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NUTRIENT CIRCULARITY IN AGROINDUSTRIAL SYSTEM: COMPOSITION OF BONE CHAR, ENVIRONMENTAL IMPACT, AND LIMITATIONS DUE TO MATTER ENTROPY

CIRCULARIDADE DE NUTRIENTES EM UM SISTEMA AGROINDUSTRIAL: COMPOSIÇÃO DO BONE CHAR, IMPACTO AMBIENTAL, E LIMITAÇÕES DEVIDO À ENTROPIA DA MATÉRIA

ADRIANA CIOATO FERRAZZA

Porto Alegre

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A ordem é uma condição transitória, pois a essência da vida é entrópica.
É no caos que as possibilidades se entrelaçam e novas realidades emergem,
construindo o futuro.
(Adriana Cioato Ferrazza).

RESUMO

A crescente demanda por recursos naturais destaca a urgência de adotar práticas que promovam a sustentabilidade. Nesse contexto, a tecnologia de pirólise se apresenta como uma solução viável, transformando resíduos em *bone char*, que, além de contribuir para a redução dos riscos sanitários associado à biomassa de origem animal, promove a fertilidade do solo, pois atua como um meio de armazenamento de carbono e recuperação de nutrientes. Entretanto, a implementação da circularidade de nutrientes enfrenta desafios significativos, especialmente à luz das Leis da física e da matéria. O planeta terra possui uma quantidade finita de matéria, que está em constante transformação. À medida que a matéria é utilizada, sua entropia tende a aumentar, manifestando-se pela diminuição da concentração de nutrientes, e pela sua dissipação no sistema terrestre. Embora a matéria dissipada ainda permaneça no sistema, a sua utilidade potencial é progressivamente reduzida. A matéria útil apresenta características de baixa entropia, ou seja, é ordenada, concentrada, disponível e capaz de atender às necessidades de processos naturais e produtivos. Na física, matéria com entropia elevada é comumente associada à desordem e dissipação. A energia pode ser empregada para reordenar e concentrar a matéria em um curto período, contudo, isso implique um aumento da entropia energética do sistema. Com base nas leis da física e nas que regem a matéria, discutem-se os limites da circularidade de nutrientes em um sistema agroindustrial. Assim, a humanidade enfrenta o desafio de preservar a utilidade da matéria sem incrementar a entropia energética do sistema. Neste contexto, o objetivo desta tese é avaliar a circularidade dos nutrientes em um sistema agroindustrial e propor um ensaio empírico sobre a máxima entropia da matéria. Metodologicamente, foi analisado o processo de recuperação de nutrientes, para a tecnologia de pirólise rápida, utilizando o teste *Tukey*. A geração de gases de efeito estufa por tonelada de nutriente recuperado foi contabilizada conforme protocolo do IPCC. Em seguida, a aplicação do método de Análise de Fluxo de Elementos permitiu quantificar os fluxos e estimar a máxima entropia da matéria recuperada. Os resultados indicam que a recuperação de nutrientes é sanitariamente segura. O nitrogênio, o carbono e o cromo reduzem conforme a temperatura de pirólise aumenta de 450 para 650^0C. A recuperação de nutrientes se mostra vantajosa quando associada ao mercado de créditos de descarbonização devido a estabilidade do carbono retido no *char*. Entretanto, os nutrientes recuperados representam apenas 4.23% do total necessário para um ciclo produtivo, e tendem à dissipação completa até o sétimo ciclo produtivo subsequente. A circularidade da matéria enfrenta os desafios entrópicos que implica em dependência de matéria de baixa entropia para a continuidade dos ciclos produtivos. Nesse sentido, para que a circularidade da matéria contribua para a redução da dependência de recursos, outros métodos de otimização de nutrientes podem ser associados ao sistema agroindustrial a fim de reduzir a entropia da matéria.

Palavras-chave: Economia Circular. Circularidade de Nutrientes. Entropia da Matéria. Limites biofísicos. Gestão de subprodutos.

ABSTRACT

The increasing demand for natural resources highlights the urgency of adopting practices that promote sustainability. In this context, pyrolysis technology emerges as a viable solution, transforming waste into bone char, which not only contributes to reducing the sanitary risks associated with animal-derived biomass but also enhances soil fertility by serving as a means of carbon storage and nutrient recovery. However, the implementation of nutrient circularity faces significant challenges, particularly in light of the laws of physics and matter. The Earth has a finite amount of matter that is in constant transformation. As matter is utilized, its entropy tends to increase, manifesting as a decrease in nutrient concentration and its dissipation within the terrestrial system. Although the dissipated matter still remains in the system, its potential utility is progressively reduced. Useful matter exhibits characteristics of low entropy, that is, it is ordered, concentrated, available, and capable of meeting the needs of natural and productive processes. In physics, matter with high entropy is commonly associated with disorder and dissipation. Energy can be employed to reorder and concentrate matter in a short period; however, this implies an increase in the energetic entropy of the system. Based on the laws of physics and those governing matter, the limits of nutrient circularity in an agro-industrial system are discussed. Consequently, humanity faces the challenge of preserving the utility of matter without increasing the energetic entropy of the system. In this context, the objective of this thesis is to evaluate the circularity of nutrients in an agro-industrial system and to propose an empirical study on the maximum entropy of matter. Methodologically, the nutrient recovery process for rapid pyrolysis technology was analyzed using the Tukey test. The generation of greenhouse gases per ton of recovered nutrients was accounted for according to the IPCC protocol. Subsequently, the application of the Elemental Flow Analysis method allowed for the quantification of flows and the estimation of the maximum entropy of the recovered matter. The results indicate that nutrient recovery is sanitary safe. Nitrogen, carbon, and chromium decrease as the pyrolysis temperature increases from 450 to 650 °C. Nutrient recovery proves advantageous when associated with the carbon credit market due to the stability of the carbon retained in the char. However, the recovered nutrients represent only 4.23% of the total required for a production cycle and tend to dissipate completely by the seventh subsequent production cycle. The circularity of matter faces entropic challenges that imply a dependence on low-entropy matter for the continuity of production cycles. In this sense, for the circularity of matter to contribute to reducing resource dependence, other nutrient optimization methods may be integrated into the agro-industrial system in order to reduce the entropy of matter.

Keywords: Circular Economy. Nutrient Circularity. Entropy of Matter. Biophysical Limits. Management of by-products.

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LIST OF ABBREVIATIONS

LCA	Life Cycle Assessment
C	Carbon
Ca	Calcium
CE	Circular Economy
CH_4	Methane
CO_2	Carbon Dioxide
$C_{\%DM}$	Pyrogenic Carbon Potential contained in Char
$C_{\%volatilized}$	Carbon volatilized during the pyrolysis process
$C_{expenditure}$	Carbon emissions from the entire pyrolysis process
DM	Dry Matter
EFA	Element Flow Analysis
EGGSHELL	Hatchery waste
EI	Emission Intensity
E_{out}	Energy produced
E_r	Energy recovery index
GHG	Greenhouse Gases
LPG	Liquefied Petroleum Gas
GWP	Global Warming Potential
HB	Hydrolyzed Chicken Bone
IPCC	Intergovernmental Panel on Climate Change
I_{PM}	Input of Matter
K	Potassium
MEM	Maximum Entropy of Matter
MJ	Megajoule
M&E	Matter and Energy
Mg	Magnesium
MSM	Mechanically Separated Meat
N	Nitrogen
N_2O	Nitrous Oxide
O_{PM}	Phosphorus Output
P	Phosphorus
Sb	Subsystem

SM	Supplementary Material
tBC	Tons of bone char

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ANNEX 58

1 INTRODUCTION

The use of natural resources should be limited to the regenerative capacity of Planet Earth, ensuring that ecological systems remain self-sustaining (Rockström *et al*., 2023). The concept of resource scarcity has become increasingly relevant in the context of the planet's biophysical limits (Bowles; Alexander; Hadjikakou, 2019; Fleischmann *et al*., 2024; Meadows, 2022; Nebel *et al*., 2023; Petraccone, 2023; Richardson *et al*., 2023; Sandström *et al*., 2023). With population growth and shifting consumption patterns, the demand for materials intensifies, leading to the accelerated depletion of natural resources (Giampietro, 2019). This issue is further exacerbated by the mismatch between the rate of resource extraction and the time required for natural reserve regeneration (Giampietro, 2023; Jakimowicz, 2023; Rockström *et al.*, 2023).

The availability of nutrients is a critical factor tied to the biophysical limits of matter, influencing the sustainability of agro-industrial systems and the resilience of ecosystems. Soil degradation, pollution, and overexploitation have contributed to a decline in the availability of essential nutrients such as nitrogen (N), phosphorus (P), and potassium (K) (Miao *et al*., 2023). This reduction not only compromises agricultural productivity but also affects food quality and global food security (Bianchi; Cordella, 2022). Additionally, competition for nutrients among sectors such as agriculture and industry exacerbates pressure on available resources. Addressing these challenges requires the implementation of sustainable management practices that promote nutrient recovery and recycling. For example, bone char— a nutrient-rich and stable carbon source— can play a crucial role in maintaining production cycles without compromising ecosystem integrity (Someus; Pugliese, 2018; Giampietro, 2023; Jakimowicz, 2023).

This growing scarcity underscores the urgency of innovative solutions for the efficient management of materials (Ahmed *et al*., 2019; Awasthi *et al*., 2019; Hart *et al*., 2022). This reduction not only compromises agricultural productivity but also affects food quality and global food security (Bianchi; Cordella, 2023; Brody, 2022). This model emphasizes the importance of maintaining the value of products, materials, and resources in the economy for as long as possible, encouraging practices such as reuse, recycling, and material recovery (Giampietro, 2023).

Although recycling is an essential component of the Circular Economy, it is crucial to acknowledge that recycling processes remain far from achieving full efficiency (Ayres, 1999; Craig, 2001; Di Maio *et al*., 2017; Kanwal; Zeng; Li, 2023; Kipp; Stüeken, 2017). Consequently, production processes require the addition of new materials to sustain subsequent production cycles (Alewell *et al*., 2020; Kipp; Stüeken, 2017; Miao *et al*., 2023). Various factors influence recycling efficiency, including material contamination, technological limitations, economic viability, and the environmental impacts associated with recycling processes (Kanwal; Zeng; Li, 2023). Furthermore, the laws of physics and the principles governing the behavior of matter impose constraints that are often overlooked by

the circular model. Therefore, it is essential to examine the limitations of material recovery imposed by entropic laws.

This thesis advocates for the inclusion of an entropic analysis of matter, focusing on the reduction of its potential utility—whether through dissipation or a decrease in the concentration of critical elements—as a limitation to the circularity of matter, based on thermodynamic principles and the laws governing matter transformations.

1.1 RESEARCH PROBLEM

An agro-industrial system is a complex production system that integrates agricultural and industrial activities, aiming to produce, process, and market agricultural and livestock product (Nan, *et al*., 2021). For this system to function efficiently and sustainably, proper management of natural resources is essential. This includes ensuring the availability of water, productive land, and favorable climatic conditions, as well as effectively managing the waste generated throughout the production process (Zwetsloot *et al*., 2015).

These agro-industrial systems rely on raw materials with high potential utility to meet production needs (Jakimowicz, 2023). The quality of a material can be defined by its "potential utility." Materials with high potential utility, or low entropy, have a greater capacity to meet the demands of natural and productive systems, as they are available, concentrated, and ordered. In contrast, high-entropy matter may remain within the system or be released into the external environment, often exhibiting low concentrations of critical elements, such as nutrients or minerals. This dispersion compromises its ability to fulfill the needs of productive or natural systems.

A clear example of this dynamic is the availability of phosphorus (P) in the soil, which is crucial for plant growth. The most useful form of this nutrient for plants is phosphorus pentoxide (P_2O_5). When plants absorb P_2O_5, it reacts with water (H_2O) to form phosphoric acid (H_3PO_4), which is utilized in biological functions. During this transformation, phosphorus is efficiently absorbed. However, the availability of P can be compromised by various factors, such as precipitation with soil metal cations, immobilization by microorganisms, and losses due to erosion and surface runoff. These and other factors contribute to the reduction of available P for plants, thereby increasing the entropy of this nutrient (Zwetsloot *et al*., 2016; Glaser, 2019).

On the other hand, the energetic entropy of forced recycling can be utilized to reorder matter. High-entropy matter, derived from by-products or waste from the production process, can be recycled through processes such as rapid pyrolysis. This technique stands out as a method for the thermal conversion of by-products, adhering to sanitary requirements and agronomic parameters. However, the consumption of diesel for biomass transportation and the energy sources powering the pyrolysis process are significant factors impacting the environment (Zwetsloot *et al*., 2015; Elkhalifa *et al*., 2019) and may contribute to energetic entropy.

In this study, the term "entropy of matter" is used to describe the state of order or concentration of matter, in contrast to the disorder or dissipation of matter within a system. Since the term "entropy" is often associated with energy in classical physics, we provide an approximation of the laws of physics and the principles governing the behavior of matter[1].

The First Law of Thermodynamics, also known as the Law of Conservation of Energy, states that energy cannot be created or destroyed but can only be transformed from one form to another (Craig, 2001; Georgescu-Roegen, 1971; Helmholtz, 1846; Joule, 1843; Mayer, 1842; Soddy, 1911). The Second Law of Thermodynamics, often referred to as the Law of Entropy, establishes that the entropy of an isolated system tends to increase over time (Fowler, 1931), indicating that entropic processes—whether natural or constructed—are irreversible (Clausius, 1850).

The laws of matter, also known as matter-dynamics, include the Law of Conservation of Mass (Lavoisier, 1789) which explains that matter can change from one state to another but cannot be created or destroyed. According to the general theory of systems, Planet Earth is a closed system, meaning it does not receive significant amounts of matter from the external environment but absorbs solar energy (Brooks *et al*., 1989; Kast; Rosenzweig, 1972; Odum, 1996). Within this system, matter is transformed from one state to another, while keeping the total amount constant, although it may exist in different concentrations, become more dissipated, or assume different molecular arrangements.

Closed systems face challenges regarding the circularity of matter, as the absence of material exchange with the external environment requires that the transformation and reuse of matter be entirely efficient to meet the needs of subsequent productive and natural cycles within the same system, thereby avoiding a reduction in the potential utility of matter. In contrast, in open systems, the reduction in the potential utility of matter can be compensated by new material inputs. Natural and productive systems are classified as open systems embedded within the closed system of Planet Earth. In this context, the circularity of matter within open systems reduces dependence on external inputs, although their circularity efficiency may fall short of full efficiency, compensated by a certain degree of disorder or external entropy.

The autonomous reordering of dissipated matter, within a timeframe usable by humanity, is unfeasible without additional energy investment for recycling. This energy utilization contributes to an increase in the energetic entropy of the system. Consequently, the challenge for economic growth lies in maintaining the availability of matter with potential utility while minimizing the increase in energetic entropy within the terrestrial system (Herbert *et al*., 2023; Petraccone, 2023).

[1] In the third article of this thesis, a parallel between Thermodynamics and Matter-dynamics is presented, which expands the discussion.

The reduction of potential utility of material impliesin critical limits that must be addressed to ensure sustainability (Miao *et al*., 2023; Richardson *et al*., 2023). In the context of thermodynamics and matter-dynamics, closed and open systems in the circular economy are considered self-sustaining, as they depend on external inputs to complete subsequent production cycles. This raises questions about the limits of circularity imposed by the laws governing matter and energy (Fleischmann *et al*., 2024), particularly the Second Law of Thermodynamics, which associates the use and interaction of matter and energy with the increase in entropy (Fleischmann *et al*., 2024; Jakimowicz, 2023; Martyushev; Seleznev, 2006).

In this context, the present thesis seeks to address the following questions: Considering nutrients as a critical element of matter, what is the quality and concentration of nutrients recovered from animal by-products biomass? What is the environmental impact on nutrient circularity? How many cycles can the recovered nutrients remain within the chicken meat productive system before being fully dissipated?

The main goal is to assess nutrient circularity in an agro-industrial system using pyrolysis, with a focus on its efficiency, environmental impacts, and the limits imposed by the maximum entropy of matter. The specific objectives are:

I. To analyze the physicochemical and sanitary parameters of nutrients recovered from biomass derived from animal by-products using rapid pyrolysis technology.

II. To quantify the generation of greenhouse gases per ton of recovered nutrients for rapid pyrolysis, in accordance with the IPCC protocol.

III. To model the limits imposed by the maximum entropy of matter on nutrient circularity in a chicken meat productive system.

The contributions of this research are structured around two pillars: relevance and originality. The relevance of the study is justified by the finite availability of low-entropy matter in a closed system, which is subject to a constant increase in irreversible entropy. Additionally, there is a scarcity of studies analyzing pyrolysis processes for animal by-products at an industrial scale. It is also necessary to define the greenhouse gas emission factors associated with the conversion of animal biomass in pyrolysis processes and to estimate the maximum dissipation of the recovered matter. Finally, Brazil is one of the largest food producers in a globalized market. Therefore, it is essential to consider the sustainability of food production for current and future generations, which is directly linked to reducing the entropic rate and enhancing resource efficiency within a system of irreversible entropy.

The originality of this research lies in its examination of the limits of matter circularity from the perspective of Matter-dynamics.

1.2 METHODOLOGICAL SYNTHESIS AND THESIS STRUCTURE

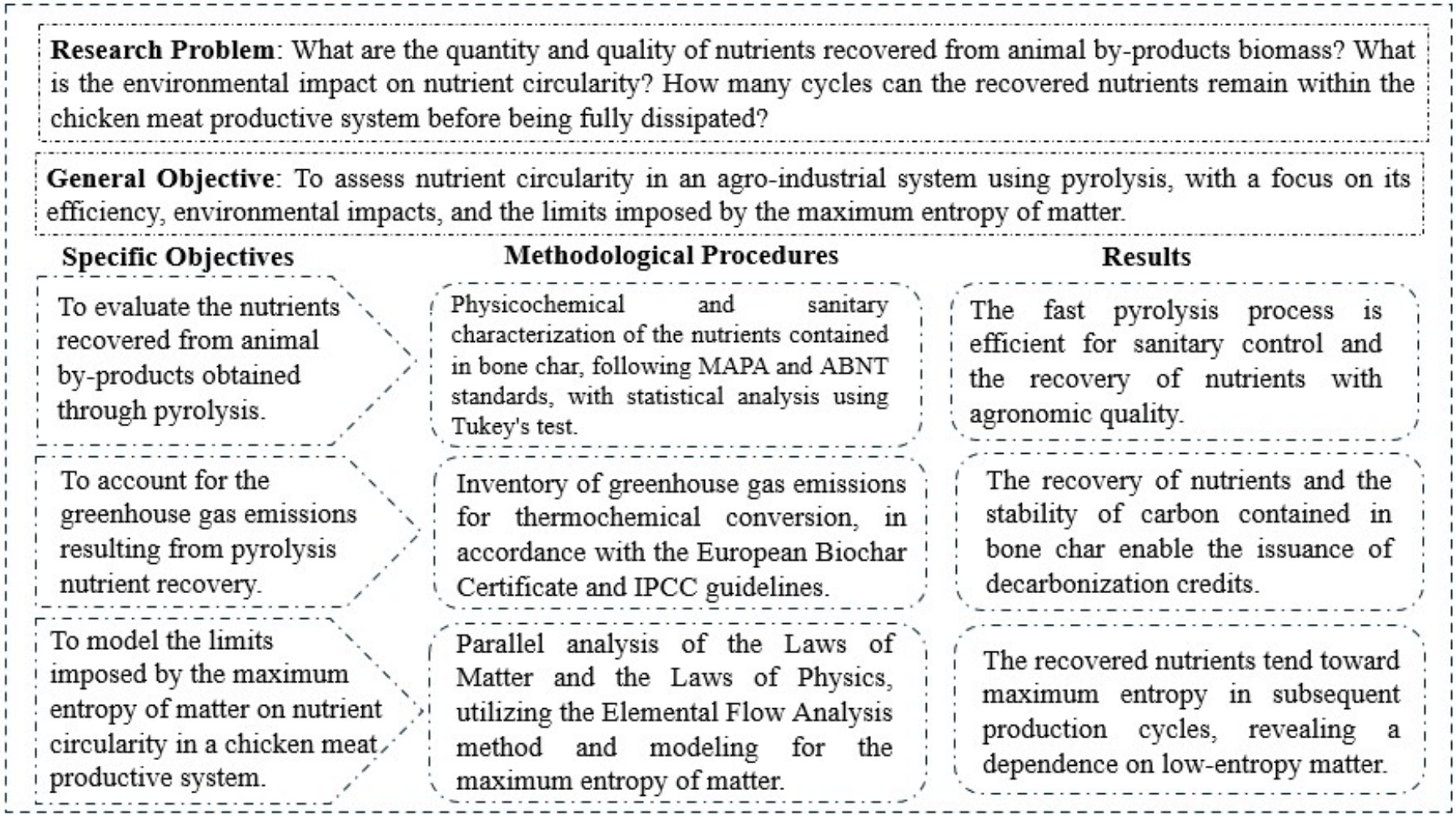
With the presented problem and outlined objectives, this thesis introduces both established and novel methods to contribute to the field, organized into three comprehensive chapters, as summarized in Figure 1.

In the first article, the aim is to validate pyrolysis technology as a viable option for recovering nutrients from biomass derived from animal by-products—particularly concerning potential sanitary risks—the physicochemical parameters, quantity and agronomic quality of the recovered nutrients, and the sanitary safety of bone char were evaluated. These indicators are designed to demonstrate the technological feasibility of achieving nutrient circularity from animal by-products.

In the second article of the thesis, a detailed inventory of the inputs and outputs of the pyrolysis process for different compositions of animal by-product biomasses enabled the accounting of decarbonization credits per ton of recovered nutrients. This study identified a significant issue regarding the renewable energy market, which provides a direct return to the meat industry. The recovery of nutrients occurs in the grain production phase, prior to meat production, and its viability is closely linked to decarbonization credits.

In the final article of this thesis, a parallel was drawn between the laws of thermodynamics and the laws of matter, referred to as matter-dynamics, to propose the maximum entropy for the recovered matter. Element Flow Analysis (EFA) was applied to the production and consumption system of chicken meat to evaluate the reduction in the concentration and quantity of a target element. The EFA flows provided data for modeling the Maximum Entropy of Matter (MEM), identified as a limiting factor for the circularity of matter.

Figure 1. Synthesis of the structure developed in this thesis.



Source: the author 2025.

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ORIGINAL PAPER

2 Circularity of Nutrients for Food Security: a Case Study of By-products from Meat Industry

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Abstract

The depletion of nutrients available in the soil is related to the long-term unsustainability of the food production system. Planetary biophysical limits make it urgent to adopt circularity practices that recover nutrients from being reused in production systems. The animal protein production system demands high amounts of nutrients, reducing the natural availability in the soil, increasing extraction from natural stocks, and dispersing nutrients abroad. However, nutrients can be recovered from slaughtered chicken by-products, such as mechanically separated meat residues and pre-hydrolyzed chicken bone. The present study compared the nutrients recovered from mechanically separated meat residues and pre-hydrolyzed chicken bone char by fast pyrolysis at 450 °C, 550 °C, and 650 °C. Results indicate that nitrogen, carbon, and chromium reduce as the pyrolysis temperature increases, while phosphorus, calcium, and magnesium increase. Nutrient recovery is less sensitive to pyrolysis temperature in pre-hydrolyzed chicken bone char than in mechanically separated meat residues-bone char (Tukey $p < 0.05$). In conclusion, the bone char production process can be fine-tuned regarding the pyrolysis temperature and the biomass loaded according to the nutrient targeted for recovery. Increasing the efficiency of nutrient cycling (soil–food–soil) can contribute to sustainable food security.

Keywords Biochar · Biofertilizer · Circular economy · Recycling · Resource use efficiency

2.1 Introduction

Biomass is the basis of our food system and future bioeconomy [1]. Still, the global biomass trade flow may modify nutrient cycling and availability [2]. Scarcity is created close to the source of biomass production, while nutrient surplus can occur in ecosystems where biomass is finally used or consumed [3, 4]. In this case, organic waste has value

Highlights

1. Nutrient recovery in pre-hydrolyzed chicken bone char is less sensitive to pyrolysis temperature.
2. Micronutrients show higher recovery rates at lower pyrolysis temperatures.
3. The solubility of P was higher in pyrolysis at higher temperatures.
4. The pyrolysis temperature should be adjusted according to the target nutrient from standardized biomass.
5. Increasing the efficiency of nutrient cycling can contribute to sustainable food security.

Extended author information available on the last page of the article

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but neglected applications in improving the food production system [5]. The recovery of critical nutrients is a potential strategy to meet growing demand, reduce potential risks, and extend the lifespan of natural reserves within a short time frame [6].

The primary macronutrients used in food production must be used judiciously. Phosphorus (P) is classified as a "critical raw material" [7]. The phosphate rock is the only primary source [8], geographically restricted [9], and without substitute for animals and plants development [10]. In 2021, the United States Geological Survey (USGS) estimated the world's economically extractable phosphate rock reserves at about 71 billion tons [8]. Assuming zero growth in extraction rate, reserves would last 260 years. The commercial formula most used in fertilizers is phosphorus pentoxide (P_2O_5), which demand grows by 2% per year [11]. Potassium (K) is also a limited natural resource. Potassium acetate increases stable carbon yield, increases P bioavailability for plants, and enhances nitrogen (N) stability recovery [12]. Nitrogen fertilizers have petroleum as their primary raw material, with relevant residual effects in the soil [13]. The recovery of N from alternative sources to petroleum arouses interest also because of the possibility of reducing the environmental impact.

Another relevant aspect of nutrient recovery is the composition of raw materials [14, 15]. Fertilizers extracted from rocks, like calcium (Ca), P, and K, contain cadmium (Cd) in their natural composition and are contributors to global soil and groundwater pollution [16]. Alternatively, nutrients can be recovered from different biomass wastes [17], such as the by-products from animal slaughter [18, 19]. The FAO (2022) estimates a global increase in animal protein consumption of 14% by 2030 [20]. Meat supply chain by-products should increase in the same proportion.

Animal by-products require a treatment that meets sanitary regulations to avoid the proliferation of diseases [21]. Thermochemical degradation is highly recommended due to its contribution to controlling pathogens [22]. Pyrolysis is a thermal process of degrading organic matter without oxygen at high temperatures (~ 300–700 °C) to produce bio-oil and bone char. Pyrolytic char can be used as a soil fertilizer since it is rich in P and other nutrients [23–28]. Another option of thermochemical treatment for animal slaughter by-products is to produce viscera meal through enzymatic hydrolysis [29]. However, the incomplete degradation of bone is a negative aspect of the enzymatic hydrolysis process.

Nutrient recovery rates vary depending on the complex interactions between the chemical elements [17], the composition of the biomass [30], and the temperature of the thermochemical process [17, 31]. Rare studies address the effect of biomass previously subjected to a thermoenzymatic process (hydrolysis) on pyrolysis bone char. Therefore, the present study aims to evaluate the nutrients recovered in bone char obtained by fast pyrolysis at different temperatures from mechanically separated meat (MSM) residues and hydrolyzed chicken bone (HB).

2.2 Methods

The industrial plant in which the processing of animal by-products was carried out using pyrolysis belongs to a large company in the Brazilian meat industry. The company has equipment with a processing capacity of up to one ton of animal by-products per 15-min cycle (fast pyrolysis). Fast pyrolysis uses higher heating rates and shorter residence times during the thermal conversion process [32, 33]. The industrial plant is installed in the state of Santa Catarina, Brazil.

In the present research, bone char is the pyrolytic biomass resulting from the pyrolysis process (output) [21, 34], applied to two raw materials (input):

i) Mechanically separated meat (MSM) is the bones and meat residues from chicken thigh and upper leg MSM processing.
ii) Chicken thigh and upper leg bones not fully dissolved by previous enzymatic hydrolysis process (HB).

In the enzymatic hydrolysis process, bones, meat, and chicken raw materials are ground and mixed with water free of contamination, pH adjustment, temperature (250 °C), and reactor pressure. After that, an enzyme is included. In our study, the papain enzyme is used, which is controlled by a specific time and undergoes an inactivation method. In the sequence, the hydrolysis output is filtered, centrifuged, separated, then sterilized, dried, and packaged. Bones not degraded in the enzymatic hydrolysis process make up the biomass destined for the pyrolysis process.

Another industrial slaughter plant of the same meat company provided MSM and HB by-products.

Three different temperatures were applied in the pyrolysis process, 450 °C, 550 °C, and 650 °C, as in the study by Wang et al. [6]. Thermometers were calibrated by an accredited laboratory for different solid materials, liquids, gases, and air following ISO 17025 standards [35]. The time variable was kept constant at 15 min, and the motor frequency was 40 Hz, with constant rotational speed. The process was carried out without oxygen.

Three sample replicates of the bone char output from each biomass (MSM and HB) loaded into the pyrolysis at each temperature (450, 550, and 650 °C) were collected and analyzed, totaling 18 samples (2 × 3 × 3). Figure 1 illustrates the methodological steps followed in the present study.

The bone char yield was calculated by the ratio (%) between the volume of output leaving the pyrolysis process and the quantity of by-products loaded to the pyrolysis equipment (input: MSM or HB), according to Eq. (1) [36, 37].

$$R\,(\%) = \frac{\text{Bone char (ton)}}{\text{By} - \text{product (ton)}} \times 100 \tag{1}$$

Physical characteristics, chemical properties, and nutrient concentration were analyzed because they are prior indicators of the desired safety and quality of fertilizers. Samples of bone char obtained were then sieved and homogenized, and the diameter of the particles was analyzed according to the Manual of Official Analytical Methods for Fertilizers and Correctives [38]. The analysis of the physical-chemical properties observed the procedures for the determination of ash content, described in the standards NBR16586 [39]; humidity [40]; volatiles [41]; carbon [42]; micro- and macronutrients; and potentially toxic elements [38]. To determine nitrogen (N), the Raney alloy macromethod was used [38, p. 9]. The chemical gravimetric method was used to determine phosphorus (P) [38, p. 21]. Atomic absorption spectrometry was used to determine the levels of potassium (K) [38, p. 46], copper (Cu) [38, p. 71], chromium (Cr), zinc (Zn) [38, p. 94], and cadmium (Cd) [38, p. 216]. Calcium (Ca) and magnesium (Mg) were determined by EDTA volumetric methods [38, p. 97], while carbon (C) by potassium dichromate volumetric method [38, p. 169].

The solubility of phosphorus in water was tested in neutral ammonium citrate and 2% citric acid [38]. The 2% citric acid extraction is commonly used to determine plant-available P from low-soluble fertilizer sources such as rock phosphate.

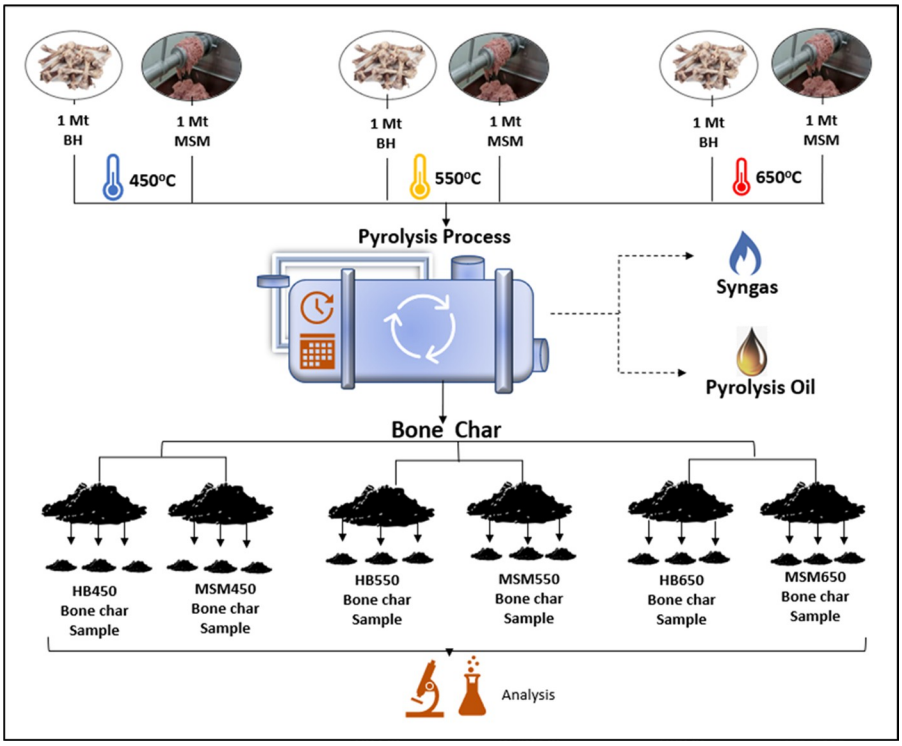


Figure 1. Methodological steps followed in the present study regarding the type of animal by-products, pyrolysis temperatures, and the bone char output.

Note. Animal by-products: MSM- mechanically separated meat residues from chicken bones and meat, and HB- chicken bone waste from previous hydrolysis process. Out- put: bone char (pyrolytic biomass). Samples: three replicates. Analysis: physical characteristics, chemical properties, nutrient concentrations, ANOVA, and Tukey test (p<0.05). Source: elaborated by the authors

Analysis of variance and test of means (Tukey $p < 0.05$) were used for the difference between the means of nutrients recovered comparing pyrolysis temperatures and biomass input.

2.3 Results

The biomass of animal by-products obtained from mechanically separated meat (MSM) and hydrolyzed chicken bone (HB) and loaded in the pyrolysis process has different physical–chemical characteristics (Table 1). The MSM biomass comprises chicken bones, waste meat, and animal fat. According to Leng et al. [43], it represents 30% of the live weight of chicken, with a high concentration of minerals, moisture, and protein compared to the HB biomass, which consists of the bones and by-products not dissolved by the enzymatic hydrolysis process.

Based on the output of the pyrolysis process, we found that the average yield was R = 20% ± 1.89% for MSM and R = 19% ± 0.87% for HB bone char. The humidity and volatiles (%) clearly show the effect of hydrolysis pretreatment for HB biomass (Table 2).

The availability of nutrients in soil depends on solubility. Therefore, solubility is an initial indicator of the bioavailability of P to plants. The results suggest that the P contained

Table 1. Physical–chemical characteristics of mechanically separated meat (MSM) and hydrolyzed chicken bone (HB) biomass loaded in pyrolysis

Physical–chemical parameters	MSM	HB
Humidity and volatiles (%)	61.15 ± 3.65	11.17 ± 1.81
Crude protein (%)	38.18 ± 2.19	13.50 ± 2.37
Mineral (% DM)	77.06 ± 5.01	91.12 ± 3.23
Ethereal extract (%)	3.37 ± 1.08	< 0.15 ± 0.0
Density (g/cm^3)	0.88 ± 4.03	0.47 ± 1.08

DM dry matter. Sample (*n*) three replicates. Data: means ± standard deviation. Source: research data

in bone char shows relatively high solubility in water and 2% citric acid for both animal by-products analyzed (Table 2). The solubility is increased with increasing temperature and is higher for HB biomass.

Regarding nutrients, the presence of N, C, and Cr decreases as the pyrolysis temperature increases, which can be explained by volatilization. The opposite trend was observed for the nutrients P, Ca, Mg, and K, whose concentration tended to increase as the pyrolysis temperature increased, except for K in the HB bone char. The presence of P tended to be higher in the HB bone char obtained from higher pyrolysis temperatures, although with no statistically significant difference (Tukey $p < 0.05$) between the averages of recovered P. On the other hand, K levels are higher and statistically different for MSM bone char obtained from lower pyrolysis temperatures (Tukey $p < 0.05$) (Table 3).

Higher temperatures (650 °C) maintained high solubility of P (Table 2) and favored the recovery of P (Tukey $p < 0.05$) from HB and MSM (Table 3). On the other hand, the recovery of calcium (Ca) was higher at the lowest pyrolysis temperature, The rates of 30.52% in the HB and 28.43% in the MSM bone char. Like N, the recovery of C tends to decrease with the increase in temperature due to the volatilization that occurred during the processing of both by-products.

The concentrations of Mg and Zn are more stable in the HB bone char. Cu, Cr, and K seem to be influenced by the previous hydrolysis process (HB) (Table 3); that is, the hydrolysis pretreatment removes these nutrients from the biomass (HB), and the temperature of the pyrolysis process has no significant influence.

Consequently, Cu, Cr, and K recovery rates are more significant for MSM biomass. In this biomass, the lowest temperature of the pyrolysis process contributes to the Cr recovery rates, and increments in temperature contribute to K recovery. Cadmium (Cd) levels were equally low (< 0.02 mg kg^{-1} DM) in both bone chars. Nutrient concentration in MSN and HB bone char at different pyrolysis temperatures is shown in Fig. 2.

2.4 Discussion

The Brazilian livestock sector slaughters more than 41 million tons of cattle, poultry, pigs, and fish per year. A significant part of this amount does not reach consumers' tables. It is estimated that 38% of the live weight of cattle, 28% of poultry, 20% of pigs, and 45% of fish are classified as unfit for human consumption by the official inspection system [44]. The animal recycling sector collects and processes about 13 million tons per year (Mt/year) of by-products from these slaughtered animals [44]. Europe, for instance, recycles 4.5 Mt/year of animal by-products destined for the production of bio-oil and fertilizer [45]. Brazil would need to open 921 more landfills if it did not recycle

Table 2. Physical–chemical characteristics of bone char from animal by-products of mechanically separated meat process (MSM) and hydrolyzed chicken bone (HB) at 450 °C, 550 °C, and 650 °C of pyrolysis temperatures.

Physical–chemical parameters	450 °C		550 °C		650 °C	
	MSM	HB	MSM	HB	MSM	HB
Humidity and volatiles (%)	23.89 ± 0.20	1.77 ± 0.04	3.48 ± 0.24	1.95 ± 0.03	1.66 ± 0.12	1.70 ± 0.07
Crude protein (%)	28.30 ± 0.19	10.51 ± 0.06	8.26 ± 0.06	15.73 ± 0.21	8.18 ± 0.13	7.42 ± 0.06
Mineral (% DM)	37.71 ± 0.57	81.22 ± 0.12	81.79 ± 0.07	76.41 ± 0.03	82.84 ± 0.06	86.35 ± 0.28
Ethereal extract (%)	2.25 ± 0.23	< 0.10 ± 0.0	< 0.10 ± 0.0	0.17 ± 0.02	< 0.10 ± 0.0	< 0.10 ± 0.0
Density (g/cm^3)	0.57 ± 0.04	0.20 ± 0.08	0.37 ± 0.03	0.23 ± 0.15	0.32 ± 0.25	0.29 ± 0.04
Phosphorus (P) (% DM)	4.88 ± 0.25	13.66 ± 0.11	13.76 ± 0.20	12.12 ± 0.03	14.15 ± 0.15	14.39 ± 0.25
Nitrogen (N) (% DM)	4.73 ± 0.23	1.68 ± 0.04	1.32 ± 0.04	2.46 ± 0.04	1.13 ± 0.03	1.24 ± 0.07
Potassium (K) (% DM)	1.09 ± 0.12	0.49 ± 0.03	2.05 ± 0.03	0.45 ± 0.03	1.57 ± 0.13	0.43 ± 0.04
Solubility of P in water (%)	10.35 ± 0.60	10.97 ± 0.09	10.96 ± 0.08	13.06 ± 0.06	12.18 ± 0.14	14.17 ± 0.13
Solubility of P in 2% citric acid (%)	80.32 ± 0.30	81.04 ± 0.06	83.99 ± 0.07	84.07 ± 0.04	87.24 ± 0.11	85.99 ± 0.06

DM dry matter; sample (*n*) three replicates. Data: means ± standard deviation. Source: research data

Table 3. ANOVA results for nutrients recovered from mechanically separated meat (MSM) and hydrolyzed chicken bone (HB) by pyrolysis at 450 °C, 550 °C, and 650 °C.

Nutrients	ANOVA		450 °C		550 °C		650 °C	
	R^2	*P*-value	MSM	HB	MSM	HB	MSM	HB
P (% DM)	77.27%	0.025	4.88Bb	13.65Aa	13.76Aa	12.12Aa	14.16Aa	14.39Aa
N (% DM)	99.54%	0.000	4.72Aa	1.68Cb	1.32Db	2.46Bb	1.31Db	1.23Db
K (% DM)	98.71%	0.000	1.09Ba	0.49Cb	2.05Aa	0.45Cb	1.58Ba	0.43Cb
Ca (% DM)	89.91%	0.001	28.4BCa	30.54Aa	27.32Ca	28.3BCa	27.51Ca	30.1ABa
C (% DM)	99.98%	0.000	39.27Aa	16.84Cb	14.35Eb	21.60Ba	15.69Db	12.09Fb
Mg (% DM)	97.85%	0.001	0.27Bb	0.65Aa	0.65Aa	0.72Aa	0.73Aa	0.74Aa
Zn (mg kg^{-1})	97.73%	0.001	161.6Db	325.7Bb	424.3Aa	296.Cab	295.Cab	233.7Cb
Cu (mg kg^{-1})	89.99%	0.001	24.75Ba	6.69Cb	46.42Aa	5.46Cb	21.41Ba	5.09Cb
Cr (mg kg^{-1})	75.67%	0.001	576.1Aa	51.6Db	507.5Ba	11.2Fb	160.1Ca	24.33Eb

Sample (*n*)=three replicates; *ANOVA*, analysis of variance test; test for averages, Tukey ($p<0.05$). Capital letters compare pyrolysis process temperatures and lowercase letters compare biomasses; *DM*, dry matter; *MSM*, mechanically separated meat; *HB*, hydrolyzed chicken bone. Pyrolysis temperature in degrees Celsius (°C); *P*, phosphorus; *N*, nitrogen; *K*, potassium; *Ca*, calcium; *C*, carbon; *Mg*, magnesium; *Zn*, zinc; *Cu*, copper; *Cr*, chromium.

Source: elaborated by the authors based on research data.

animal by-products. By-product recycling collaborates with the National Solid Waste Plan and avoids an increase of approximately 30% in landfills [44].

Besides the pathogen control provided by the heat treatment, reducing the volume of by-products contributes to reducing the environmental impact. The main effects of the hydrolysis pretreatment (Table 1) on the biomass that enters the pyrolysis process are reduction of humidity, protein, and mineral and consequent increase in the proportion of minerals. We found that the average yield of the pyrolysis process was nearly 20%. The yield of the pyrolysis process is generally low, with approximately 20–22% of the weight of biomass entering the pyrolysis process [46–48]. The weight reduction is mainly explained by the loss of carbon (C), which boosts the performance of bone carbonization. The C loss was more pronounced for HB by-products previously treated by hydrolysis ($R = 19\%$) since it had been subjected to a thermochemical treatment before the pyrolysis. The European Biochar Foundation [49] recognizes a difference between "biochar" and "bone char" compositions. Biochar originates mainly from plant biomass with a high carbon concentration. For this reason, "bone char" cannot be categorized as "biochar," but as "pyrogenic carbonated material" [49]. Pyrolysis materials derived from mineral-rich input materials (e.g., manure, animal bones) are much lower in organic C [23], in contrast with a high concentration of other nutrients.

Carbon bioavailability is temperature-dependent [32], and higher pyrolysis temperatures tend to stabilize C [50]. By-product type plays a crucial role in catalyzing biomass conversion to bone char and assisting in its stabilization [51]. A stable carbon has an average time of 556 years in the soil [50]. Biochar application in the soil may play a role in climate change mitigation since it rests stably by hundreds to thousands of years [32, 52]. According to Wang et al. [6], the stability of C ratios in pyrolysis bone char at 450 °C, 550 °C, and 650 °C is 0.26, 0.73, and 0.85, respectively. The relationship between O, H, and C can be used to estimate the time retention of C in the soil [53].

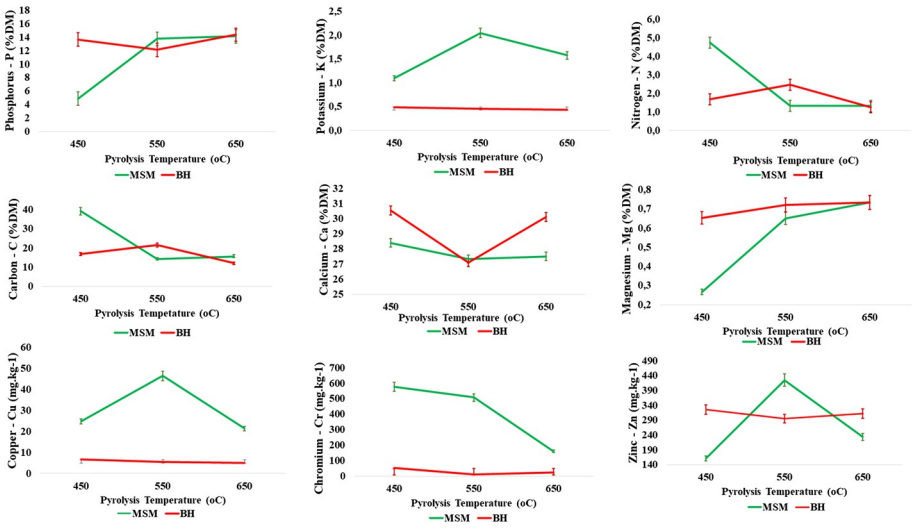


Figure 2. Nutrient concentration in MSN and HB bone char at different pyrolysis temperatures.
Note: MSM, mechanically separated meat; HB, hydrolyzed chicken bone; DM, dry matter. Pyrolysis temperature. Date = means ± standard deviation. Source: elaborated by the authors based on research data.

Even though increasing the pyrolysis temperature reduces C retention in bone char while significantly growing its stability [17], the retention rate of C as organic carbon was reported as approximately 10% by Zupančič and Čelan Korošin [30], while the low rate (11%) was found in the cattle bone at 800 °C [34] since bone carbonization promotes the loss of C [54]. As the pyrolysis temperature increases, the quantity of C is lost (Fig. 2 and Table 3) but increases the stability of carbon in the soil (quality carbon).

The results for P concentration, transformed to the agronomic formula P_2O_5, were like those found by Someus and Pugliese [23] (28%) using pyrolysis for chicken bone at a temperature of 850 °C and higher than that reported by Santos et al. [55] at 400 °C (20.66%). Accordingly, temperatures and biomass are less relevant to describe the P_2O_5 concentration for different processes because efficiency is a "critical element" in any industrial-scale pyrolysis process. The quality of technology design is unique and impacts the output characteristics from the pyrolysis [23].

Equally important is the high solubility of P in 2% citric acid (> 80%) and water (> 10%) found in our study, indicating the bioavailability of P for plant uptake. According to Mayer and Kaltschmitt [3] and Ahmad et al. [56], P uptake by plants depends on solubility, among other factors. In quick-release fertilizer, 70% of total P is soluble in 2% citric acid [57]. In the result presented by Someus and Pugliese [23] for chicken bone pyrolysis at 850 °C, the solubility was 64.6% and classified as a controlled release. This means that the nutrients solubilize in the soil slowly, which ensures a prolonged presence of the nutrient in the soil [55]. Furthermore, small average density granulometry (0.28 g/cm^3) contributes to P uptake by plants.

Pyrolysis volatilizes a substantial part of N in both biomasses. Moreover, the remaining N is mainly unavailable for plant uptake [12], becoming a limiting factor in N recovery by pyrolysis (Fig. 2 and Table 3). However, the increase in pyrolysis temperature favors the formation of oxide, hydroxide, and carbonate mineral phases of Ca, Mg, Na, and K [32].

Meanwhile, the hydrolysis pretreatment interferes with the recovery of K because increasing the temperature in pyrolysis does not increase the rates of K recovered (Fig. 2 and Table 3).

In the same way, adding calcium (Ca) makes C retention more efficient [17]. In our study, on average, 30% of Ca was recovered (Fig. 2 and Table 3). The relatively high concentration of Ca and P is natural in the animal bone composition. Sixty to 70% of bone's weight is composed of hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$] [58]. Ca is an acidity neutralizer widely used in agriculture [59], which controls the uptake of Cd by plants [15, 59] and is classified as an anti-nutrient neutralizing [51] with a relevant contribution to soil nutrition [23].

Considering the current depletion of the soil, all nutrients contribute to the regenerative process [32, 51]. Nutrients like Mg showed no significative variations related to temperature and by-products (Tukey $p<0.05$, Table 3). However, the Cu and Cr mean concentration differs significantly concerning the MSM and HB bone char (Tukey $p < 0.05$, Table 3). Cr is essential for chicken nutrition and is used as a feed supplement, remaining concentrated mainly in chicken meat [60]. This explains the lower concentration of Cr in HB bone char or biomass dependent.

The fact that Zn concentration is higher in HB bone char is important for soil remediation, because the bone char has the property to degrade toxic materials. The ZnO, for instance, can degrade methylene blue [61]. Likewise, its potential can be enhanced with hydrolysis pretreatment.

Another important advantage of this P-recovered source is its purity compared to rock phosphate [62]. Nearly null or low concentrations of heavy metal contents could be found in bone char [63]. In fact, bone char from both by-products has no significant levels of cadmium (Cd < 0.02 mg kg^{-1} DM) irrespective of pyrolysis temperature, same result for castle bone char [64]. In comparison with rock phosphate, sedimentary deposits average Cd 21 mg kg^{-1} with a range of less than 1 to 150 mg kg^{-1} [65]. Consequently, based on studies of Cd accumulation in soil, the European Commission proposed a limit from 60 to 20 mg Cd kg^{-1} P_2O_5 over 15 years [65].

Pyrolysis modifies the availability of nutrients in bone char by changing how each nutrient is bound in the material [12] regarding the type of biomass and pyrolysis temperature. There is evidence that the increase in temperature favors the recovery of P, Ca, and Mg and contributes to the volatilization of Cd, K, C, Cr, and N. The biomass with the greatest contribution to the recovery of nutrients is MSM, compareted with the HB hydrolysis pretreatment. This last one increased nutritional losses, in pyrolysis process. The nutritional contributions of the hydrolysis process were not considered. Likewise, the physical–chemical characteristics of bone char can be optimized during its production through optimal selection of raw material and processing conditions [66].

The results of this study of using biomass in cascade contribute to formulate public policies in the context of the circular economy. The European Biochar Certificate is in the process of defining parameters for bone char certification [49]. First, to achieve the SDG 2 "zero hunger" target, there is an increment to SDG 2.3, which sets the target of doubling the production in smallholder farms. To improve the yield in small farms, it is necessary to increase P fertilization by 22–30%. The estimate suggests that applying 50 kg P ha^{-1} $year^{-1}$ during 2015–2030 would eliminate the P constraint for crop yields [67], but not every additional nutrient needs to come from a primary nature reserve.

Another usage example on the potential of cascading biomass use presented in the Polish Agro-food consortium suggests that cooperation between local actors can strongly contribute to the circular bioeconomy [45]. Clearly, the implementation of circular bioeconomy at the microeconomic level in production units causes a company to implement

various strategies to improve the production system and cooperate with other companies [68], like feed animals and energy production [45].

In addition to nutrient recovery, the use of cascading biomass also contributes to renewable energy production. Oliveira Pavan et al. [69] quantifies that the state of São Paulo can generate 1.69 GW of energy using regional waste streams in circular model cooperation. In the energy matrix of Brazil, in 2019, the forest biomass it was transformed into 3.24 GW of energy [70]. The use of by-products can reduce dependence on forest biomass for energy production by 47.8% and release land destined to wood production for food production or forest preservation. In this case study, the bio-oil and biogas from the pyrolysis process are used to reduce and neutralize the energy consumption in the process by up to 70%, which helps to counteract the energetic impact of nutrient recovery.

Therefore, our findings may contribute to this emerging topic by providing new values for nutrient recovery from two by-products bone char at different pyrolysis temperatures.

2.5 Conclusions

The physicochemical characteristics and maximization of nutrient recovery rates contained in bone char can be optimized by adjusting the processing conditions. In addition, the type of biomass to be loaded into the pyrolysis process plays a major role, influencing the stability of the results. Processing more homogeneous biomass results in more stable recovery rates.

New investigations are emerging to measure and discuss the environmental impact of nutrient recovery. Researches can advance in overcoming these limitations and evaluate the effects of additives in processing these by-products and their impact on nutrient recovery. Also, the analysis of the volumes, characteristics, and uses of pyrolysis oil and syngas can be investigated.

The results of nutrient recovery from by-product treatment by pyrolysis on an industrial scale confirm this process as a technological possibility for nutrient management. Nutrient recovery from by-products balances the use of natural resources with improved soil health and contributes to sustainable food security.

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Declarations

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5 FINAL REMARKS

The evaluation of the physicochemical and sanitary parameters of nutrients recovered from biomass derived from animal by-products using rapid pyrolysis technology (Chapter 1) indicates that the pyrolysis process is a technologically viable method for nutrient recovery. The nutrients incorporated into bone char exhibit agronomic quality and sanitary safety. Additionally, the process parameters and biomass composition can be adjusted to optimize both the quantity and quality of the recovered nutrients.

When greenhouse gas emissions per ton of recovered nutrients are calculated according to the IPCC protocol (Chapter 2), the results indicate that for the analyzed technological process, powered by electricity and liquefied petroleum gas (LPG), nutrient recovery must be linked to the quantification of stable carbon stored in bone char to generate decarbonization credits, which connects its use to fertilizer applications. Additionally, producing renewable energy through the combustion of bone char offers a more direct application in the meat processing plant. However, this combustion releases the carbon retained in the char and degrades the nutrients. While both the generation of decarbonization credits and the production of renewable energy are considered sustainable practices, one is achieved at the expense of the other.

The modeling of the limits imposed by the maximum entropy of matter for nutrient circularity in the agroindustrial system (Chapter 3) reveals that the supply of renewable energy may be a less significant factor among the limitations for food production compared to the demand for nutrients. However, recovered nutrients contribute to reducing the temporary dependence on low-entropy matter, which is dissipated in subsequent production cycles. Consequently, the productive system remains dependent on the input of low-entropy matter. The European Commission (2022), a proponent of the Circular Economy, recognizes this limitation and emphasizes that consumption patterns must become more sustainable to ensure environmental integrity, as technological solutions alone are insufficient to bridge the gap between supply and demand.

The depletion of natural reserves and the compromise of the planet's natural regeneration capacity emphasize that traditional economic models, whether linear or circular, fall short of promoting true sustainability. This failure stems from their disregard for the laws of thermodynamics and the principles governing matter transformations, referred to in this study as matter dynamics. In essence, achieving sustainability within the planet's biophysical limits cannot rely solely on technological solutions.

Although society has access to technologies such as pyrolysis, presented in Chapter 1 of this thesis, which can safely and effectively promote the circularity of critical elements of matter within a short timeframe, these technologies require energy. Even if the pyrolysis process is powered by renewable energy, as a potential solution to reduce dependence on non-renewable energy sources, the issue of entropy associated with energy transformation resulting from forced recycling remains.

The accounting of greenhouse gases as a measure of sustainability, detailed in the second chapter of this thesis, following the standard protocols of the Intergovernmental Panel on Climate Change (IPCC, 2019) and the European Biochar Certificate (2023), illustrates the complexity industries face in the context of sustainability. Some choices classified as sustainable may be highly entropic, to the detriment of other, less entropic options. This occurs because greenhouse gas accounting is strongly influenced by the selection of renewable energy sources and the choice of comparison benchmarks, such as GHG emissions from rock fertilizer production or gases from biomass decomposition, compared to the GHG emissions from nutrients recovered from by-products in the pyrolysis process. Furthermore, the production of greenhouse gases may be directly associated with energetic entropy, reflecting inefficiencies in transformation processes and the degradation of available energy quality.

In addition to energetic entropy, the entropy of matter can manifest in other aspects, as discussed in the third chapter of this thesis. In an open system, such as productive systems, the efficiency of matter recovery may be reduced because the internal entropy of the system—both for matter and energy—is compensated by inputs of low-entropy matter and energy, meaning these systems depend on external inputs. Both in Element Flow Analysis and in the modeling of the Maximum Entropy of Matter, empirical evidence indicates the inefficiency of these systems in closing the cycle, either through the reduction in the amount of matter classified as waste that returns to the productive system or through the dissipation of the critical element analyzed—in this case, the nutrient phosphorus. With each new production cycle, a quantity of concentrated low-entropy matter must be added to complete production.

The analyzed agro-industrial system also reveals additional opportunities to optimize nutrient flow, whether through domestic organic waste, human feces, improved absorption of nutrients applied to the soil, or the recycling of organic matter without the use of energy, as in biodecomposition.

In light of this, the evaluation of nutrient circularity in an agroindustrial system through pyrolysis—considering its efficiency, environmental impacts, and the limits imposed by the maximum entropy of matter—reveals that, although the circularity of matter contributes to reducing temporary dependence on low-entropy matter, it is intrinsically entropic and unsustainable.

5.1 SUGGESTIONS FOR THE AGRO-INDUSTRY

The production of the agro-industry is intrinsically linked to environmental conditions and the availability of high-quality natural resources, which are essential for meeting the needs of both the productive and environmental systems. To continue fulfilling its noble role of producing food on a large scale, it is crucial for the agro-industry to adopt a proactive stance towards sustainability, aiming to preserve its business model both in the present and in the future.

A critical aspect to consider is the finiteness of natural nutrient reserves, which makes the implementation of strategies for the recovery and recycling of these resources urgent. In this context, technologies such as pyrolysis stand out, as they promote the necessary sanitary safety for animal by-products and contribute to carbon retention. However, this recovery currently meets only 4.24% of the phosphorus (P) nutrient requirements necessary for production, and this nutrient still lacks viable substitutes. Therefore, it is imperative to adopt a variety of nutrient recovery solutions in order to reduce the rate of consumption and promote the reconstitution of critical nutrient reserves, as well as to prioritize nutrient recovery and carbon retention in char over renewable energy production, since burning char releases carbon and denatures nutrients.

5.2 STUDY LIMITATIONS

It should be noted that some limitations were encountered regarding the resources for laboratory analyses. Various tests are necessary to meet the methodological analysis parameters for bone char, as outlined by MAPA (2017) and ABNT (2016, 2017a, 2017b, 2018). Part of the laboratory analyses for bone char was funded by the partner industry, while another part was conducted at UFRGS university. Among the analyses, the characterization of the physicochemical parameters for the bio-oil and biogas outputs was excluded, and tests with additives or mixtures of the biomasses were not included. Although most scientific publications on bone char use parameters estimated from laboratory-scale prototypes—which may differ from the industrial scale of this study—the absence of these tests was compensated by parameters presented in the literature.

Limitations were also encountered regarding the greenhouse gas accounting parameters available in the Intergovernmental Panel on Climate Change (2019) method, which is designed for the incineration of biomass and the production of biochar from plant biomass. The European Biochar Certificate (2023) recognizes the need for advancements in determining parameters for GHG estimates related to the conversion of animal biomass into bone char, which are anticipated in future publications. The parameters were adapted from the consolidated IPCC (2019) method for biomass incineration and the guidelines for biochar quality certification recognized by the European Biochar Certificate (2023).

The Element Flow Analysis faced limitations due to uncertainties in the data representing the flows, as highlighted in the uncertainty analysis provided in the Supplementary Material of the third article in this thesis. These challenges have also been noted by authors such as Ott and Rechberger (2012) and Sinha (2022). To address these uncertainties, the modeling utilized Stan software, approximating the data to a normal distribution. This approach enables the application of methods such as error propagation and data reconciliation.

It is important to highlight that limitations may arise in the discussion of results related to the physicochemical parameters of the pyrolysis process, greenhouse gas accounting per

ton of recovered nutrients, and estimates for element flow analysis, based on the approximations of the indicators and their respective standard deviations.

5.3 SUGGESTIONS FOR FUTURE STUDIES

The recycling of matter requires low-entropy energy. The use of energy can incur energetic entropy, depending on the type of energy utilized, which may be linked to climate change. Including the energetic entropy of recycling in the modeling of the Maximum Entropy of Matter (MEM) appears to be a coherent approach. This opens opportunities for future research to expand discussions on MEM. Additionally, the relationship between recovered matter and the different forms of energy used in recycling can be further explored.

Another important factor to consider is time. According to Kummel (2011), the entropy of systems always increases over time. Thus, it is recommended to explore the impact of time on entropy, both in natural reordering processes (negentropy) and in reducing the rate of entropy through the forced recycling of matte, as well as to analyze the entropy for biomass recycling methods with no energy, such as biodegradation by bacteria and other opportunities to reduce the flow of nutrients in the system.

Finally, an entropic velocity can serve as a benchmark for the limits of unsustainability, emphasizing the inability of current consumption levels to meet the needs of future generations by mapping the reduction in the potential utility of matter associated with each production cycle and specific product.

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ANNEX

PETEK
TRADUÇÕES

CERTIFICATE OF PROOFREADING

I, the undersigned Nina Petek, translator in the City of Porto Alegre in the State of Rio Grande do Sul, Brazil, hereby attest:

1. That I am a qualified Translator in the Portuguese to English language combination, and the owner of company *Petek Traduções*, a translation company duly registered in Brazil, created in 2012.
2. That I have performed a proofreading of the attached English scientific article for publication, namely:

"NUTRIENT CIRCULARITY IN AGROINDUSTRIAL SYSTEMS: COMPOSITION OF BONE CHAR, ENVIRONMENTAL IMPACT, AND LIMITATIONS DUE TO MATTER ENTROPY"

3. That my proofreading is a true and correct interpretation of said documents to the best of my knowledge and ability.

Signed this on January 17th, 2025, in City of Porto Alegre, in the State of Rio Grande do Sul, Brazil.

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