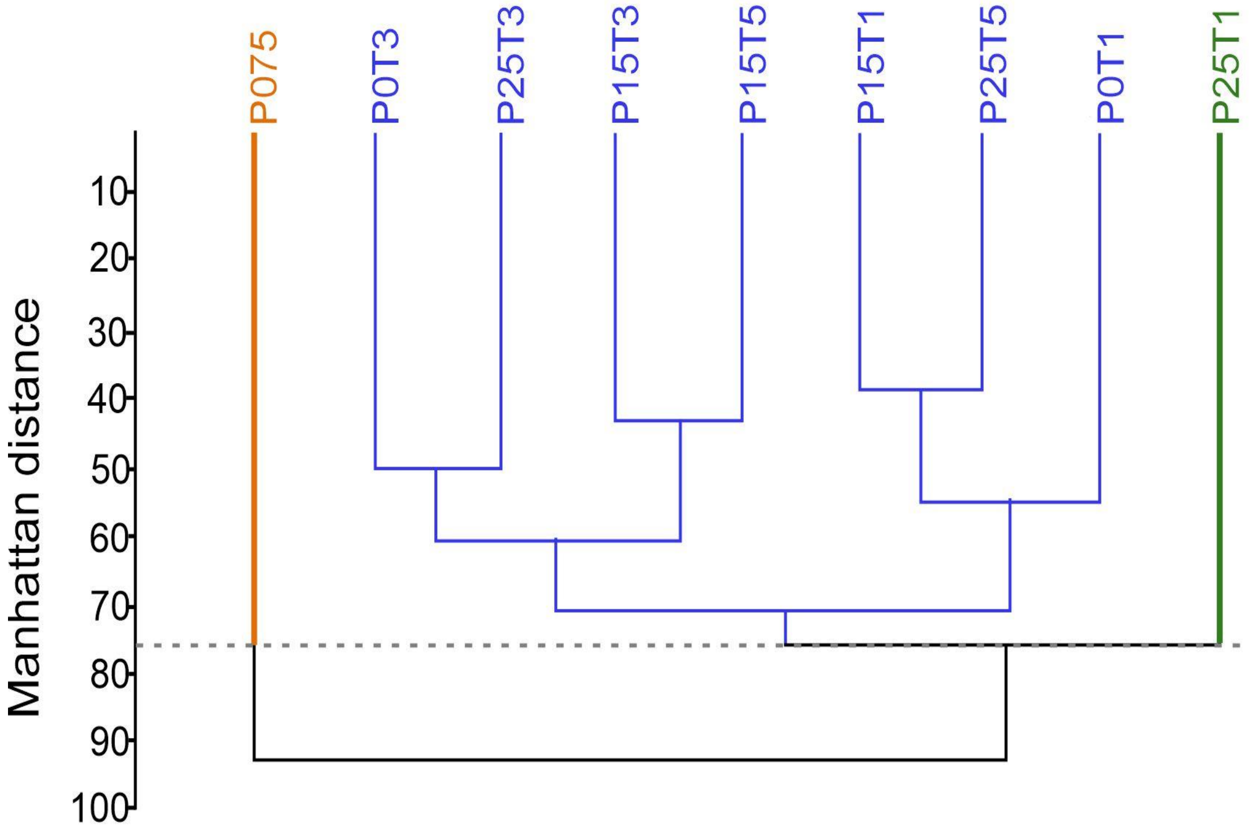
Figure 8. Distribution of charcoal treatment as a function of scores and the ordering diagram of the eigenvectors of our first two main components, where: A = P0T1; B = P15T1; C = P25T1; D = P0T3; E = P15T3; F = P25T3; G = P0T5; H = P15T5; and I = P25T5.



The PCA results suggest that charcoal produced at lower heating rates and higher PET proportions (P25T1) and that at higher heating rates without PET (P0T5) had properties unlike other co-pyrolytic materials. The group formed by the P25T1 treatment was positively correlated with the higher, lower, and net heating value; bulk density; apparent density; and energy density vectors; and negatively correlated with ash content (Figure 8). The thermogravimetric analysis showed a particularity of this treatment (Figure 5), indicating that the material was thermally stable at combustion temperatures with higher heating rates and lower PET proportions. The second group comprised most of the studied treatments (Figure 8). It showed moderate results when compared to the others. Finally, charcoal produced with the highest heating rate and without PET addition (P0T5) also showed particular behavior, which was positively correlated with the ash content and fixed carbon vectors (Figure 8). In general, all the obtained clusters showed that co-pyrolysis can be a strategy for energy generation.

Figure 9 shows a dendrogram from the cluster analysis which more clearly discriminates the groups formed.

Figure 9. Dendrogram obtained by UPGMA using the Manhattan distance between the different analyzed treatments. Cophenetic correlation coefficient = 0.7366, significant at 95% probability. A = P0T1; B = P15T1; C = P25T1; D = P0T3; E = P15T3; F = P25T3; G = P0T5; H = P15T5; and I = P25T5.



To minimize the number of groups and homogenize them, we chose 75% of the Manhattan distance as our cutoff point. Table 1 shows the treated group means.

Table 1. Average of the groups formed by the UPGMA cluster analysis.

Analyzed variables	Groups		
	Group 1	Group 2	Group 3
CH (%)	30.2	30.5	32.76
PL (%)	45.87	38.87	25.84
NCG (%)	23.93	31.17	41.88
AD (g cm^{-3})	0.162	0.187	0.231
BD (kg m^{-3})	129.55	146.97	161.74
M (%)	4.584	4.739	5.118
ASH (%)	0.81	0.652	0.58
VM (%)	23.88	24.29	24.54
FC (%)	75.31	75.06	74.9
HHV (kcal kg^{-1})	7011.8	7426.5	7684.5
LHV (kcal kg^{-1})	6687.8	7102.5	7360.5
NHV (kcal kg^{-1})	6353.3	6762.7	6954.1
ED (Gcal m^{-3})	3.438	4.143	4.704

Where: CH = charcoal yield; PL = pyroligneous liquid yield; NCG = non-condensable gases yield; AD = apparent density; BD = bulk density; M = moisture; ASH = ash; VM = volatile materials; FC = fixed carbon; HHV = higher heating value; LHV = lower heating value; NHV = net heating value; ED = energy density.

Figure 9 clearly shows that the properties of ash and fixed carbon contents, heating values (higher, lower and net), and energy density especially influenced the formation of three distinct groups. From the assessed properties, all three groups (Figures 8 and 9) have the potential to produce energy via pulverized charcoal. However, they may differ in energetic performance. Group A will perform the best, followed by B and C. In general, we found that the lowest heating rate (1 ºC min^{-1}) and highest PET proportion (25%) produced charcoal with the best energy properties. Thus, our results can support further research to understand the properties of co-pyrolytic charcoal for energy purposes and its byproducts (such as pyroligneous liquid), which can help optimize co-pyrolysis.

3.3.Practical applications and future research

Called the “contemporary symbol of modernity,” plastic has transformed the modern world, providing many benefits while also posing environmental, social and economic problems due to its slow decomposition in nature. Characterized by low price, it is ubiquitous in society. It is difficult to find any objects people use or interact with that contain no type of plastic (WILLIAMS; RANGEL-BUITRAGO, 2022). But the waste generated endangers humans; impacts tourism and recreation; threatens rivers, coasts and aquatic life; and constitutes an aesthetic eyesore.

Environmental pollution by plastic waste disposal has become a global challenge. Thus, one of the Sustainable Development Goals developed by the United Nations is to manage this waste to minimizing its negative impacts on the environment, by reducing use while increasing reuse and recycling. It is necessary to apply measures to reverse the present trend of incorrect disposal, in line with the tenets of the circular economy. From this perspective, evaluating the potential of charcoal produced by the co-pyrolysis of biomass and PET can encourage changes in policies, promoting the innovative and sustainable use of plastic waste.

The results of this study are encouraging for the idea of a green economy, by recovering waste, previously seen as a problem rather than a potentially profitable alternative. This can promote a pioneering strategy to manage plastic waste, especially PET, in Brazil, aiming at generating a sustainable and profitable energy product which can satisfy the Brazilian National Solid Waste Policy. Future studies can assess the environmental feasibility of using this material for energy generation, including by evaluating the gases emitted during its combustion. This study showed that the properties of biomass and PET charcoal can satisfy industrial needs, especially those in the steel sector. Thus, we recommend reactivity and resistance analyses of the studied material to evaluate if it is sufficiently resistant for iron ore reduction reactions. Our results and future research evaluating the technical, environmental, and economic viability of this production can promote public policies aimed at better management of plastic waste.

4. CONCLUSION

The synergistic effects obtained between biomass and polyethylene terephthalate (PET) during co-pyrolysis improved the properties of interest in the charcoal produced. The layer of liquefied plastic on the surface of co-pyrolytic charcoal resulted in a maximum heating value of 7684 kcal kg^{-1} and energy density of 4.7 Gcal m^{-3} with 25% PET added to biomass, positively indicating its use in the energy sector. Optimizing the properties of co-pyrolytic charcoal for its use as an energy product can improve the economic and environmental viability of co-pyrolysis while contributing to sustainable waste management and resource recovery. We suggest that future studies should focus on evaluating the technical, environmental, and economic feasibility of the material, producing data which enable industrial implementation.

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6. SUPLEMENTARY MATERIALS

Table S1. Immediate analysis of the raw materials involved in the process (biomass and PET)

Material	M (%)	VM (%)	ASH (%)	FC (%)	HHV (kcal kg^{-1})	LHV (kcal kg^{-1})	NHV (kcal kg^{-1})
PET	3.10	91.14	0.103	8.75	5743.05	5439.05	5232.46
Biomass	8.25	85.50	0.398	14.09	4758.29	4454.29	4039.32

Where: M = moisture; ASH = ash; VM = volatile materials; FC = fixed carbon; HHV = higher heating value; LHV = lower heating value; and NHV = net heating value.

Figure S1. TGA and DTG curves for biomass and PET, where A = biomass; B = PET.

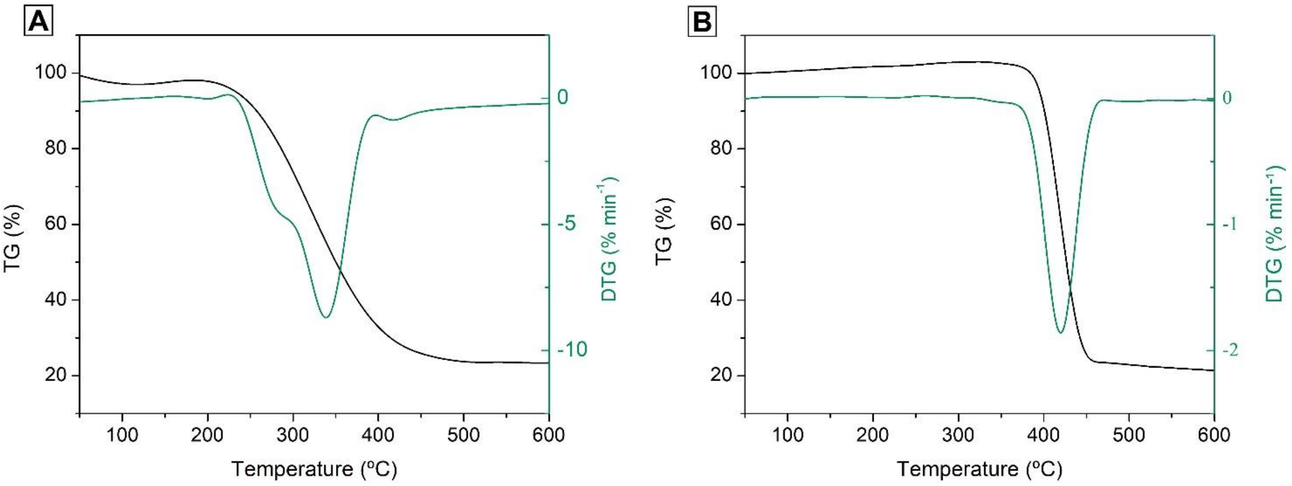
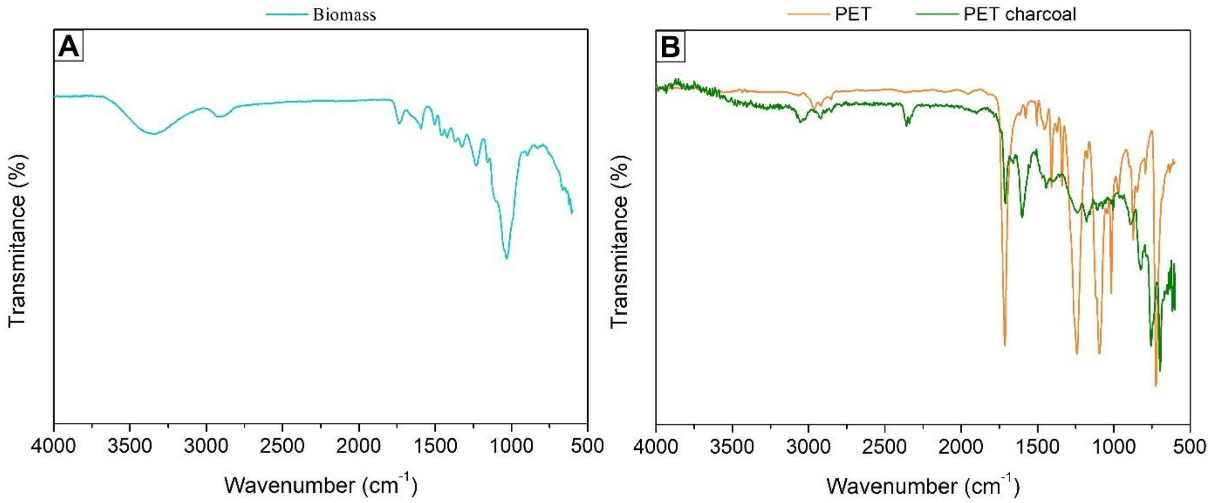


Figure S2. FTIR spectra of biomass and PET, where A = biomass and B = PET and PET charcoal.



$CY = \left(\frac{Mc}{Mw}\right) \times 100$ (Equation S1)

$PY = \left(\frac{Mpl}{Mw}\right) \times 100$ (Equation S2)

Where: CY = charcoal yield (%); Mc = mass of co-pyrolytic charcoal (g); Mw = mass of dried wood (g); PY = pyroligneous liquid yield (%); and Mpl = mass of pyroligneous liquid (g).

$NHV = LHV\left(\frac{100-U}{100}\right) - 6 \times M$ (Equation S3)

Where: NHV = net heating value (MJ kg^{-1}); LHV = lower heating value (MJ kg^{-1}); and M = moisture (%).

Figure S3. Co-pyrolysis yield and properties of the produced charcoal, where CH = charcoal yield (%); PL = pyroligneous liquid yield (%); NCG = non-condensable gas yield (%); AD = apparent density (g cm^{-3}); BD = bulk density ($g.cm^{-3}$); M = moisture (%); ASH = ash content (%); VM = volatile material content (%); FC = fixed carbon content (%); HHV = higher heating value (kcal kg^{-1}); LHV = lower heating value (kcal kg^{-1}); NHV = net heating value (kcal kg^{-1}); and ED = energy density (Gcal m^{-3}).

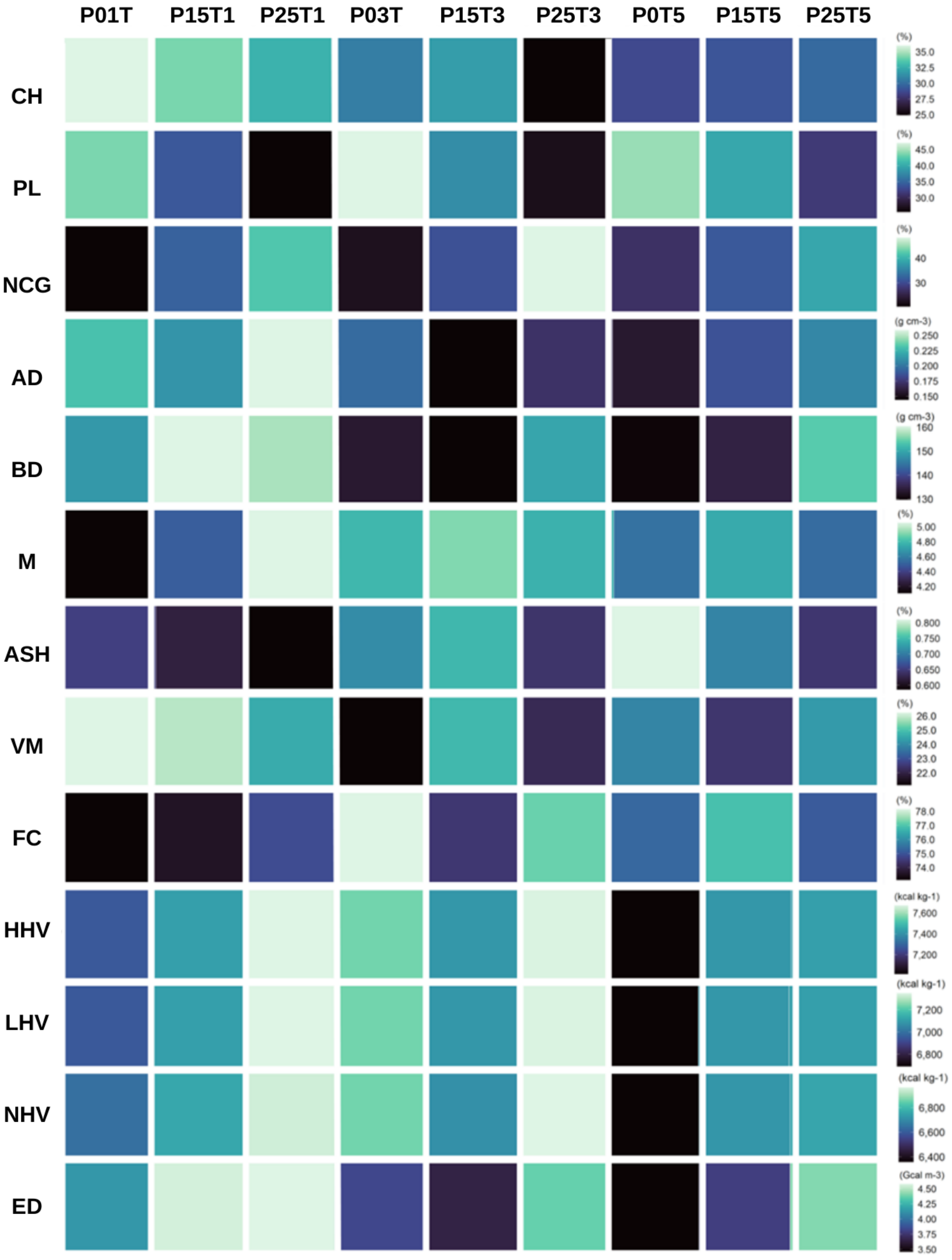


Figure S4. Behavior of non-condensable gases in the co-pyrolysis of biomass and PET.

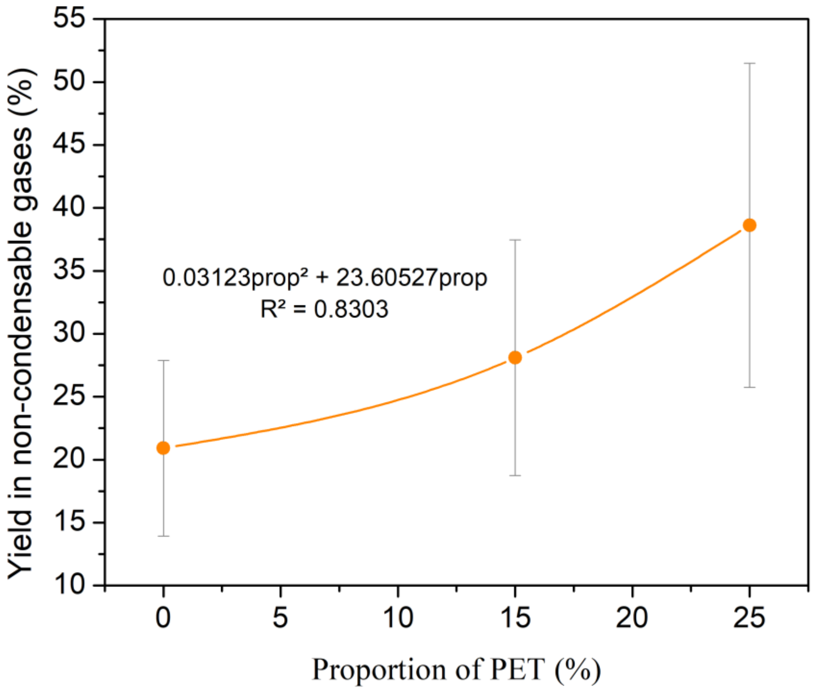


Figure S5. Apparent density of charcoal produced by the co-pyrolysis of biomass and PET.

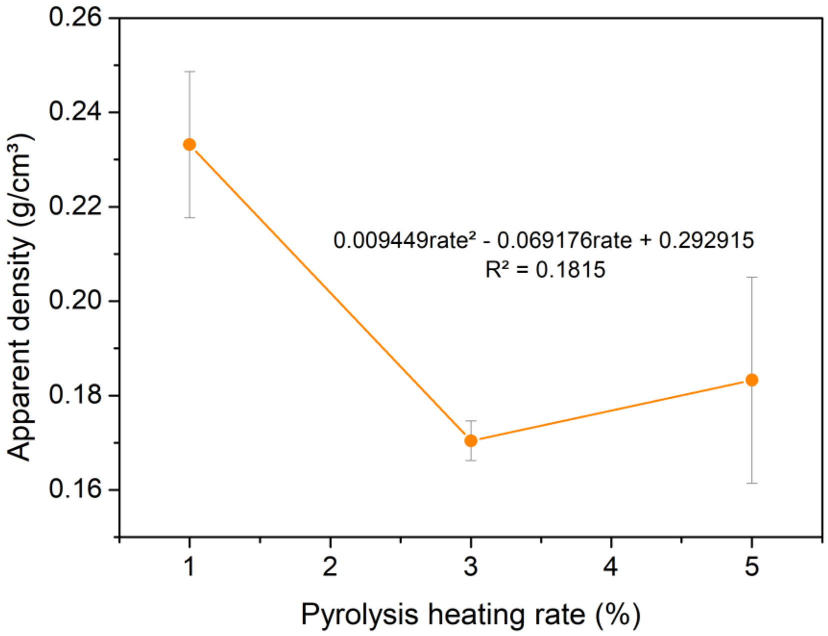


Figure S6. Moisture in charcoal produced by the co-pyrolysis of biomass and PET.

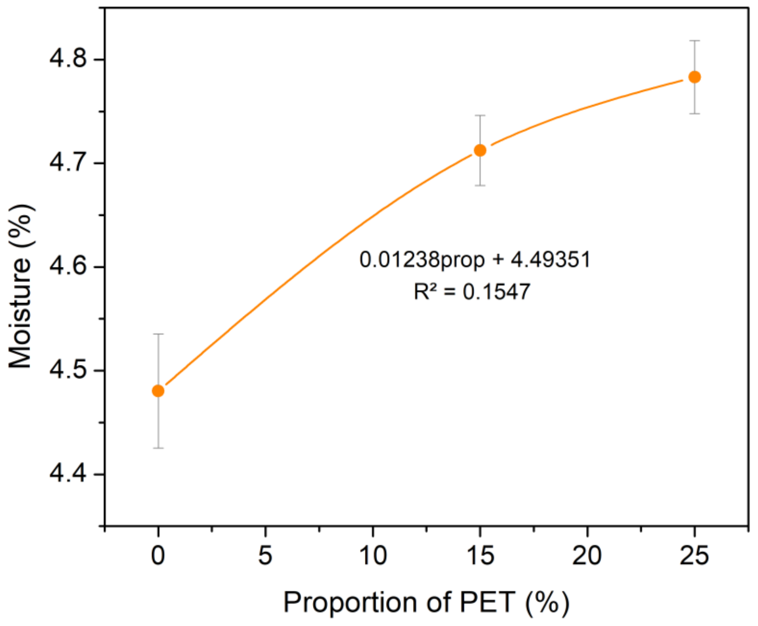
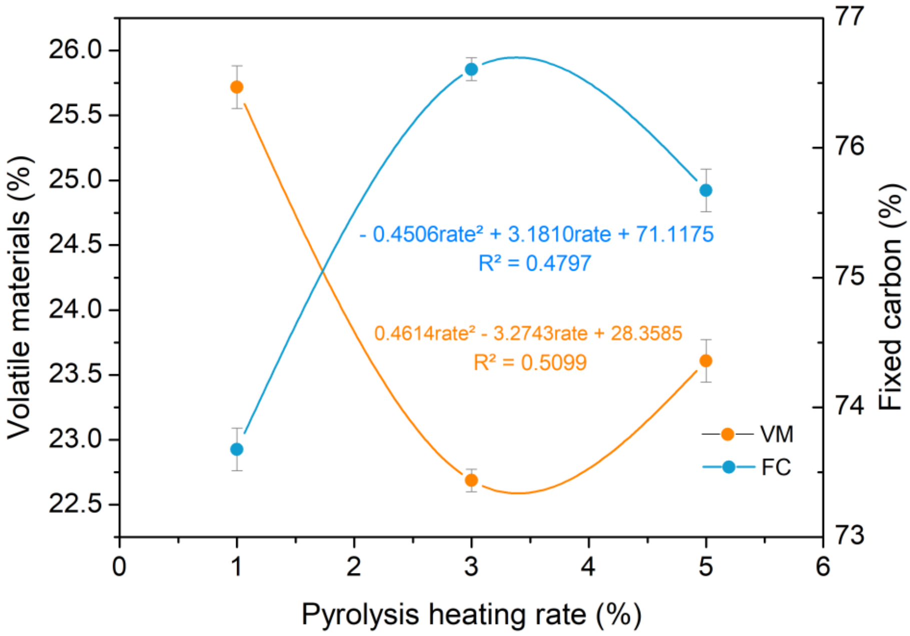


Figure S7. Percentage of volatile materials and fixed carbon in charcoal produced by the co-pyrolysis of biomass and PET.



4. CHAPTER 2. Co-pyrolysis of biomass and polyethylene terephthalate: perspectives for the use of chemical products of wood vinegar

ABSTRACT

Plastic is a problem of significant concern worldwide. The co-pyrolysis of biomass and polyethylene terephthalate (PET) can be a strategy to reuse this material and transform it into value-added products. Thus, this study aims to understand the influence of the co-pyrolysis of biomass and PET on wood vinegar. The PET proportions used were 0%, 15%, and 25% of the dry mass of eucalyptus biomass. The co-pyrolysis was performed in a fixed-bed reactor, in a low-oxygen atmosphere without gas entry, at a final temperature of 450°C, and three heating rates (1, 3, and 5°C.min^{-1}). The liquid fraction was double distilled at 100°C and purification yields were estimated. After purification, the pH, density, and viscosity of wood vinegar were analyzed. The chemical composition of wood vinegar was subject to GC-MS analysis. The addition of PET and the heating rate variation influenced the composition of the wood vinegar produced. The liquid density decreased as the PET proportion in the biomass increased. The increase in the heating rate reduced the pH of wood vinegar from 2.75 to 2.61. Therefore, lower heating rates and PET proportions tend to increase the viscosity of wood vinegar. Ketones were the most representative organic compounds in all evaluated materials, followed by phenols, furans, and pyrans.

Keywords: gas chromatography; circular economy; reuse of plastics.

Resumo

O plástico é um problema de grande preocupação em todo o mundo. A co-pirólise de biomassa e polietileno tereftalato (PET) pode ser uma estratégia de reaproveitamento desse material, possibilitando transformá-lo em produtos de valor agregado. Assim, este estudo tem como objetivo compreender a influência da co-pirólise da biomassa e do PET no vinagre de madeira. As proporções de PET utilizadas foram 0%, 15% e 25% da massa seca da biomassa de eucalipto. A co-pirólise foi realizada em um reator de leito fixo, em atmosfera com baixo teor de oxigênio, sem entrada de gás, a uma temperatura final de 450°C e três taxas de aquecimento (1, 3 e 5°C.min^{-1}). A fração líquida foi duplamente destilada a 100°C e os rendimentos de purificação foram estimados. Após a purificação, o pH, densidade e viscosidade do vinagre de madeira foram analisados. A composição química do vinagre de madeira foi submetida à análise GC-MS. A adição de PET e a variação da taxa de aquecimento influenciaram na composição do vinagre de madeira produzido. A densidade do líquido diminuiu à medida que a proporção de PET na biomassa aumentou. O aumento da taxa de aquecimento reduziu o pH do vinagre de madeira de 2,75 para 2,61. Portanto, taxas de aquecimento e proporções de PET mais baixas tendem a aumentar a viscosidade do vinagre de madeira. As cetonas foram os compostos orgânicos mais representativos em todos os materiais avaliados, seguidos pelos fenóis, furanos e piranos.

Palavras-chave: cromatografia gasosa; economia circular; reaproveitamento de plásticos.

5. GENERAL CONCLUSION

The heating rate and the proportion of PET added to the biomass influenced the yields and characteristics of the pyroligneous liquid and the co-pyrolytic charcoal produced. In general, the addition of PET resulted in a lower yield of the solid and liquid products. Considerable synergistic effects were observed between the materials during the co-pyrolysis reaction, resulting in the improvement of some properties of interest in the co-pyrolytic charcoal. Higher heating rates and a higher proportion of PET resulted in improvements in some properties of interest in charcoal, such as increased heating value, reduced ash content, and increased energy density. These results suggest that co-pyrolytic charcoal from biomass and PET can be a strategy for reusing plastic waste and generating energy products, mainly for injection into blast furnace tuyeres. Ketones were the main compounds found in wood vinegar. In short, higher heating rates and higher proportions of PET resulted in the inhibition of some wood vinegar compounds. It was observed that the addition of PET did not inhibit the formation of compounds of interest to the industry. Furthermore, it is noted that the addition of PET at a rate of 1 ºC.min^{-1} favored the formation of Diethyl phthalate, a compound of great interest to the cosmetics industry.

We recommend the evaluation of the technical, environmental, and economic feasibility of the production of co-pyrolytic charcoal and wood vinegar, providing data that allow its implementation on an industrial scale. With the results of our study, we aim to provide insights into the reuse of PET on an industrial scale. In the future, the products generated by the co-pyrolysis of biomass and PET can be a pioneering strategy and model of innovation and sustainability, bringing the ecological character to the industry in general.