SÃO PAULO STATE UNIVERSITY (UNESP)
JABOTICABAL CAMPUS

VALORIZING BY-PRODUCTS FROM CROP HARVESTING INTO ANTIOXIDANTS TO CONTROL PELLET OFF-GASSING

Bruno Rafael de Almeida Moreira
Agronomy, M.S.

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AUTHOR’S ACADEMIC PROFILE

Bruno Rafael de Almeida Moreira was born on June 1, 1995, in Dracena, São Paulo, Brazil, to Agnaldo da Silva Moreira and Jaqueline Pereira de Almeida. Raised by his grandparents, Maria Francisca and Aparecido Pereira, he completed his elementary and high school education in his hometown from 2002 to 2012. In 2014, Bruno embarked on his academic journey by enrolling in the undergraduate program for Agronomic Engineering at the College of Agricultural and Technological Sciences (FCAT/Unesp). In 2018, he graduated with academic distinction, having excelled in a diverse range of subjects and during his mandatory supervised internships. Continuing his academic pursuit, he obtained a Master's degree in Agronomy at the Faculty of Engineering (FEIS/Unesp) in 2019. By 2020, he had earned his Master's degree, specializing in Production Systems. His master's thesis focused on the application of hydrothermal carbonization and microwave irradiation to convert waste into pellets for bioenergy generation and carbon capture. Advancing further, Bruno commenced his Ph.D. studies in Agronomy (Plant Production) at the College of Agricultural and Veterinary Sciences (FCAV/Unesp) in 2021. Under the guidance of Prof. Dr. Rouverson Pereira da Silva, his doctoral research delved into the conversion of residual biomass from agricultural crop harvests. He explored its potential as antioxidants to manage degasification and self-combustion in pellets, while simultaneously contributing significantly to the scientific output of his research group.

If what I know, I don’t transmit, then I’m no use

Bruno Rafael

I dedicate the culmination of my academic journey and achievements to my grandparents, Maria Francisca and Aparecido Pereira, and family.

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The completion of this dissertation marks a transformative journey that has significantly enriched my life. I am profoundly grateful for the steadfast support and guidance bestowed upon me by numerous individuals and institutions.

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I am indebted to my grandparents, Maria Francisca and Aparecido Pereira, whose enduring love and nurturing guidance have played a pivotal role in shaping the person I am today. Their unswerving belief in my potential and tireless encouragement have laid a robust foundation for my academic endeavors. The values of determination, diligence, and familial bonds that they imparted have served as the bedrock of my journey.

My appreciation extends to my family, particularly my mother Jaqueline Pereira and stepfather Valdeir Siqueira, who have been unwavering pillars of support. Their sacrifices, encouragement, and steadfast faith in my abilities have propelled me forward. To my brother Paulo Roberto, your companionship and unyielding belief in me have been an enduring source of motivation. I also wish to convey my gratitude to my aunt Katia Pereira, uncle Marcos Souza, cousin Gabriel Felipe, and grandaunt Claudete for their love, encouragement, and invaluable insights that have enriched my path.

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In conclusion, this dissertation not only attests to my personal dedication but also to the collective support, encouragement, and belief vested in me by a remarkable array of individuals and discerning institutions. To all those mentioned, and even those whose contributions may have gone unmentioned but are equally cherished, I extend my heartfelt appreciation. Your influence on my journey is immeasurable, and I carry your unwavering support with me as I embark on new horizons.

With profound appreciation,

Bruno Rafael

SUMMARY

VALORIZAÇÃO DE SUBPRODUTOS DE COLHEITA MECÂNICA DE CULTURAS EM ANTIOXIDANTES AO CONTROLE DE DESGASEIFICAÇÃO DE PÉLETES

RESUMO – A dissertação abrange os capítulos I, II, III, IV e V, com o objetivo de examinar o fenômeno da liberação de gases e suas implicações sociais, ambientais e econômicas para o desenvolvimento sustentável. Eles contribuem com insights para aprimorar a compreensão e o gerenciamento desse problema crítico, fornecendo conhecimentos acionáveis para partes interessadas como formuladores de políticas, produtores e pesquisadores, impulsionando progressos na segurança ocupacional, na saúde humana, na higiene industrial e na proteção ambiental dentro das cadeias de valor de biocombustíveis sólidos. O Capítulo I é introdutório e revisa, criticamente, a literatura existente, explora práticas e técnicas preventivas e mitigadoras relacionadas à liberação de gases e aprofunda-se nas dimensões sociais, ambientais e econômicas associadas à liberação de gases da biomassa, enfatizando sua importância na indústria global de biocombustíveis sólidos. Além disso, o capítulo investiga cenários de liberação de gases em ambientes residenciais, comerciais e industriais. O Capítulo II foca nos aspectos tecnocêntricos da liberação de gases da biomassa. Realiza uma rigorosa metanálise de várias estratégias empregadas para a prevenção e mitigação da liberação de gases. O capítulo explora o impacto específico e a natureza das práticas e técnicas utilizadas, como ventilação, secagem, pré-tratamento termoquímico (por exemplo, torrefação e explosão a vapor), ozonização, extração com fluido supercrítico e adição de antioxidantes. Para garantir rigor metodológico, o capítulo utiliza abordagens estatísticas como análise de curva de densidade, análise de modelo de efeito misto linear e análise fatorial bayesiana. Também incorpora a utilização da transformação logarítmica natural de dados bibliométricos complexos e análise de funil para avaliar robustamente o viés de publicação. Através desta análise abrangente, o Capítulo II fornece uma compreensão profunda da eficácia de vários métodos no controle das emissões de monóxido de carbono (CO), dióxido de carbono (CO_2), metano (CH_4) e compostos orgânicos voláteis (COVs). O Capítulo III apresenta pesquisa original realizada pelo autor. Concentra-se na seleção de resíduos agrícolas, especificamente cascas de amendoim, grãos de café usados e folhas de cana-de-açúcar, como biorresíduos para o desenvolvimento de extratos antioxidantes biogênicos destinados a controlar a liberação de gases em pellets de madeira. O capítulo destaca o potencial desses materiais naturais na redução das emissões de CO_2 e no aprimoramento da reatividade e estabilidade do material por meio de suas capacidades e funcionalidades antioxidantes. A pesquisa realizada neste capítulo demonstra abordagens inovadoras para o controle da liberação de gases na produção de energia de biomassa e destaca o valor do uso de biorresíduos como soluções sustentáveis. O Capítulo IV se beneficia dos resultados dos capítulos anteriores e oferece uma análise aprofundada dos grãos de café usados como meio de controle de gases que não o CO_2 na liberação de gases da biomassa. O capítulo examina a eficácia dos grãos de café usados no controle de emissões de gases como CO, CH_4 e COVs em diversas condições atmosféricas. Investiga o impacto de doses adicionais variadas e temperaturas ambientais na atividade e controle da liberação de gases. Além disso, o capítulo caracteriza extensivamente a utilização de grãos de café usados como substitutos na composição de pellets de biomassa. Avalia seu potencial para minimizar a formação de incrustações e escórias nos equipamentos de conversão de biomassa, otimizando a eficiência da combustão. No Capítulo V, resumimos a importância e as implicações de nossa pesquisa original sobre antioxidantes biogênicos para a sociedade, o meio ambiente e a economia. Destacamos a importância de nossas descobertas no avanço do controle da liberação de gases, no desenvolvimento sustentável de energia e na gestão de resíduos na agricultura, ao mesmo tempo em que exploramos oportunidades econômicas potenciais para a indústria de valorização de resíduos, produtos de valor agregado e expansão de mercado. Além disso, aprofundamos os benefícios sociais e ambientais, incluindo redução de impactos, gestão de recursos, promoção da economia circular, bem-estar das pessoas e práticas agrícolas sustentáveis. Ao elucidar esses aspectos, pretendemos contribuir para a discussão acadêmica em torno do tema e fornecer uma compreensão abrangente das implicações mais amplas de nossa pesquisa.

Palavras-chave: biomassa de madeira para combustível sólido, compostos orgânicos voláteis, desenvolvimento sustentável de energia, monóxido de carbono, resíduo agrícola.

VALORIZING BY-PRODUCTS FROM CROP HARVESTING INTO ANTIOXIDANTS TO CONTROL PELLET OFF-GASSING

ABSTRACT – The dissertation encompasses the chapters I, II, III, IV, and V, with the objective of examining the phenomenon of off-gassing and its social, environmental, and economic implications for sustainable development. They contribute insights to enhance the understanding and management of this critical issue, providing actionable knowledge for stakeholders such as policymakers, producers, and researchers, ultimately driving progress in occupational safety, human health, industrial hygiene, and environmental protection within solid biofuel value chains. Chapter I serves as a comprehensive and in-depth introduction to the dissertation. It goes beyond a superficial overview and provides a rigorous examination of the phenomenon of biomass off-gassing and its implications for sustainable energy development. The chapter critically reviews existing literature, explores preventive and mitigatory practices and techniques related to off-gassing, and delves into the social, environmental, and economic dimensions associated with biomass off-gassing, emphasizing its significance within the global solid biofuel industry. Moreover, the chapter investigates off-gassing scenarios in residential, commercial, and industrial settings, analyzing the potential risks and implications involved. It highlights the crucial role of education, training, and the dissemination of scientific information in preventing or mitigating the autogenous generation of toxic chemicals. Chapter II focuses on the technocentric aspects of biomass off-gassing. It conducts a rigorous meta-analysis of various strategies employed for the prevention and mitigation of off-gassing. The chapter explores the specific impact and nature of practices and techniques utilized, such as ventilation, drying, thermochemical pretreatment (e.g., torrefaction and steam explosion), ozonation, supercritical fluid extraction, and antioxidant addition. To ensure methodological rigor, the chapter employs statistical approaches such as density curve analysis, linear mixed-effect model analysis, and Bayesian factor analysis. It also incorporates the utilization of the natural logarithm transformation of intricate bibliometric data and funnel plot analysis to robustly assess publication bias. Through this comprehensive analysis, Chapter II provides a profound understanding of the efficacy of various methods in controlling emissions of carbon monoxide (CO), carbon dioxide (CO_2), methane (CH_4), and volatile organic compounds (VOCs). Chapter III presents original research conducted by the author. It focuses on the selection of agricultural residues, specifically peanut shells, spent coffee grains, and sugarcane leaves, as bioresources for the development of biogenic antioxidant extracts aimed at controlling off-gassing in wood pellets. The chapter showcases the potential of these natural materials in reducing CO_2 emissions and enhancing the reactivity and stability of the material through their antioxidant capabilities and functionalities. The research conducted in this chapter demonstrates innovative approaches to off-gassing control in biomass energy production and highlights the value of utilizing bioresources as sustainable solutions. Chapter IV benefits from the findings of the previous chapters and offers an in-depth analysis of spent coffee grains as a means of controlling gases other than CO_2 in biomass off-gassing. The chapter examines the effectiveness of spent coffee grains in controlling emissions of gases such as CO, CH4, and VOCs under various atmospheric conditions. It investigates the impact of varying additive doses and environmental temperatures on off-gassing activity and control. Additionally, the chapter extensively characterizes the utilization of spent coffee grains as substitutes within the composition of biomass pellets. It evaluates their potential to minimize fouling and slagging formation within biomass conversion equipment while optimizing combustion efficiency. In Chapter V, we summarize the significance and implications of our original research on biogenic antioxidants for society, the environment, and the economy. We highlight the importance of our findings in advancing off-gassing control, sustainable energy development, and waste management in agriculture, while exploring potential economic opportunities for the waste valorization industry, value-added products, and market expansion. Additionally, we delve into the social and environmental benefits, including impact reduction, resource management, circular economy promotion, people's well-being, and sustainable agricultural practices. By elucidating these aspects, we aim to contribute to the scholarly discussion surrounding the topic and provide a comprehensive understanding of the broader implications of our research.

Keywords: agricultural residue, carbon monoxide, sustainable energy development, volatile organic compounds, wood biomass-to-solid fuel.

CHAPTER I – General Considerations

Chapter I is under review as a systematic paper titled 'Fuel-Flexible Biomass Off-Gassing: A Critical Review of Practices and Technologies for Mitigatory Control' for potential inclusion in the Journal of Cleaner Production (Manuscript number: JCLEPRO-D-23-18195; date of submission: July 2nd, 2023). Consequently, the forthcoming text strictly conforms to the formatting and structural guidelines set forth by this esteemed journal.

Highlights

The solid biofuel industry plays a vital role in sustainable development and clean energy solutions.

Inadequate storage and handling of biomass leads to the release of toxic gases, posing occupational and health risks.

Drying, grinding, and carbonization techniques improve biofuel stability by removing oxidizable compounds.

Pelletizing improves product's durability and reduces the generation of fine particles, minimizing off-gassing potential.

Ventilation, filtration, and effective combustion equipment management help control off-gassing risks.

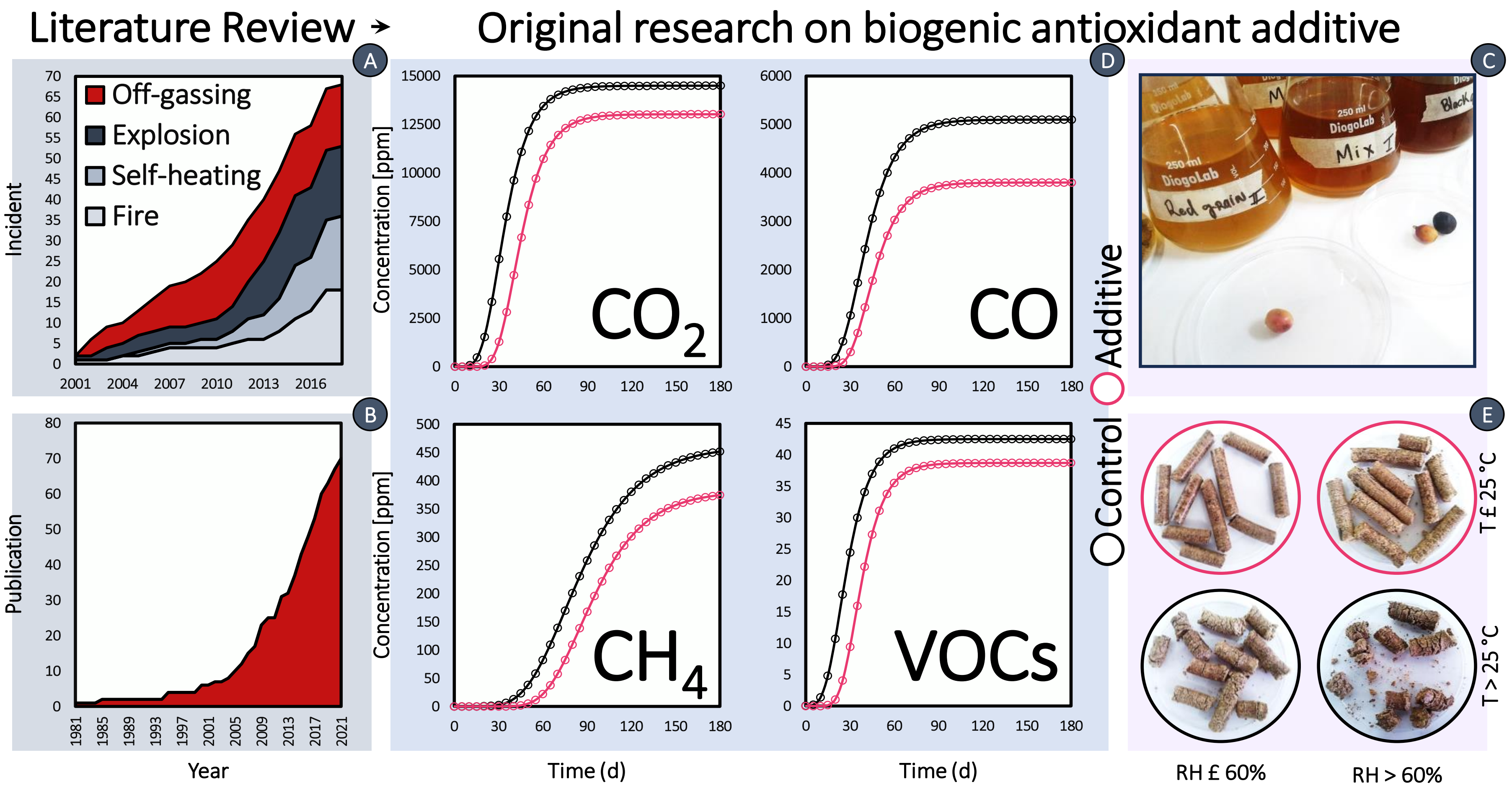
Early detection and alarming systems are valuable for prompt identification.

Abstract

Energy biomass plays a pivotal role in the global bioeconomy, offering a disruptive and sustainable solution for clean and affordable biofuels while mitigating climate change. However, improper handling of biomass-to-solid (BTS) fuels poses significant risks to occupational safety and human health. Storing BTs fuels without proper ventilation intensifies off-gassing, leading to the concentration of toxic gases such as carbon monoxide (CO), carbon dioxide (CO2), methane (CH4), and volatile organic compounds (VOCs). Exposure to these fast-acting toxic chemicals can result in accidents and adverse health effects. To address this issue, a comprehensive review was conducted, analyzing practices to control off-gassing in the solid biofuel industry. Pre-production strategies, such as drying, grinding, and carbonization, are found to improve the stability of the final product by removing oxidizable compounds. During production, pelletizing enhances the durability of the biofuels and reduces the generation of fine particles. Post-production solutions involve the implementation of ventilation, filtration, and combustion equipment management, as well as early detection systems. These measures collectively contribute to protecting occupational safety, human health, and the environment, thereby fostering sustainable energy development. In conclusion, energy biomass presents an essential component of the global bioeconomy, providing a disruptive and sustainable solution for clean biofuels while addressing climate change. However, careful handling and management of biomass-to-solid fuels are crucial to avoid off-gassing risks. The review's insights into controlling off-gassing offer valuable guidelines for the solid biofuel industry to ensure occupational safety, human health, and environmental protection while advancing sustainable energy development.

Keywords: carbon monoxide; occupational safety; oxidation; reactive oxygen species; volatile organic compounds; wood pellets.

Graphical Review



1. Introduction

Biomass is a renewable and sustainable energy source with significant societal, environmental, and economic impacts (**Tab 1**) (Gunnarsdottir et al., 2021). Its utilization offers diverse benefits, including enhancing energy security, promoting rural development (Sharma et al., 2016), and providing equitable energy access (Smith et al., 2022). By offering a reliable energy resource, biomass reduces dependence on fossil fuels, enhancing energy resilience. Moreover, it creates employment opportunities, improves living standards, and curtails rural-urban migration (Yu et al., 2022).

Environmentally, biomass plays a crucial role in climate change mitigation (Narnaware and Panwar, 2022), waste management (Srivastava and Mishra, 2022), and biodiversity preservation (Pierrehumbert, 2022). It is considered carbon-neutral since the carbon dioxide emitted during combustion is offset by the carbon dioxide absorbed during plant growth (Narnaware and Panwar, 2022), reducing greenhouse gas emissions. Additionally, biomass manages organic waste materials, leading to decreased methane emissions and waste reduction (Srivastava and Mishra, 2022). Sustainable biomass production practices, such as reforestation and agroforestry, also enhance biodiversity, restore habitats, safeguard soil health, and create ecological corridors (Pierrehumbert, 2022).

Economically, biomass energy fosters job creation, stabilizes energy costs (Bragg-Sitton et al., 2020), and stimulates economic growth (Bui et al., 2021). Throughout the value chain, biomass generates employment opportunities, contributing to local and national economies (Gunnarsdottir et al., 2021). As an alternative to fossil fuels, biomass reduces price volatility and stabilizes energy costs (Bragg-Sitton et al., 2020). Moreover, it attracts investments in research, development, and infrastructure, opening new markets and export opportunities for biomass-derived products (Bui et al., 2021). Biomass thus offers a sustainable solution for energy security, climate change, waste management, rural development, and economic growth while promoting sustainable practices and minimizing environmental impacts.

Tab 1. Synthesis of pros and cons of energy biomass for society, the environment, and the economy

Pros	Description
Energy Security	Biomass offers a sustainable and renewable energy source, reducing reliance on fossil fuels. This enhances energy security by diversifying the energy mix and decreasing vulnerability to fluctuations in fossil fuel prices and availability
Rural Development	Biomass production can have significant positive impacts on rural communities. It creates employment opportunities in various sectors such as agriculture, forestry, and bioenergy industries. This leads to improved livelihoods, higher income levels, and reduced rural-urban migration, contributing to rural development and socio-economic progress
Equitable Energy Access	Biomass can be produced locally, making it a valuable energy source for remote or underdeveloped areas that lack access to traditional energy infrastructure. By utilizing biomass resources, these communities can have access to affordable and sustainable energy, empowering them to improve their living conditions and foster economic growth
Climate Change Mitigation	Biomass is considered carbon-neutral as the carbon dioxide emitted during its combustion is offset by the carbon dioxide absorbed during plant growth. By using biomass as an alternative to fossil fuels, greenhouse gas emissions can be reduced, thus mitigating climate change and promoting a more sustainable future
Waste Management	Biomass utilization provides an effective solution for managing organic waste materials. By utilizing agricultural residues, forest residues, or food waste as biomass feedstock, these materials are diverted from landfills, reducing methane emissions and minimizing the environmental impact of waste disposal
Biodiversity Preservation	Sustainable biomass production practices, such as reforestation and agroforestry, can have positive impacts on biodiversity. These practices promote habitat restoration, protect soil health, and create ecological corridors, enhancing ecosystem resilience and conserving biodiversity
Job Creation	Biomass energy production requires a range of activities, including biomass cultivation, harvesting, transportation, and conversion processes. This generates employment opportunities throughout the biomass value chain, supporting local and national economies and contributing to job creation
Energy Cost Stabilization	Biomass resources, such as agricultural and forestry residues, can be utilized locally, reducing dependence on imported fossil fuels. By utilizing locally available biomass feedstock, communities and industries can stabilize energy costs, minimizing the impact of price fluctuations in the global energy market
Economic Growth	The biomass sector attracts investments in research and development, technological innovations, and infrastructure development. This fosters economic growth by creating new markets and export opportunities for biomass-derived products. Additionally, biomass production contributes to the growth of related industries, such as equipment manufacturing and biomass supply chains
Cons	
Feedstock Availability	Biomass feedstock availability may be limited and subject to competition with other uses, such as food production or animal feed. This can create challenges in securing a reliable and sustainable supply of biomass, especially in regions where there is high competition for land resources
Land and Water Use	Scaling up biomass production requires significant land and water resources. If not managed sustainably, this expansion can lead to land-use conflicts, deforestation, loss of natural habitats, and depletion of water resources. Balancing the demand for biomass with the need to protect ecosystems and ensure sustainable land use is a critical consideration
Net Carbon Emission	While biomass is considered a renewable energy source, the overall sustainability of biomass utilization depends on various factors. The transportation, processing, and conversion of biomass feedstock can result in net carbon emissions and environmental impacts, including deforestation for feedstock cultivation and emissions from biomass combustion. Careful consideration of feedstock selection, cultivation practices, and energy conversion efficiency is necessary to ensure the environmental benefits of biomass utilization outweigh any potential drawbacks
Technology and Infrastructure	Biomass utilization often requires specialized technologies and infrastructure for efficient conversion and utilization. Establishing and maintaining such infrastructure can involve significant investments and ongoing operational costs. This includes the development of biomass power plants, biomass processing facilities, and transportation systems. Upgrading or retrofitting existing energy infrastructure to accommodate biomass integration may also pose challenges and incur additional expenses
Off-gassing	Indoor facilities, such as biomass heating systems or cooking stoves, pose a particular concern as poor ventilation or inadequate combustion conditions can lead to the release of harmful substances. Carbon monoxide (CO), a colorless and odorless gas, is highly toxic when inhaled, and certain volatile organic compounds (VOCs) present in biomass combustion emissions, such as benzene and formaldehyde, can cause respiratory irritation and long-term health effects. Ensuring proper ventilation, maintenance of biomass combustion systems, and adherence to safety guidelines are crucial to mitigate the risk of automatic release of toxic chemicals and protect human health

Nonetheless, addressing challenges associated with biomass utilization is crucial. These challenges include feedstock availability and competition concerns (Barry et al., 2022), impacts on land and water use (Kumar et al., 2022), net carbon emissions, sustainability considerations (Christoforou and Fokaides, 2019), technology and infrastructure requirements, particulate matter emissions (Xu et al., 2021), and the release of toxic chemicals (Alakoski et al., 2016). Ensuring safety, minimizing environmental impacts, and optimizing the benefits of biomass utilization require careful feedstock selection, sustainable practices, adherence to emissions regulations, technological advancements, and proper handling.

2. Materials and Methods

Our review provides a rigorous and systematic analysis of the existing literature on preventing and mitigating off-gassing from biomass-to-solid (BTS) fuels, with a specific focus on wood pellets. The review process was conducted using a collaborative approach, engaging expert reviewers to enhance the quality and comprehensiveness of the analysis. To ensure credibility and reliability, we conducted a thorough search for scholarly sources in reputable databases. Our inclusion criteria focused on papers discussing practices and techniques for controlling off-gassing and emissions of toxic chemicals such as carbon monoxide (CO), carbon dioxide (CO_2), methane (CH_4), nitrous oxides (NO_x), sulfur oxides (SO_x), and volatile organic compounds (VOCs). The selected papers were critically evaluated, considering their technical capabilities, advantages, and limitations, particularly in residential and industrial contexts. The review encompasses a wide range of relevant literature, ensuring a comprehensive and in-depth analysis of the topic. To enhance readability and facilitate information retrieval, we employed visual aids such as tables. These aids help present the information in a clear and organized manner.

3. Results and Discussion

3.1. The Phenomenon of Biomass Off-Gassing: Significance and Implications for Occupational Safety and Human Health

Biomass off-gassing is a significant concern during decomposition or combustion processes of biomass materials (Sheng and Yao, 2022). This release of gases has environmental and safety implications, observed in various biomass-related processes like anaerobic digestion, composting, gasification, and biomass combustion. Anaerobic digestion produces biogas through off-gassing, while composting emits gases like CO_2 and methane (Kunatsa and Xia, 2022). Gasification generates syngas, and biomass combustion releases gases such as CO_2, CO, NO_x, SO_x, VOCs, and particulate matter (Sheng and Yao, 2022).

Off-gassing can have positive implications when utilized as renewable energy sources in processes like anaerobic digestion and gasification (Ren et al., 2020). However, during biomass combustion and storage (**Tab 2**), it contributes to air pollution, climate change, and health impacts (Gauthier et al., 2012). Minimizing off-gassing is crucial to reduce the environmental footprint of the solid biofuel industry and maintain fuel's quality and efficiency (Pecha et al., 2021).

Occupational safety risks arise from the hazardous nature of certain released gases (Gauthier et al., 2012). To mitigate health and safety risks, proper handling, storage, and transportation practices are necessary. Regulations and emission limits govern off-gassing, requiring solid biofuel producers and suppliers to comply. Responsible management and emission reduction measures not only mitigate risks but also enhance the reputation and marketability of solid biofuels (Gauthier et al., 2012).

Tab 2. Summary of the off-gassing potential of biomass-to-solid fuels

Source	Description
Pellets	Pellets are manufactured through a process that involves compressing biomass feedstock under high pressure. This compression results in a denser and more uniform fuel with low moisture content. The low moisture content of pellets contributes to efficient combustion, as moisture can hinder the release of energy and increase emissions. Additionally, the uniform size and shape of pellets allow for consistent airflow and combustion in pellet stoves, boilers, and power plants. When burned in modern, well-designed pellet combustion systems, pellets generally have low off-gassing potential, as they can achieve high combustion efficiency and minimize emissions
Briquettes	Briquettes are similar to pellets in terms of their production process and characteristics. They are compressed solid fuel blocks made from biomass materials. Like pellets, briquettes have low moisture content and high energy density, leading to efficient combustion. The compact and uniform nature of briquettes allows for consistent combustion, resulting in reduced off-gassing potential. However, the specific composition and production methods used for briquettes can vary, which can affect their combustion properties and emissions. It is important to ensure that briquettes are produced from high-quality biomass feedstock and with appropriate binding agents to minimize off-gassing during combustion
Wood chips	Wood chips are larger pieces of wood typically derived from forestry residues, logging by-products, or wood processing waste. They have higher moisture content compared to pellets and briquettes, which can affect their combustion efficiency and off-gassing potential. The combustion of wood chips requires specialized combustion systems designed to handle their larger size and higher moisture content. When properly burned in well-designed wood chip combustion systems, efficient combustion can be achieved, reducing emissions and off-gassing. However, inadequate drying or combustion in inefficient appliances can lead to incomplete combustion, resulting in higher emissions and increased off-gassing potential
Wood logs	Wood logs are the most traditional and commonly used form of solid biofuel. They have higher moisture content and lower energy density compared to pellets, briquettes, and wood chips. The combustion of wood logs can result in higher emissions and increased off-gassing potential if burned in inefficient or poorly maintained appliances. Proper seasoning and drying of wood logs before burning are crucial to reduce moisture content and improve combustion efficiency. Inefficient combustion, such as incomplete burning or smoldering, can lead to the release of pollutants and increased off-gassing potential. It is essential to ensure proper ventilation, appliance design, and maintenance when using wood logs for combustion
Energy crops	Energy crops, such as switchgrass, miscanthus, or fast-growing trees, are cultivated specifically for their use as biomass feedstock in bioenergy production. The off-gassing potential of energy crops can vary depending on the specific crop, cultivation practices, and processing methods. Energy crops cultivated for solid biofuel production are typically harvested at optimal times to ensure low moisture content and high energy yield. When sustainably managed and used in well-designed combustion systems, energy crops can contribute to low emissions and reduced off-gassing potential. However, it is crucial to consider the environmental impacts and land-use implications associated with large-scale cultivation of energy crops
Agricultural residues	Agricultural residues, such as crop straws, husks, stalks, and shells, are by-products of agricultural activities. Their off-gassing potential depends on factors such as crop type, moisture content, storage conditions, and combustion technology used. Agricultural residues often have higher moisture content compared to pellets and briquettes, which can impact combustion efficiency. Proper pre-processing, such as drying or pelletizing, can help reduce moisture content and improve combustion efficiency, thereby reducing off-gassing potential. The specific composition of agricultural residues can also affect their combustion properties and emissions. For example, some crop residues may contain higher levels of silica or alkali metals, which can influence ash formation and emissions during combustion. Proper handling and storage of agricultural residues are important to prevent excessive moisture absorption or decomposition, which can lead to increased off-gassing potential
Municipal solid waste	Municipal solid waste is a complex mixture of various organic and inorganic materials, including food waste, paper, plastics, and other household and commercial waste. The off-gassing potential of MSW can be influenced by factors such as waste composition, sorting, treatment methods, and combustion technologies employed. Advanced waste-to-energy processes, such as incineration with energy recovery or anaerobic digestion, can help reduce off-gassing potential by maximizing energy conversion efficiency and minimizing the release of harmful pollutants. These processes involve controlled combustion or biochemical decomposition of MSW, resulting in energy generation while reducing the volume of waste that needs to be landfilled. Proper waste sorting and treatment, such as removing hazardous materials or recyclables, are crucial to minimize the off-gassing potential of MSW during combustion or digestion processes

3.1.1. Carbon Monoxide (CO)

Carbon monoxide (CO) is a toxic gas resulting from incomplete combustion of carbon fuels, posing severe health risks, including headaches, loss of consciousness, and even fatality (Guo et al., 2022). Prolonged exposure can lead to cardiovascular and neurological disorders (**Tab 3**).

CO accumulation is primarily attributed to poorly maintained fuel-burning appliances and inadequate ventilation (Svedberg and Johanson, 2017). To mitigate risks, preventive measures should be taken. Adequate ventilation ensures proper airflow, reducing CO buildup (Gauthier et al., 2012). Regular maintenance of fuel-burning appliances is crucial to prevent leaks or malfunctions that may produce CO. Educating individuals about CO dangers and promoting safe practices is vital (Lehna et al., 2017).

Early detection is crucial for safety (Fernandez-Anez et al., 2021). CO detectors serve as an early warning system, alerting occupants to dangerous levels of the gas. Prompt response to CO alarms includes evacuating, opening windows for ventilation, and contacting emergency services. Immediate medical attention for CO poisoning symptoms is essential to protect health.

Tab 3. Summary of significance and implications of fast-acting toxic chemicals for occupational safety and health

Gas	Description
CO	Acute exposure can lead to symptoms such as headaches, dizziness, and in severe cases, loss of consciousness and death. Safety measures include proper ventilation and CO detectors
CO_2	Not directly toxic, but high concentrations can lead to oxygen deprivation. Excessive CO_2 emissions contribute to climate change and global warming
CH_4	Direct exposure does not pose significant risks, but methane contributes to climate change
NO_x	Contributes to air pollution, smog formation, and respiratory health issues. Safety measures include optimizing air-fuel ratios, controlling combustion temperatures, and effective emission control measures.
SO_x	Contributes to air pollution. Exposure can cause respiratory irritation. Safety measures include emission control measures, using low-sulfur biomass or fuel, and proper combustion techniques.
VOCs	Wide range of organic chemicals released from biomass. Can cause diverse health effects depending on the specific compounds involved. Safety measures include proper storage, handling, and combustion practices, implementing ventilation systems, using low-VOC materials, and employing control measures to remove VOCs from exhaust gases.

3.1.2. Carbon Dioxide (CO_2)

Excessive concentrations of CO_2 can pose significant risks to occupational safety and human health, primarily due to the potential displacement of oxygen in confined spaces, jeopardizing workers' well-being (Shaffer et al., 2009). Monitoring CO_2 levels and ensuring proper ventilation are crucial preventive measures.

In addition to the direct impact on oxygen levels, elevated CO_2 concentrations can adversely affect respiratory function, leading to symptoms like breathlessness and headaches. These health effects are particularly pronounced in indoor spaces with limited ventilation, where CO_2 levels can increase, compromising air quality and cognitive function (Jacobson et al., 2019).

To address these risks, occupational health regulations establish exposure limits for CO_2. Employers are required to monitor CO_2 levels in the workplace (Fernandez-Anez et al., 2021), implement ventilation (Emhofer et al., 2015), provide comprehensive employee training, and supply appropriate PPE to ensure their safety (Gauthier et al., 2012; Lehna et al., 2017). Compliance with these regulations is essential for creating a secure working environment and safeguarding the health of workers.

3.1.3. Methane (CH_4)

Methane, a flammable gas commonly found in natural gas, poses significant occupational safety and health risks (Rezaei et al., 2021). Ensuring the well-being of workers in environments where methane is present requires taking necessary precautions.

Continuous monitoring of methane levels is essential, and gas detection systems can provide early warnings in case of leaks or accumulation. Preventing fires or explosions involves eliminating potential ignition sources. Adequate ventilation systems help maintain safe air quality and reduce methane concentration. Proper storage practices are crucial to minimize the risk of leaks or releases (Alakoski et al., 2016).

Methane's ability to displace oxygen in confined spaces is a specific hazard, leading to potential asphyxiation. Thorough risk assessments, especially in environments with other hazardous substances, should be conducted to mitigate these risks. Implementing safety measures, such as ventilation systems and gas detection, is vital in such scenarios (Svedberg and Johanson, 2017).

Comprehensive training on methane safety protocols is essential for personnel in methane-prone environments (Lehna et al., 2017). This includes knowledge of proper handling, emergency procedures, and the use of personal protective equipment. Compliance with occupational health and safety regulations is paramount, and regular equipment maintenance is necessary for proper functioning. Adherence to safety procedures and protocols is crucial for maintaining a safe work environment.

3.1.4. Nitrogen Oxides

Nitrous oxides, including nitric oxide (NO) and nitrogen dioxide (NO_2), have significant implications for occupational safety, human health, and the environment. Elevated NO_x levels can cause respiratory irritation, coughing, and wheezing, particularly in industries involving combustion processes or the use of nitrogen-based chemicals (Asghar et al., 2021). Prolonged exposure increases the risk of developing occupational asthma and other respiratory conditions.

Moreover, NO_x contributes to air pollution, smog, and ground-level ozone formation, exacerbating respiratory illnesses and affecting human health. Nitrogen dioxide, a component of NO_x, harms the respiratory system and impairs lung function (Bilsback et al., 2020). Additionally, NO_x emissions have environmental consequences, contributing to acid rain that damages ecosystems and infrastructure (Amoatey et al., 2019; Menezes and Popowicz, 2022). Nitrous oxide (N_2O) is a potent greenhouse gas contributing to global warming and climate change (Desantes et al., 2020).

To mitigate NO_x risks, several measures can be implemented. Engineering controls and ventilation systems can minimize NO_x exposure in workplaces. Cleaner technologies and fuels can reduce NO_x emissions during combustion processes (Moreira et al., 2021). Regular air monitoring helps identify and address high NO_x levels, and personal protective equipment can protect workers from exposure. Moreover, emission controls and environmental regulations play a crucial role in limiting NO_x emissions from industrial processes, mitigating their negative impacts on human health and the environment (Alves et al., 2020).

3.1.5. Sulfur Oxides

Sulfur oxides, particularly sulfur dioxide (SO_2), have significant implications for occupational safety, human health, and the environment. Exposure to SO_x can lead to respiratory irritation, exacerbating pre-existing respiratory conditions (Amoatey et al., 2019; Bilsback et al., 2020).

Sulfur oxides emissions contribute to environmental issues such as acid rain, air pollution, particulate matter, and smog (Menezes and Popowicz, 2022). These pollutants have detrimental effects on air quality and human health, leading to respiratory illnesses (Amoatey et al., 2019; Bilsback et al., 2020).

To mitigate SO_x risks, several measures can be implemented. Emission controls can limit the release of SO_x into the atmosphere by employing technologies that capture or remove sulfur compounds during combustion processes. The use of low-sulfur fuels, such as low-sulfur coal or cleaner energy sources, can reduce SO_x emissions (El-Sheikh et al., 2020; Jiang et al., 2020).

In the workplace, monitoring SO_x levels is crucial for occupational safety and health. PPE, such as respiratory masks or breathing apparatus, can protect workers from hazardous SO_x exposure (Gauthier et al., 2012; Lehna et al., 2017). Regulations and policies play a vital role in promoting cleaner technologies and reducing SOx emissions. They encourage the adoption of emission controls and low-sulfur fuels, contributing to improved air quality and reduced health risks associated with SO_x.

3.1.6. Volatile Organic Compounds

Volatile organic compounds (VOCs) are chemicals that can evaporate and contribute to indoor and outdoor air pollution. Elevated VOC levels pose risks to occupational safety and human health, particularly for workers in industries like painting and chemical manufacturing (Borén et al., 2018, 2017).

Inhaling VOC fumes can cause respiratory irritation, headaches, nausea, and acute toxicity. Prolonged exposure increases the risk of developing chronic health conditions, including respiratory disorders and cancer. VOCs can also trigger asthma attacks and worsen existing respiratory conditions (Poole and Basu, 2017; Xu et al., 2021).

Moreover, VOCs degrade indoor air quality, leading to sick building syndrome with symptoms such as headaches, fatigue, and eye, nose, and throat irritation (Nakaoka et al., 2014; Shim et al., 2023). Additionally, VOCs contribute to outdoor air pollution, contributing to smog formation and environmental issues (Turner et al., 2020).

To mitigate VOC exposure risks, several measures can be implemented. Engineering controls, such as ventilation and local exhaust systems, limit VOC release and concentration in the workplace (Emhofer et al., 2015). The use of low-VOC materials, including adhesives, can significantly reduce VOC emissions. Proper storage and handling of VOC-containing substances are essential in preventing accidental releases and exposure (Svedberg et al., 2008).

Raising awareness among workers about VOC hazards is crucial (Lehna et al., 2017). Providing education on safe handling practices, promoting the use of personal protective equipment, and encouraging proper ventilation in work areas with VOCs are important preventive measures.

3.1.7. Specifications and Regulatory Frameworks

In major solid biofuel markets like Europe and North America, biomass off-gassing control is governed by specific regulations and specifications that prioritize safe and environmentally responsible biomass utilization. These regulations ensure compliance with stringent requirements and promote sustainable practices.

In Europe, the Renewable Energy Directive (RED) (Long et al., 2021) and the Industrial Emissions Directive (IED) (Romero-Castro et al., 2022) play crucial roles in promoting sustainable biomass use. The RED establishes sustainability criteria for biofuels, emphasizing greenhouse gas emissions reduction and the use of certified sustainable biomass. The IED focuses on emissions control, setting limits for air and water emissions from industrial installations, including biomass facilities. Additionally, certification schemes like the Sustainable Biomass Program (SBP) (Kashanian et al., 2020) and the Forest Stewardship Council (FSC) (Schepers, 2010) ensure responsible sourcing of biomass. These schemes verify and certify sustainably sourced biomass materials, considering factors like forest management practices and biodiversity protection. In North America, regulations from organizations such as the Occupational

Safety and Health Administration (OSHA) and the Environmental Protection Agency (EPA) address off-gassing control (Hoppin and Jacobs, 2013). These regulations provide guidelines for handling, storage, and emission control to safeguard worker safety and environmental protection.

Importantly, these specifications and regulatory frameworks are periodically updated to reflect advancements in knowledge, technology, and best practices. This continuous evolution ensures the biomass industry operates safely and sustainably. Compliance with these regulations and responsible biomass sourcing and utilization are essential for biomass facilities to contribute effectively to renewable energy goals while minimizing the negative impacts of off-gassing.

3.2. Determinant Factors of Off-Gassing

3.2.1 Type of Biomass

The chemical composition of biomass significantly influences the emission of VOCs throughout its life cycle. Distinct biomass sources, such as wood, agricultural residues, and energy crops, have distinct chemical profiles, leading to variations in VOC emissions (Soto-Garcia et al., 2015). Wood biomass contains terpenes found in wood resin, while agricultural residues and energy crops may have their own unique volatile compounds (Soto-Garcia et al., 2015). Moisture content also affects VOC release, with high moisture content promoting microbial activity and VOC production. Storage conditions, including ventilation, temperature, and duration, play a crucial role in off-gassing potential. Processing techniques like drying and pelletizing can alter biomass properties and increase VOC emissions (Narron et al., 2020). Combustion of biomass for heating purposes can release VOCs, affecting indoor air quality. Proper burning conditions and ventilation are necessary to minimize VOC emissions and ensure safe indoor environments (Moreira et al., 2021).

3.2.2. Moisture Content

Excessive moisture in biomass facilitates off-gassing through microbial decomposition and fermentation (**Tab 4**), leading to the release of VOCs, such as alcohols and organic acids (He et al., 2020; Granström and Javeed, 2016). Poor ventilation worsens off-gassing risks related to moisture. High moisture content in biomass hinders combustion efficiency, requiring extra energy for evaporation, increasing the chances of incomplete combustion and pollutant generation (He et al., 2020; Paris et al., 2022). Proper moisture management during biomass storage is crucial to mitigate off-gassing, prevent microbial growth, and minimize mold or mildew formation. Ensuring adequate drying and storage practices helps prevent excessive moisture and mitigates off-gassing risks (Granström and Javeed, 2016).

3.2.3. Lignocellulose

Lignin, cellulose, and hemicellulose are crucial components of biomass with implications for off-gassing. Lignin, a complex polymer, provides structural integrity to cell walls, particularly in woody biomass (Siwale et al., 2022). During thermal decomposition, lignin releases aromatic compounds such as phenols and guaiacols. It can also serve as a precursor for VOCs like alcohols and organic acids (Borén et al., 2018). Additionally, cellulose, abundant in plant cell walls, can undergo enzymatic hydrolysis, leading to VOC production during microbial fermentation. Breakdown products of cellulose, including furans and aldehydes, contribute to off-gassing (Borén et al., 2018). Similarly, hemicellulose, a polysaccharide, easily degrades, producing VOCs like alcohols and organic acids (Borén et al., 2018, 2017). Understanding these components aids biomass utilization optimization, efficient energy conversion, and emission control strategies.

3.2.4. Extractives

Extractives in biomass are non-structural compounds that can be extracted using solvents, such as oils, waxes, resins, and tannins (Attard et al., 2016). They play a significant role in biomass off-gassing. During combustion, extractives can impact pollutant emissions, including particulate matter, NO_x, and SO_2. Their composition influences pollutant levels and characteristics. Some extractives have catalytic or inhibitory effects on pollutant formation, while others affect energy conversion efficiency. Volatile organic compounds released from extractives during off-gassing or combustion contribute to air pollution, including smog, ozone, and particulate matter formation (Svedberg et al., 2008). The health effects depend on VOC composition and concentration. Proper management of biomass, including storage, drying, and combustion practices, is crucial to mitigate off-gassing and reduce environmental and health impacts. Understanding extractives is essential for assessing off-gassing risks, implementing emission control measures, and optimizing biomass utilization (Attard et al., 2016).

3.2.5. Microbial Activity

Microbes play a crucial role in biomass off-gassing, breaking down organic matter and releasing volatile compounds (Sheng and Yao, 2022). They accelerate the decomposition of biomass components like cellulose and hemicellulose, leading to the release of VOCs. The types and quantities of VOCs produced depend on the specific microbes, environmental conditions, and biomass composition. Microbes can also ferment sugars in biomass, generating alcohols, organic acids, and additional VOCs. Moisture content and temperature influence microbial activity, with higher moisture promoting increased off-gassing. Proper moisture control, ventilation, and monitoring are essential for mitigating off-gassing risks and minimizing VOC emissions (Huang et al., 2023). Understanding and managing microbial activity is crucial for safe biomass utilization and addressing health and environmental concerns.

Tab 4. Summary of significance and implications of biomass' components for off-gassing

Component	Description
Moisture Content	Influenced by environmental conditions like humidity, temperature, and storage. Higher moisture content in biomass leads to increased microbial activity and off-gassing. Fluctuations in conditions can quickly impact moisture content and trigger off-gassing
Lignocellulose	Includes lignin, cellulose, and hemicellulose. These are stable and less sensitive to environmental changes but can degrade and off-gas in the presence of certain enzymes or microorganisms. Factors like moisture content, temperature, and presence of these enzymes or microorganisms can influence off-gassing
Extractives	These vary in sensitivity based on their chemical composition and properties. Some, like volatile terpenes, can readily off-gas with minor environmental changes. Others may require specific triggers, like high temperatures during combustion, to release VOCs. Their sensitivity can vary widely depending on their chemical nature, concentration, and interactions with other biomass components

3.3. Best Available Practices and Technologies (BAPT) for Preventive and Mitigatory Off-Gassing Control

3.3.1. Drying

Mechanical drying plays a crucial role in controlling biomass off-gassing by reducing moisture content (**Tab 5**), which in turn limits microbial activity and the release of VOCs. Techniques such as hot air drying or kiln drying are effective in lowering the moisture levels of biomass (Arshadi et al., 2009; Manninen et al., 2002).

By reducing moisture content, mechanical drying creates unfavorable conditions for microbial growth, resulting in a decrease in VOC release and an improvement in air quality. Furthermore, it enhances the combustion efficiency of biomass, leading to reduced emissions and improved energy output. Additionally, mechanical drying helps minimize the generation of odors associated with biomass off-gassing. Excess moisture removal mitigates the formation of odor-causing compounds, creating a more pleasant and healthier environment (Arshadi et al., 2009; Manninen et al., 2002).

Standardized drying processes ensure consistency in controlling off-gassing and managing emissions, thereby improving air quality and enhancing safety in biomass operations. These processes establish guidelines and procedures that facilitate effective moisture control and off-gassing mitigation (Arshadi et al., 2009; Manninen et al., 2002).

When selecting and utilizing drying techniques, it is important to consider factors such as biomass type, desired moisture content, scale of operation, and available resources. By integrating mechanical drying into biomass operations, effective moisture control can be achieved, off-gassing can be mitigated, and efficient and sustainable practices can be promoted (Arshadi et al., 2009; Manninen et al., 2002).

Tab 5. Summary of advantages, trade-offs, and challenges of Best Available Practices and Technologies

Practice/Technique	Advantage	Trade-off	Challenge
Drying	Reduces moisture content, minimizes microbial growth and VOC emissions, and improves combustion efficiency	Requires energy input, additional equipment, and careful moisture control	Ensuring effective and efficient drying processes, managing energy consumption
Grinding	Increases surface area for drying, improves combustion efficiency, enhances homogeneous mixing	Requires energy input, specialized equipment, potential for increased dust generation	Proper equipment selection, control of particle size and dust emissions
Carbonization	Converts biomass into charcoal, reduces off-gassing potential, enhances energy density	Requires high temperatures, prolonged processing time, and energy input	Controlling pyrolysis conditions, managing carbonization process and byproducts
Torrefaction	Enhances biomass properties, reduces moisture content and off-gassing potential, improves fuel characteristics	Requires energy input, specialized equipment, and careful temperature control	Achieving optimal torrefaction conditions, managing process parameters and equipment maintenance
Steam explosion	Breaks down biomass structure, improves accessibility for drying and combustion, reduces off-gassing potential	Requires high-pressure steam, specialized equipment, and potential energy consumption	Controlling steam-explosion conditions, managing process safety, and optimizing biomass treatment
Gasification	Converts biomass into syngas, reduces off-gassing potential, enables energy production	Complex process, requires specialized equipment, careful gas cleaning and emissions control	Achieving efficient gasification, minimizing tar and pollutant emissions, optimizing syngas utilization
Ozonation	Oxidizes and degrades volatile compounds, reduces off-gassing and odor	Requires ozone generation equipment, careful control of ozone concentration	Proper ozone dosage, managing ozone byproducts and potential safety hazards
Supercritical Fluid Extraction	Removes volatile compounds and contaminants, reduces off-gassing potential	Requires specialized equipment, high-pressure operation, potential energy consumption	Selecting appropriate extraction solvents, optimizing extraction conditions, managing extraction byproducts
Antioxidant Addition	Inhibits oxidation reactions, reduces off-gassing potential, improves stability	Requires suitable antioxidants, proper dosage, and compatibility with biomass	Selecting appropriate antioxidants, optimizing dosage levels, ensuring long-term stability
Ventilation	Dilutes and disperses off-gassing emissions, reduces pollutant concentration, improves indoor air quality	Requires energy consumption, proper system design and maintenance, potential air distribution challenges	Determining appropriate airflow rates, achieving proper air exchange, optimizing air distribution
Filtration	Captures and removes particulate matter, VOCs, and odorous compounds, improves air quality	Requires filtration systems, regular maintenance, and potential pressure drop	Selecting suitable filters, optimizing filtration efficiency, managing filter replacement and waste disposal
Combustion Equipment	Optimizes combustion efficiency, reduces off-gassing and emissions, enhances energy production	Requires proper equipment maintenance, fuel supply management, and emissions control measures	Ensuring proper combustion conditions, minimizing pollutant emissions, complying with regulatory standards, and managing operational and maintenance practices
Electrostatic Precipitation	Efficiently captures and removes particulate matter, reduces emissions, improves air quality	Requires specialized equipment, periodic cleaning and maintenance, potential for ozone generation	Ensuring proper electrode charging, optimizing collection efficiency, managing system operation and maintenance
Scrubbing	Removes acidic gases, VOCs, and particulate matter, enhances air quality, aids in regulatory compliance	Requires chemical solutions or sorbents, maintenance of scrubbing systems, potential waste disposal challenges	Selecting appropriate scrubbing techniques, optimizing pollutant removal efficiency, managing waste streams and treatment

3.3.2. Grinding

Grinding biomass plays a crucial role in off-gassing control by reducing particle size, which increases the surface area of the biomass material (Ferreira et al., 2020; Gu et al., 2019). This enhanced surface area improves the efficiency of drying processes by facilitating quicker moisture removal. By reducing moisture content more effectively, grinding helps minimize microbial growth and the release of VOCs during storage.

The finer particle size achieved through grinding also has benefits for biomass combustion. It increases the surface-to-volume ratio of the biomass particles, promoting more complete combustion and reducing emissions. The increased surface area allows for better interaction between the biomass and combustion air, leading to improved combustion efficiency and reduced pollutant emissions (Guo et al., 2020; Thieu Trinh et al., 2023; Whittaker and Shield, 2017).

Grinding biomass also contributes to the creation of a homogeneous mixture. This homogeneity ensures consistent drying and off-gassing behavior throughout the biomass material. It facilitates the implementation of effective management strategies for moisture control and off-gassing mitigation. By achieving a uniform particle size distribution, grinding enables more accurate and controlled drying processes, leading to improved air quality and reduced environmental impact (Guo et al., 2020; Thieu Trinh et al., 2023; Whittaker and Shield, 2017).

When selecting equipment and determining operating conditions for grinding biomass, it is essential to consider the specific characteristics of the biomass material. Distinct biomasses may require specific grinding methods and equipment. Care should be taken to avoid excessive energy consumption, material damage, or excessive generation of fine particles during the grinding process. Proper equipment selection and operating conditions ensure efficient grinding while minimizing potential drawbacks (Guo et al., 2020; Thieu Trinh et al., 2023; Whittaker and Shield, 2017).

3.3.3. Carbonization

Carbonization, also known as pyrolysis, is a thermal process that decomposes biomass in the absence of oxygen. This process releases volatile compounds such as water, CO_2, CH_4, and tars (Hu and Gholizadeh, 2019). By limiting complete combustion, carbonization effectively controls off-gassing by reducing the formation and emission of volatile compounds (Hu and Gholizadeh, 2019).

During carbonization, biomass is transformed into stable biochar (Hu and Gholizadeh, 2019). Biochar has a reduced off-gassing potential due to the removal of volatile compounds during the process. It is an inert material, rich in carbon, and resistant to microbial degradation. As a result, biochar minimizes off-gassing during storage, handling, and utilization, contributing to improved safety and environmental performance (Tumuluru et al., 2015).

In addition to off-gassing control, carbonization improves the combustion characteristics of biomass. The resulting biochar has enhanced properties that contribute to more efficient combustion, leading to improved energy conversion and reduced pollutant formation during biomass utilization (Xi et al., 2021). Furthermore, carbonization plays a role in carbon sequestration. By converting biomass into stable biochar, carbonization locks carbon within the charred biomass material. This process contributes to the long-term storage of carbon, effectively sequestering it and reducing carbon dioxide emissions to the atmosphere (Tumuluru et al., 2015; Xi et al., 2021).

3.3.4. Torrefaction

Torrefaction is a thermochemical pre-treatment method that plays a significant role in controlling off-gassing. By subjecting biomass to elevated temperatures in the absence of oxygen, torrefaction effectively reduces the moisture content of biomass, limiting microbial activity and off-gassing (Tumuluru et al., 2015; Xi et al., 2021).

The elevated temperatures used in torrefaction help remove moisture from biomass, resulting in improved air quality and reduced health risks associated with microbial growth. Additionally, torrefaction induces chemical changes in biomass, leading to the degradation of volatile components known for off-gassing. This removal of volatile compounds allows for better control over off-gassing and minimizes the release of odorous substances. Moreover, torrefaction alters the physical properties of biomass, enhancing its stability and ease of handling. The torrefied biomass exhibits improved grindability, reduced hygroscopicity, and increased resistance to biological degradation. These properties contribute to reduced off-gassing potential during storage, handling, and transportation (Tumuluru et al., 2015; Xi et al., 2021).

Torrefaction also has the advantage of reducing emissions of VOCs, odorous compounds, and gases during biomass utilization. The modified chemical composition of torrefied biomass results in improved combustion characteristics, including reduced greenhouse gas emissions and improved combustion efficiency. Torrefied biomass can be directly substituted for conventional biomass in existing combustion systems without requiring significant modifications (Tumuluru et al., 2015; Xi et al., 2021).

By incorporating torrefied biomass, sustainable energy generation can be promoted, as it offers several environmental advantages, including reduced off-gassing potential and improved combustion efficiency. The utilization of torrefied biomass contributes to minimizing the environmental impacts associated with off-gassing from biomass and supports the transition towards a more sustainable and cleaner energy sector.

3.3.5. Steam Explosion

Steam explosion is a thermochemical pre-treatment process that significantly contributes to the control of off-gassing from biomass by reducing moisture content, fragmenting biomass, and weakening lignin, among other effects (Borén et al., 2018, 2017).

During steam explosion, biomass is subjected to high-pressure steam followed by rapid decompression. This process leads to the fragmentation of biomass, resulting in smaller particle sizes (Sarker et al., 2021). The reduction in particle size increases the surface area-to-volume ratio, enhancing drying efficiency and promoting faster moisture evaporation. This limits water availability for microbial activity and reduces the potential for off-gassing during storage and utilization (Borén et al., 2018, 2017).

Steam explosion also weakens lignin, a complex polymer that binds biomass fibers together. By breaking down lignin, steam explosion improves the accessibility of cellulose, another component of biomass. This enhanced accessibility allows for more efficient conversion of cellulose during downstream processes (Sarker et al., 2021).

The process of steam explosion creates cracks and pores within the biomass structure, enhancing porosity. This improved porosity facilitates moisture release and the diffusion of volatile compounds. The enhanced airflow and moisture evaporation resulting from the steam explosion reduce the favorable conditions for microbial activity, further reducing the risks of off-gassing (Borén et al., 2018, 2017).

Additionally, steam explosion reduces biomass recalcitrance, making the biomass more amenable to processing and enhancing downstream conversion processes. The weakened lignin and improved accessibility of cellulose contribute to improved bioconversion efficiency (Borén et al., 2018, 2017).

The parameters of steam explosion, such as steam pressure, duration, and temperature, can be customized to achieve effective pre-treatment for specific biomass types and desired outcomes (Borén et al., 2018, 2017). This flexibility allows for optimization and ensures environmentally sustainable pre-treatment processes tailored to biomass utilization (Borén et al., 2018, 2017).

3.3.6. Gasification

Gasification is a highly controlled biomass conversion process that allows for precise regulation of off-gassing compounds by manipulating various factors such as temperature, residence time, and oxygen availability. Unlike direct combustion, it takes place in a limited oxygen environment, which significantly reduces the formation of VOCs and results in the production of a cleaner fuel gas known as syngas. Syngas is primarily composed of CO, H_2, and CH_4. Due to its lower reactivity and emission potential, syngas is less prone to off-gassing compared to other combustion processes (Akhtar et al., 2018).

Gasification systems can incorporate tar removal mechanisms to address complex organic compounds that may still be present in the gasification process. These tar removal systems help to further reduce off-gassing and ensure the production of cleaner syngas. Additionally, it offers environmental benefits beyond off-gassing control. Furthermore, it minimizes the generation of pollutants such as NO_x, SO_x, and particulate matter. By replacing fossil fuels with biomass-derived syngas, gasification contributes to reducing greenhouse gas emissions and promotes carbon sequestration. This is achieved through the production of stable biochar, a byproduct of gasification that can be utilized for applications such as soil amendment and carbon sequestration (Valizadeh et al., 2022).

3.3.7. Ozonation

Ozonation is a chemical process that is utilized to effectively control off-gassing from biomass by oxidizing VOCs present in the biomass. In the process, ozone (O_3) is employed to react with VOCs, leading to their conversion into simpler compounds or mineralization into CO_2 and water (H_2O). This chemical reaction effectively reduces the concentrations of volatile compounds, resulting in improved air quality (Rahman et al., 2017).

Ozonation also plays a role in eliminating microorganisms present in biomass. By removing these microorganisms, which contribute to off-gassing through their metabolic activities and release of volatile compounds, ozonation helps minimize off-gassing potential. This leads to a reduction in odorous emissions associated with biomass. Furthermore, ozonation promotes the biodegradation of complex organic components within the biomass. This acceleration of biomass breakdown helps to reduce the potential for off-gassing by facilitating the breakdown of volatile compounds and their transformation into simpler forms (Rahman et al., 2017).

One notable environmental benefit of ozonation is that ozone decomposes into oxygen (O_2) molecules without leaving harmful residues or by-products. This makes ozonation an environmentally friendly method for controlling biomass off-gassing (Rahman et al., 2017).

3.3.8. Supercritical Fluid Extraction

Supercritical fluid extraction (SFE) is a process that utilizes CO_2 as a solvent to selectively extract valuable compounds from biomass. This extraction method is non-toxic and environmentally friendly, as CO_2 is a naturally occurring gas and does not leave harmful residues (Arshadi et al., 2012; Attard et al., 2016).

In SFE, CO_2 is brought to a supercritical state, where it exhibits properties of both a liquid and a gas. In this state, CO_2 permeates the biomass, allowing for efficient extraction of target compounds. One advantage of SFE is its ability to selectively extract volatile compounds while leaving non-volatile components behind. This selectivity is advantageous for off-gassing control as it allows for the extraction of specific compounds relevant to the control of volatile emissions (Arshadi et al., 2012; Attard et al., 2016).

The solubility of compounds in the supercritical fluid is influenced by their polarity and molecular weight. This property enables targeted extraction, as compounds with specific characteristics can be efficiently extracted using SFE (Arshadi et al., 2012; Attard et al., 2016). Another benefit of SFE is the easy removal of the supercritical fluid solvent. After extraction, the supercritical CO_2 can be depressurized and converted back into a gas, leaving minimal residual solvent content. This feature reduces the potential for solvent off-gassing and ensures the safety and environmental friendliness of the extraction process (Arshadi et al., 2012; Attard et al., 2016).

Additionally, SFE operates at relatively low temperatures, which helps preserve the integrity of heat-sensitive compounds present in the biomass. This characteristic is particularly important for off-gassing control, as it minimizes off-gassing resulting from thermal degradation during the extraction process (Arshadi et al., 2012; Attard et al., 2016).

3.3.9. Antioxidant Addition

Antioxidants play a crucial role in controlling off-gassing in biomass by inhibiting oxidation reactions and reducing the formation of volatile and odorous compounds.

Distinct antioxidants, such as acetylsalicylic acid (ASA) (Sedlmayer et al., 2020), tert-butyl hydroquinone (TBHQ), propyl gallate (Arshadi et al., 2018), and tobacco extract (Moreira et al., 2021), are being investigated for their potential in controlling off-gassing from biomass. These antioxidants work by scavenging free radicals and inhibiting oxidative reactions that can lead to the formation of volatile and odorous compounds. By reducing the formation of these compounds, antioxidants effectively control off-gassing and improve the air quality associated with biomass utilization. Furthermore, antioxidants have additional benefits beyond off-gassing control. They help preserve the quality and nutritional integrity of biomass by protecting it from oxidative degradation. This preservation extends the shelf life of biomass and enhances its suitability for various applications (Moreira et al., 2021).

The use of antioxidants in biomass processing also creates a safer working environment for workers. By reducing the formation and release of volatile and odorous compounds, antioxidants minimize health risks associated with occupational exposure to these compounds. This promotes a healthier and safer workplace for individuals involved in biomass processing (Arshadi et al., 2018; Moreira et al., 2021; Sedlmayer et al., 2020).

In addition to their role in off-gassing control and occupational safety, antioxidants contribute to environmental sustainability. By mitigating the formation of volatile and odorous compounds, antioxidants help reduce air pollution resulting from biomass off-gassing. This reduction in air pollution has positive effects on the overall ecological impact of biomass utilization (Arshadi et al., 2018; Moreira et al., 2021; Sedlmayer et al., 2020).

3.3.10. Pelletizing

Pelletizing biomass is a beneficial method for controlling off-gassing (Alakoski et al., 2016). The pelletization process involves reducing the moisture content of biomass through drying, which limits the availability of water for microbial activity. By reducing the moisture content, pelletization minimizes the potential for off-gassing associated with microbial activity (Alakoski et al., 2016)

One of the advantages of pelletizing biomass is that it densifies the material into compact pellets. The dense structure of pellets confines gases and volatile compounds, minimizing their emission into the environment. This confinement contributes to improved air quality by reducing the release of volatile compounds and odors. The pellet structure also enhances combustion efficiency during biomass utilization. The compact nature of pellets allows for more efficient and controlled combustion, leading to reduced emissions of pollutants. This improved combustion efficiency further contributes to better air quality by minimizing the release of harmful substances (Whittaker and Shield, 2017).

Additionally, pelletization facilitates better handling, storage, and transportation of biomass (Cui et al., 2021). The compact and uniform size of pellets makes them easier to handle and store compared to uncompacted biomass materials. This improved manageability reduces the likelihood of off-gassing during storage and transportation, enhancing overall safety and reducing the potential for environmental contamination. Moreover, the compactness of pellets reduces surface contact, which in turn lowers the emissions of volatile compounds and odors. The minimized surface area limits the potential for off-gassing, resulting in improved air quality (Whittaker and Shield, 2017).

The process of pelletization also contributes to occupational safety and air quality by reducing dust generation. Pellets have reduced dust compared to uncompacted biomass materials, improving the working environment for individuals involved in biomass handling and processing (Whittaker and Shield, 2017). Standardization in pellet production allows for precise off-gassing management (Cui et al., 2021). By adhering to standardized processes and regulations, pellet manufacturers can ensure the control of off-gassing and compliance with environmental and safety regulations.

3.3.11. Handling

Proper handling of biomass is crucial for controlling off-gassing, ensuring worker safety, and maintaining biomass quality (Rahman et al., 2018; Svedberg and Johanson, 2017).

Using personal protective equipment (PPE) such as gloves, masks, goggles, and protective clothing is important to minimize direct exposure to volatile compounds and potential risks during biomass handling (Rahman et al., 2018; Svedberg and Johanson, 2017). Additionally, providing adequate training to workers on proper handling techniques, safety protocols, hazard identification, and emergency response procedures helps reduce the risk of accidents or incidents and contributes to off-gassing control (Svedberg and Johanson, 2013).

Furthermore, adopting gentle handling practices, such as careful stacking, lifting, and transferring of biomass, minimizes the release of volatile compounds and helps control off-gassing (Svedberg et al., 2008; Svedberg and Johanson, 2017, 2013). Moreover, implementing effective dust control measures, such as using dust suppression systems, dampening techniques, or covered conveyors, reduces the dispersion of dust particles, improves air quality, and minimizes respiratory health risks (Whittaker and Shield, 2017; Svedberg and Johanson, 2013). Equally relevant is the prevention of spills and leaks through the use of secure containers and careful handling practices. It helps mitigate off-gassing and environmental contamination (Svedberg and Johanson, 2017).

Compliance with regulations and guidelines governing safe handling, storage, and transportation of biomass materials ensures a safe working environment and minimizes off-gassing risks (Gauthier et al., 2012; Svedberg et al., 2008; Svedberg and Johanson, 2017, 2013). By prioritizing worker safety, environmental protection, and regulatory compliance in biomass handling, off-gassing can be effectively controlled. Proper handling practices reduce the release of volatile compounds, enhance worker safety, and preserve biomass quality. Additionally, ensuring sustainability in biomass handling contributes to environmental conservation and the overall goal of reducing off-gassing and its impact on air quality and human health.

3.3.12. Transportation

Transportation plays a critical role in controlling biomass off-gassing, and various measures can be implemented for effective management (Svedberg et al., 2008).

Minimizing agitation and movement during transportation is essential to reduce the release of volatile compounds from biomass materials. Secure fastenings and shock-absorbing materials help minimize disturbance and movement, thus reducing off-gassing (Svedberg et al., 2008; Svedberg and Johanson, 2017). Additionally, dust control techniques are crucial for improving air quality and reducing respiratory risks during biomass transportation. Covered trucks, suppression systems, and dampening methods minimize dust particle dispersion into the air, ensuring better air quality and reducing health hazards (Gauthier et al., 2012; Svedberg et al., 2008).

Preserving biomass quality during transportation is vital to maintain its energy content and minimize off-gassing risks. Proper packaging, insulation, and temperature control measures ensure the biomass retains its quality throughout the transportation process (Svedberg et al., 2008; Svedberg and Johanson, 2017, 2013). Additionally, preventing spills and leaks during biomass transportation is essential to mitigate off-gassing and environmental contamination. Secure fastenings, appropriate container design, and quick response protocols help minimize the release of volatile compounds and prevent environmental pollution (Svedberg et al., 2008; Svedberg and Johanson, 2017, 2013).

Compliance with transportation regulations ensures safe and responsible practices. Adhering to regulations regarding secure fastenings, container design, labeling, and handling procedures minimizes off-gassing risks and environmental pollution (Svedberg et al., 2008; Svedberg and Johanson, 2017, 2013). Promoting sustainability in biomass transportation involves reducing environmental impact and greenhouse gas emissions. Utilizing low-emission vehicles, optimizing logistics to minimize transportation distances, and implementing efficient routing strategies support sustainability goals and climate change mitigation efforts (Svedberg and Johanson, 2013).

By implementing proper transportation practices, including vehicle sealing, dust control, spill prevention, regulatory compliance, and sustainability measures, biomass facilities can effectively manage off-gassing, protect the environment, enhance transportation safety, and ensure the quality of the transported biomass.

3.3.13. Storage

Storage conditions are crucial in controlling biomass off-gassing, and several factors should be considered for effective management (Alakoski et al., 2016; Svedberg and Johanson, 2017).

Moisture control is essential to minimize off-gassing potential. Dry storage areas inhibit microbial growth, which can contribute to off-gassing. Appropriate moisture levels through covered storage areas and humidity control preserve biomass quality and reduce off-gassing risks (Alakoski et al., 2016; Svedberg and Johanson, 2017). Additionally, preventing exposure to oxygen and heat is crucial in controlling biomass degradation and off-gassing. Properly sealed containers and oxygen-free environments reduce the potential for off-gassing. Preventing excessive heat minimizes biomass degradation and subsequent off-gassing (Alakoski et al., 2016).

Furthermore, proper ventilation in storage areas allows for the exchange of air, preventing the accumulation of gases and volatile compounds. Adequate airflow and ventilation systems help dissipate off-gassing emissions, maintaining air quality and reducing health risks (Alakoski et al., 2016; Svedberg and Johanson, 2017). Moreover, adhering to storage regulations ensures safety, environmental protection, and occupational health (Alakoski et al., 2016). Proper storage practices, such as covering biomass piles and implementing safety measures, reduce off-gassing and environmental pollution (Svedberg and Johanson, 2017).

By considering these factors and implementing effective practices, biomass and sold biofuel facilities can effectively control off-gassing, protect air quality, and promote environmental sustainability. Proper storage conditions not only mitigate off-gassing risks but also maintain biomass quality, optimize energy value, and ensure regulatory compliance (Alakoski et al., 2016; Svedberg and Johanson, 2017).

3.3.14. Ventilation

Ventilation is a crucial element in controlling off-gassing in solid biofuels, encompassing key aspects that enhance its effectiveness (Emhofer et al., 2015). It serves to dilute and disperse emissions, reduce particulate matter accumulation, manage odors, and control moisture. Proper ventilation systems, whether natural or mechanical, play a vital role in mitigating the risks associated with biomass off-gassing (Emhofer et al., 2015).

Ventilation dilutes and disperses emissions by introducing fresh air, reducing pollutant concentrations. Airflow patterns carry pollutants away from occupied areas, minimizing potential harmful conditions to human health. It also prevents particulate matter buildup by promoting air movement, thus reducing respiratory irritations and health risks (Svedberg and Johanson, 2017). Odor management is another crucial function of ventilation (Emhofer et al., 2015). By constantly introducing fresh air and carrying away volatile compounds responsible for unpleasant odors, ventilation creates a more pleasant indoor environment, reducing complaints related to biomass off-gassing smells. Moisture control is closely related to ventilation since excessive moisture promotes microbial growth and off-gassing. Effective ventilation reduces humidity, manages moisture levels, and inhibits mold and mildew growth, minimizing the release of VOCs and other off-gassing byproducts linked to microbial activity, thus improving indoor air quality and reducing health risks (Svedberg and Johanson, 2017).

In occupational settings where biomass processing or combustion occurs, proper ventilation is crucial for worker safety. It reduces workers' exposure to harmful emissions, gases, and particulate matter released during biomass off-gassing. Adequate ventilation systems tailored to specific needs ensure compliance with safety regulations and create a safer working environment (Simpson et al., 2016). Various ventilation strategies and systems can be employed for effective biomass off-gassing control. Natural ventilation uses openings like windows, doors, and vents, while mechanical ventilation systems actively introduce and circulate fresh air using fans and blowers. Local exhaust ventilation captures and removes contaminants directly at their source using hoods and extraction systems. The choice of ventilation approach depends on factors such as the scale of operations, off-gassing activities, and desired air quality standards (Svedberg and Johanson, 2017).

Design, installation, and maintenance is critical for optimizing ventilation systems. Calculating appropriate airflow rates, determining air exchange rates, and controlling airflows contribute to sufficient air exchange, dilution of pollutants, and proper distribution of fresh air. Integrating filtration systems like high-efficiency filters into ventilation systems can capture and remove particulate matter and contaminants. Regular maintenance and inspection, including filter cleaning or replacement, airflow rate checks, and indoor air quality monitoring, ensure optimal performance, informing system adjustments and improvements (Svedberg and Johanson, 2017).

3.3.15. Filtration

Filtration plays a crucial role in biomass off-gassing control (Still et al., 2018). It effectively captures and removes particulate matter, permanent gases (CO, CO_2, and CH_4), and VOCs from the air (Lang et al., 2021). Particulate matter, including ash and soot, can have adverse effects on air quality and human health. Filtration systems, such as HEPA filters, efficiently capture and retain these particles using interception, impaction, and diffusion mechanisms (Cornette et al., 2020).

In addition to particulate matter, off-gassing releases harmful permanent gases and VOCs (Kim et al., 2022). Filtration systems with adsorbent materials like activated carbon or zeolite effectively capture and retain these gases through surface-based processes, reducing their concentration in the air and minimizing health impacts. These systems can also address odorous compounds by incorporating activated carbon or odor-removal media, improving overall air quality (Kim et al., 2022).

Filtration systems are crucial for maintaining indoor air quality in settings where biomass combustion occurs (McNamara et al., 2017). They are commonly integrated into ventilation systems to continuously circulate and filter the air. In addition to capturing particulate matter, gases, and odorous compounds, filtration systems remove other airborne contaminants, such as allergens, mold spores, and bacteria, creating a healthier indoor environment and reducing respiratory issues for occupants (McNamara et al., 2017).

The selection and design of filtration systems depend on specific characteristics of the biomass off-gassing, the intended application, and desired filtration efficiency. Factors like filter media type, filtration velocity, and system maintenance should be carefully evaluated to ensure optimal performance and longevity of the filtration system (McNamara et al., 2017).

3.3.16. Management of Combustion Equipment

Effective combustion equipment management plays a vital role in controlling biomass off-gassing. Proper handling and operation of furnaces, water heaters, stoves, and fireplaces are essential for efficient combustion, reducing emissions of pollutants and volatile compounds. This improves air quality and reduces the environmental impact of biomass utilization (Thomson and Liddell, 2015).

Maintaining optimal combustion temperatures is crucial for promoting complete combustion, minimizing the release of hazardous substances. Proper temperature control ensures efficient combustion, enhances occupational safety, and reduces off-gassing (Thomson and Liddell, 2015). Adequate air supply is another key factor in achieving complete combustion and controlling off-gassing. Managing combustion equipment involves providing sufficient air for combustion, facilitating complete oxidation, and minimizing the formation and release of volatile compounds, thus improving personnel safety (Thomson and Liddell, 2015).

Additionally, advanced combustion control systems optimize equipment performance by regulating parameters such as temperature and air-fuel ratio. These systems enhance combustion efficiency and reduce off-gassing by providing better control over the release of volatile compounds, thus improving air quality (Thomson and Liddell, 2015). Equally significant is the regular maintenance and monitoring. Routine maintenance ensures proper equipment functioning, reducing the risk of malfunctions that can lead to off-gassing incidents. Continuous monitoring of gas composition and emissions enables timely detection of issues, preventing the release of hazardous volatile and semi-volatile compounds (Thomson and Liddell, 2015).

The integration of emission control technologies further enhances off-gassing control. Technologies like electrostatic precipitators, bag filters, and scrubbers capture and remove particulate matter, gases, and volatile compounds, ensuring compliance with regulatory standards and reducing emissions (Thomson and Liddell, 2015). By incorporating appropriate emission control technologies, biomass combustion facilities minimize pollutant release, enhancing air quality and mitigating environmental impact.

3.3.17. Electrostatic Precipitation

Electrostatic precipitation mitigates particulate matter emissions during biomass combustion (Nandan et al., 2021; Vicente et al., 2022). It uses electrostatic principles to capture and remove fine particles, like ash, soot, and microscopic debris, from flue gases or exhaust streams (Schittl et al., 2021).

High-voltage electrodes create an electric field in a chamber, charging the particles in the gas stream. Oppositely charged collection plates or surfaces in the chamber attract and accumulate the charged particles over time. The technique's efficiency depends on various factors, including electrode design, electric field intensity, particle size, composition, and collection surface geometry (Cid et al., 2022). Regular removal of accumulated particles is necessary to maintain system efficiency.

Electrostatic precipitation offers several advantages for biomass off-gassing control. It efficiently captures fine particles, including health-risky PM2.5, enhancing air quality and protecting human health (Varshney et al., 2022). The adaptability of the technique to different biomass combustion systems allows integration into existing or new installations. By minimizing the release of particulate matter and associated pollutants like heavy metals and organic compounds, electrostatic precipitation contributes to environmental protection and ensures compliance with regulatory standards (Varshney et al., 2022).

The technique's relatively low energy consumption compared to alternatives, such as baghouse filters, enhances energy efficiency and reduces environmental impact (Varshney et al., 2022). However, the electrical energy required for operating electrostatic precipitation systems should still be considered, and proper maintenance and monitoring are essential for sustained efficiency in capturing and removing particulate matter during off-gassing (Jaworek et al., 2021).

3.3.18. Scrubbing

Scrubbing is a highly effective technique for controlling biomass off-gassing by extracting pollutants from flue gases or exhaust streams. It targets gaseous pollutants like acidic gases, nitrogen oxides, and VOCs produced during biomass combustion. Flue gases are subjected to scrubbing with chemical solutions or sorbents, leading to the capture and elimination of pollutants (Costa et al., 2023).

Scrubbing efficiently removes particulate matter and specific VOCs from flue gases using impaction, diffusion, and absorption mechanisms, thereby improving air quality and reducing health and environmental risks associated with particulate matter (Costa et al., 2023; Darbandi et al., 2021). The technique ensures compliance with air quality regulations and emission standards, making it crucial for managing pollutant emissions in biomass facilities, promoting environmental sustainability, and avoiding penalties (Costa et al., 2023).

Scrubbing offers versatility with various systems available, such as wet scrubbers, dry scrubbers, and hybrid systems, providing customized solutions for specific pollutants (Darbandi et al., 2021; Xu et al., 2021). However, scrubbing operations generate waste streams that require proper handling and disposal (Susastriawan et al., 2021). Proper sizing, configuration, regular maintenance, and monitoring are essential for optimal performance and efficiency of scrubbing systems, which come with initial capital investments and ongoing operational costs (Costa et al., 2023).

3.3.19. Early Detection and Alarming

Early detection (Fernandez-Anez et al., 2018) and alarm systems (Jiang et al., 2016) are essential for effective control of biomass off-gassing. They offer several advantages that enhance safety and management of off-gassing incidents. Early detection systems provide timely information and initiate alarms when volatile compounds or permanent gases are detected, enabling swift responses and implementation of emergency plans. This prompt notification minimizes the potential for injuries, damages, and environmental impact (Fernandez-Anez et al., 2018; Jiang et al., 2016).

These systems also provide continuous monitoring and surveillance of off-gassing conditions, allowing for proactive interventions. By maintaining constant vigilance, potential off-gassing issues can be identified before they escalate, ensuring a safer working environment and preventing long-term exposure to harmful compounds. Moreover, early detection systems contribute to data collection and analysis, offering insights into off-gassing incidents. This data-driven approach helps understand the root causes of off-gassing and informs mitigation strategies, leading to improvements in process management, equipment maintenance, and safety protocols (Fernandez-Anez et al., 2018).

Early detection systems serve as training tools, raising awareness and reinforcing safety protocols among personnel. Regular drills and exercises familiarize workers with alarm signals, evacuation procedures, and response protocols, enhancing preparedness and effective response. Additionally, these systems help meet regulatory requirements and compliance standards. They demonstrate a commitment to safety and prevent penalties or legal issues associated with non-compliance (Fernandez-Anez et al., 2018; Jiang et al., 2016).

3.3.20. Education, Training, and Provision of Scientific Information

Education and training are essential components in effectively addressing the risks associated with fast-acting chemicals and off-gassing incidents (Lehna et al., 2017). Prioritizing education as a preventive measure, alongside control strategies, can significantly minimize these risks. Developing informative Health and Safety Data Sheet (HSDS) templates is crucial for communicating potential hazards to customers. These templates provide comprehensive information on safe handling, storage, and use of chemicals, enabling users to make informed decisions and take appropriate precautions (Lehna et al., 2017).

Supplemental data on dust is important, as certain concentrations of dust particles can lead to respiratory diseases (Whittaker and Shield, 2017). Detailed information on the health hazards associated with specific types of dust, along with exposure limits and guidelines for controlling dust emissions, helps mitigate off-gassing risks. Chemicals involved in off-gassing, such as alpha-pinene, require comprehensive information on health effects, safe handling practices, and appropriate personal protective equipment (PPE). Guidance on PPE selection, use, and maintenance ensures adequate protection (Svedberg and Johanson, 2017; Whittaker and Shield, 2017).

Awareness and communication through clear signage and warnings are crucial for promoting safety and accident prevention (Lehna et al., 2017). Additional measures like lockable doors and physical barriers enhance safety and restrict access to hazardous areas. Outreach and training efforts are important for educating the public, including homeowners and community members, about the risks of off-gassing and preventive measures. Collaboration between government agencies, private companies, and educational institutions ensures the dissemination of accurate and accessible information. Government agencies, such as Health Canada, play a vital role in setting limits for toxic substances and providing occupational safety guidelines in residential settings.

4. Conclusion

This review offers a comprehensive analysis of biomass off-gassing prevention and mitigation. It goes beyond a superficial overview and critically examines the phenomenon, investigating its implications in both residential and industrial scenarios. The review achieves this by conducting an extensive synthesis of existing literature, encompassing a wide array of preventive and mitigatory practices and techniques. The preventive measures discussed in the review include drying, grinding, and thermochemical pre-treatment techniques such as carbonization, torrefaction, and steam explosion. Additionally, advanced technologies like ozonation and SFE are explored as effective ways to manage biomass off-gassing. Handling, storage, and transportation practices are also addressed, given their crucial roles in preventing off-gassing incidents. Furthermore, the review discusses the integration of combustion equipment management with electrostatic precipitation and scrubbing to control emissions during solid biofuel combustion. The importance of early detection and alarming systems is emphasized to enable prompt responses to potential off-gassing events. Moreover, the review underscores the pivotal role of education, training, and the dissemination of scientific knowledge in averting the autogenous generation of toxic chemicals, particularly CO and VOCs. Ultimately, the main objective is to drive advancements in occupational safety, human health, industrial hygiene, and environmental protection within the solid biofuel value chains. By implementing the preventive and mitigatory practices outlined in the review, stakeholders can work towards a safer and more sustainable utilization of biomass resources.

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CHAPTER II – Fuel-Flexible Biomass Off-Gassing: A Meta-Analysis for Research and Development in Preventive and Mitigatory Practices and Techniques

An alternate version of Chapter II is presently accessible as a review paper on the web at https://doi.org/10.1016/j.indcrop.2023.117508

Highlights

The utilization of biomass in residential and industrial settings generates hazardous gases, posing risks.

Meta-analysis identified effective strategies, including drying, ventilation, torrefaction, ozonation, supercritical fluid extraction, and antioxidant addition.

Implementation of these strategies resulted in a 25% decrease in emissions, supported by strong evidence.

Adoption of these measures safeguards occupational safety, human health, and the environment.

These strategies contribute to the development of cleaner and safer biomass energy, ensuring a sustainable future.

Abstract

Biomass, a renewable energy source, poses substantial risks in residential and industrial settings due to the generation of hazardous gases, including carbon monoxide (CO), carbon dioxide (CO_2), methane (CH_4), and volatile organic compounds (VOCs). To evaluate the impact of technocentric solutions on these emissions, a comprehensive meta-analysis was conducted using statistical approaches, such as density curve analysis, linear mixed-effect model analysis, and Bayesian factor analysis. Between 2001 to 2017, multiple distressing incidents were documented, with alarmingly high carbon monoxide concentrations (480,000-750,000 ppm), tragically resulting in fatalities and injuries. In response to these significant risks, a series of strategies have been identified, encompassing drying, ventilation, thermochemical pre-treatment (torrefaction and steam explosion), ozonation, supercritical fluid extraction (SFE), and antioxidant addition. Implementation of these measures has demonstrated an average 25% reduction in emissions, robustly supported by a Bayes factor ($\log_e$ BF) estimation of 4.5, unequivocally signifying a noteworthy decrease in off-gassing and emissions of CO, CO_2, CH_4, and VOCs. These findings distinctly emphasize the paramount importance of safeguarding occupational safety, human health, and environmental integrity when utilizing biomass energy. Through the adoption of these strategies, we can actively contribute to the advancement of cleaner and safer biomass energy, ensuring an enduringly sustainable future.

Keywords: carbon monoxide; occupational safety; reactive oxygen species; volatile organic compounds; wood pellets.

1. Introduction

Between 2001 and 2017, multiple distressing incidents occurred in residential and commercial settings, involving hazardous off-gassing of CO from wood pellets (**Fig 1**). These incidents had severe consequences for human health, resulting in fatalities and injuries, with CO concentrations reaching alarmingly high levels (480,000 to 750,000 ppm). Notable incidents were reported in Rotterdam, the Netherlands (2002), and Helsingborg, Sweden (2006), during wood pellet unloading and handling, leading to tragic outcomes (Gauthier et al., 2012). The release of carbon monoxide caused elevated carboxyhemoglobin (COHb) levels, impairing oxygen delivery to the brain and muscles, leading to compromised judgment, lethargy, and other adverse effects.

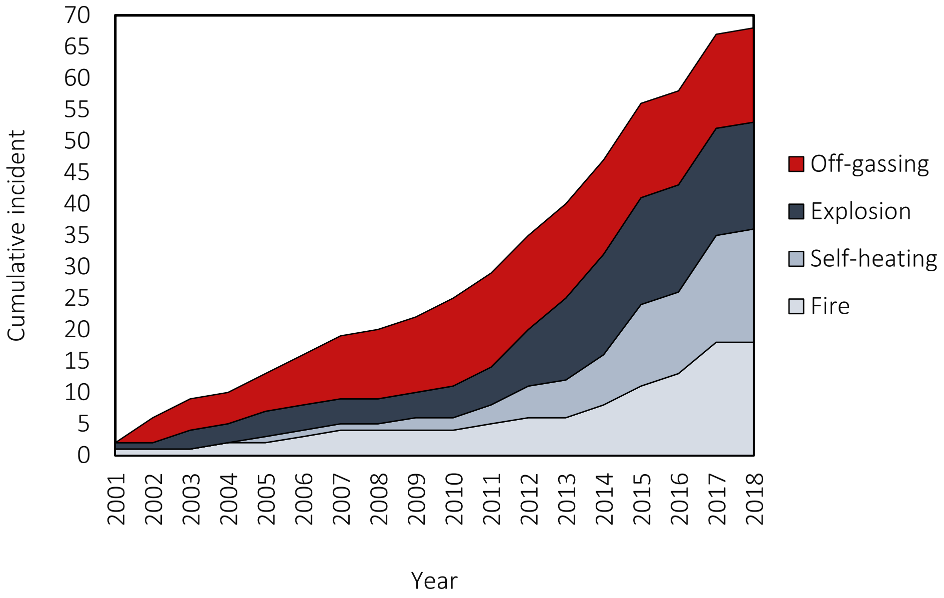

Fig 1. Incidents of hazardous off-gassing from wood pellets (2001-2017). During the specified timeframe, incidents occurred with extremely high carbon monoxide (CO) concentrations (480,000-750,000 ppm), resulting in loss of life and serious injuries during wood pellet handling. The CO release led to increased carboxyhemoglobin (COHb) levels in victims, causing impaired cognitive and physical functionality. To address CO off-gassing hazards from wood pellets and prioritize safety, robust protocols are crucial during transportation, storage, and handling. These include implementing proper ventilation systems and continuous monitoring, along with providing education and training programs to raise awareness and foster a safety-oriented culture. Prioritizing safety measures effectively minimizes the risk of CO exposure and its detrimental consequences.

Similar incidents in Finland, Ireland, Germany, and Switzerland have also underscored the inherent dangers associated with wood pellet off-gassing. The occurrence of fatalities and injuries emphasizes the urgent need for preventive and mitigatory measures (Alakoski et al., 2016; Gauthier et al., 2012). Addressing these risks and safeguarding well-being and environmental integrity necessitates the implementation of sustainable alternatives in the biomass and bioenergy sector.

To systematically evaluate technocentric solutions for reducing biomass off-gassing, we conducted a meta-analysis. We examined the integration of techniques such as ventilation, drying, thermochemical pre-treatment, ozonation, SFE, and antioxidant addition. Through our meta-analysis, we seek to provide evidence-based insights into the technical effectiveness of these practices, offering actionable knowledge to promote occupational safety, human health, and environmental protection in residential and industrial facilities.

2. Systematic Review Protocol

2.1. Bibliometric and Altimetric Data Collection

We conducted a systematic review to evaluate the effectiveness of various biomass off-gassing control practices and techniques. To ensure a thorough search, we utilized reputable databases, specifically Science Direct® and Web of Science™. Our search strategy incorporated relevant indexing terms and Boolean operators, which allowed us to gather a comprehensive set of relevant studies. The primary focus of our review was on assessing the emissions of CO, CO_2, CH_4, and VOCs, as they are of higher intellectual interest in the context of biomass off-gassing compared to other gases like nitrogen oxides (NO_x) and sulfur oxides (SO_x). Additionally, we explored several technocentric solutions, including ventilation, drying, thermochemical pre-treatment (torrefaction and steam explosion), ozonation, SFE, and antioxidant addition. These practices have been widely discussed in the literature, and their potential in mitigating biomass off-gassing throughout the entire life cycle of solid biofuels highlights their significance in the field. To maintain a clear and focused scope, we excluded papers unrelated to biomass-to-solid (BTS) fuels. Specifically, we avoided materials like particleboard, cardboard, and chemicals to ensure our analysis remains relevant to the topic at hand. Moreover, we were meticulous in selecting studies with robust methodologies, ensuring the reliability and validity of our meta-analytical procedures. This involved eliminating experiments with insufficient and inconclusive data on certain practices and strategies, such as grinding, carbonization (pyrolysis), management of combustion equipment (including electrostatic precipitation and scrubbing), and filtration. Our review placed a particular emphasis on assessing the impact of significant toxic chemicals on critical aspects, including occupational safety, human health, industrial hygiene, and environmental protection. To ensure the credibility of our findings, we relied solely on peer-reviewed papers, adhering to the highest standards of quality in our analysis. Furthermore, expert reviewers thoroughly evaluated the selected articles to maintain accuracy and validity. Throughout the review process, we actively encouraged regular discussions to uphold scientific rigor and minimize potential biases that could influence the impartiality of our conclusions. This approach allowed us to derive reliable and credible insights into the effectiveness of biomass off-gassing control practices and their implications for various critical aspects.

2.2. Statistical Data Analysis

We employed well-established and accepted techniques in the scientific community, including density curve analysis (Cacioppo et al., 2013), linear mixed-effect model analysis (Luutu et al., 2022), Bayesian factor analysis (Zhang and Schuster, 2021), natural logarithmic transformation (Rodríguez-Barranco et al., 2017), and Begg's funnel plot analysis (Hariyanto et al., 2021). These methodologies were carefully selected and justified to maintain statistical rigor and reliability, addressing distinct aspects of our research question.

3. Results

Our research provides strong evidence supporting the effectiveness of preventive and mitigatory practices and techniques in reducing emissions of CO, CO_2, CH_4, and VOCs from wood pellets (**Fig 2–4**). Strategies like ventilation, drying, torrefaction, steam explosion, ozonation, SFE, and antioxidant addition significantly improved material quality and storage environments, leading to substantial decreases in off-gassing emissions, indicated by negative central estimates of LeRR for fast-acting toxic chemicals (**Fig 2**).

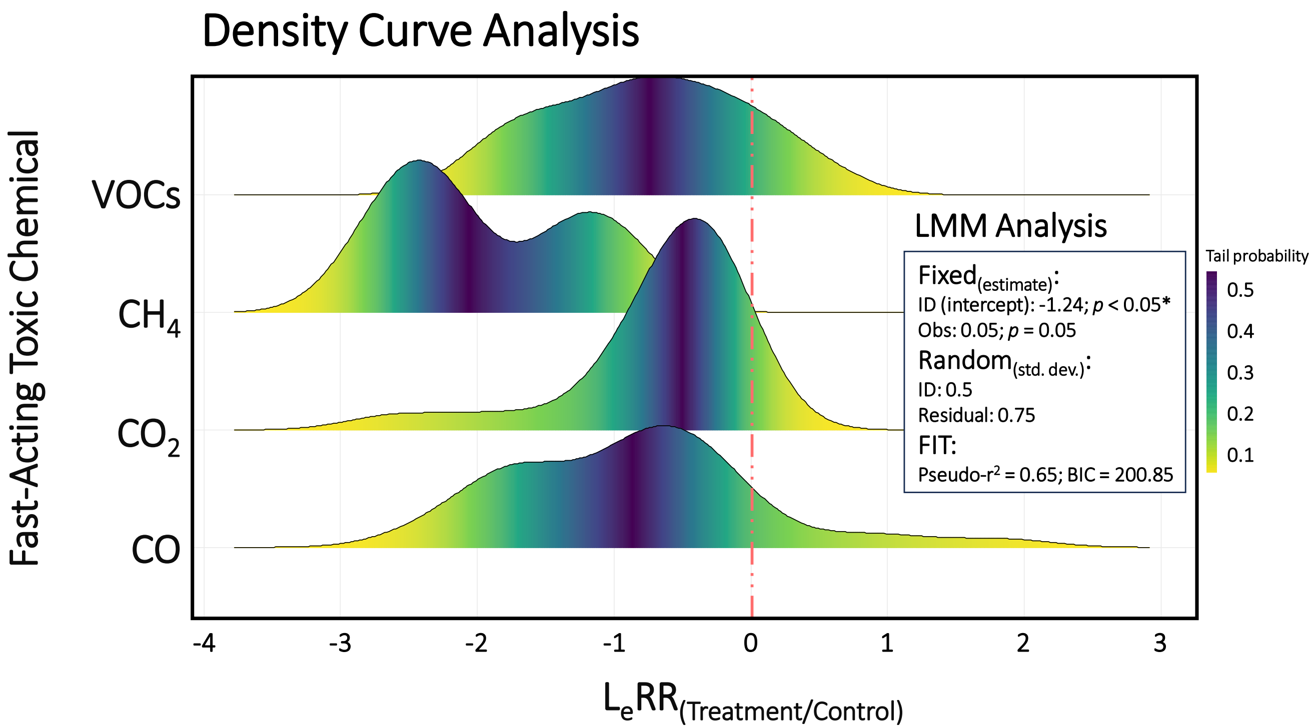

Fig 2. Density curve analysis of the natural logarithmic response of emissions of off-gassing in systems with and without the implementation of technocentric solutions for preventive and mitigatory control. To assess the effectiveness of techniques in mitigating off-gassing emissions from wood pellets, a natural logarithmic transformation is applied to achieve a symmetrical, normally distributed response variable for robust statistical analysis. The density curve and summary statistics offer insights into data characteristics and variations, identifying potential deviations. Integration of LMM addresses heterogeneity, accounting for variations from different practices and techniques, ensuring robustness in the analysis for informed decision-making and mitigation strategies.

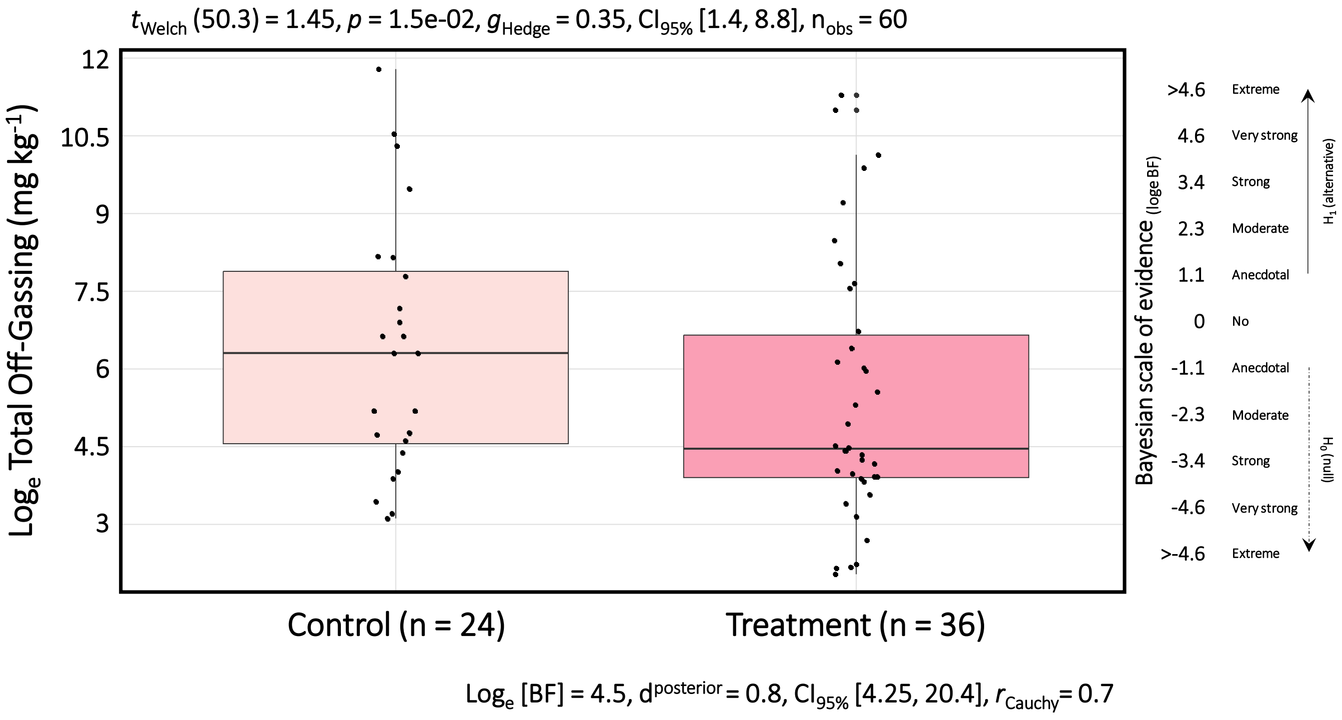

Fig 3. Bayesian factor analysis and Welch's test for the total off-gassing generation in systems with and without the implementation of technocentric solutions for preventive and mitigatory control. BFA evaluates the null hypothesis (no significant differences in emissions) against the alternative hypothesis (substantial differences) using Bayesian factor analysis. A factor >1 indicates significant differences, while <1 suggests no significant differences. Welch's test addresses sample size and variance heterogeneity for robust comparisons. BFA and Welch's test provide insights into emissions variations and the effectiveness of mitigation techniques, facilitating informed decision-making and enhancing credibility.

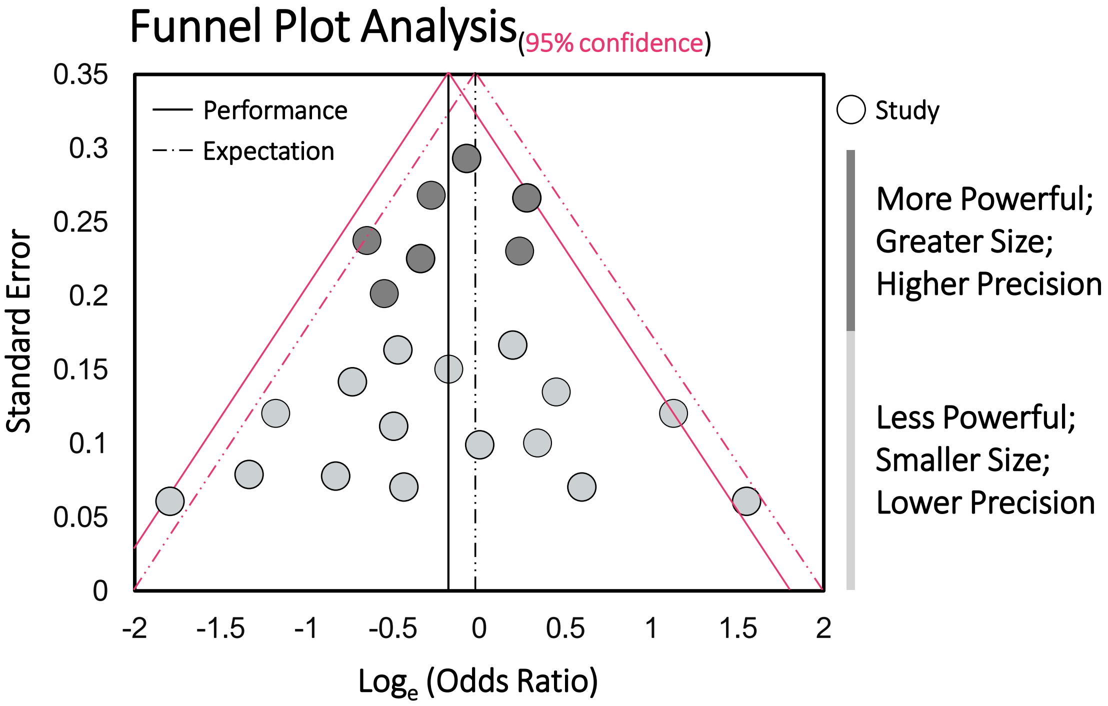

Fig 4. Funnel plot analysis of bias in the meta-analysis of total off-gassing generation in systems with and without the implementation of technocentric solutions for preventive and mitigatory control. FPA is a statistical technique used in meta-analyses to detect potential publication bias and assess study distribution. In emissions of off-gassing meta-analysis, the funnel plot represents study distribution, with symmetry indicating larger studies with smaller errors. Asymmetry suggests potential publication bias. FPA also assesses small study effects, where smaller studies may show larger effects due to biases or lower quality. By examining the funnel plot, researchers identify biases and improve the interpretation of meta-analysis results, ensuring objectivity and reliability.

The linear mixed-effects model (LMM) analysis allowed us to predict a 25% disparity between treatment and control groups with 65% accuracy, objectively evaluating the impact of prevention or mitigation on emissions reduction. Bayes factor analysis (BFA) (**Fig 3**) and funnel plot analysis (FPA) (**Fig 4**) further supported the effectiveness of these strategies. Bayes factor analysis yielded a logarithm of the Bayes factor ($\log_e$ BF) estimation of 4.5, strongly indicating significant differences in off-gassing emissions between treatment and control groups. However, we must consider potential biases introduced by smaller-sized studies. FPA identified potential publication bias, particularly in smaller-sized studies, which may impact conclusions due to their lower statistical power and precision.

4. Discussion

4.1. The Significance of Woody Resources

Solid biofuel production primarily relies on wood as the dominant feedstock, with softwoods accounting for approximately 95% of the composition, while non-wood sources make up about 5%. Among softwoods, Scots pine is the most prevalent feedstock, followed by Norway spruce, Douglas fir, western red cedar, Chinese fir, and southern yellow pine (**Fig 5**).

Off-gassing in organic matter is driven by autoxidation initiated by free radicals (R•) and reactive oxygen species (ROS) (Porter et al., 1995). Softwoods exhibit higher susceptibility to autoxidation and off-gassing compared to hardwoods. Hydroxyl radicals (OH•) significantly contribute to CO generation from softwoods, particularly those rich in glucomannans, at temperatures of 30-35°C, while unsaturated fatty acids also contribute to CO formation, though to a lesser extent (Porter et al., 1995).

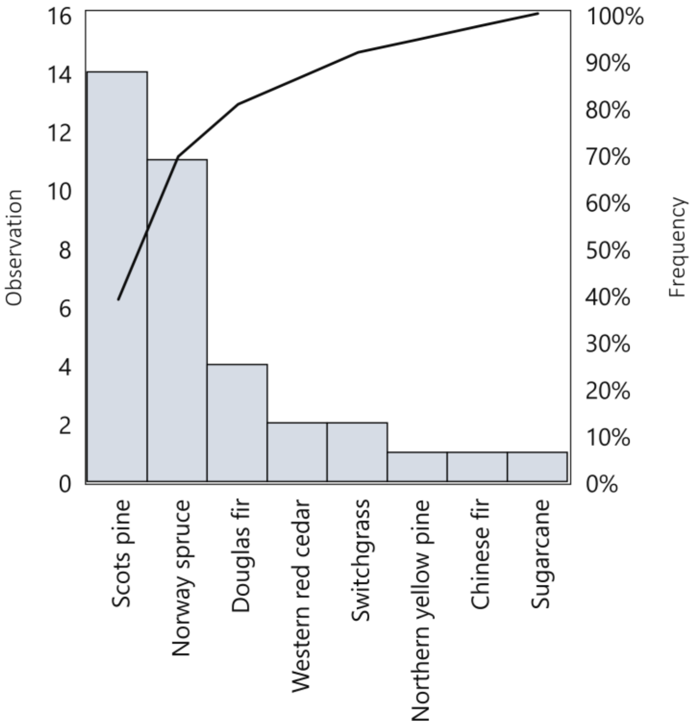

Fig 5. Distribution of feedstocks for solid biofuel production. Approximately 95% of solid biofuel feedstock is sourced from softwood materials, including Scots pine, Norway spruce, Douglas fir, western red cedar, Chinese fir, and southern yellow pine. Softwoods are more susceptible to autoxidation and off-gassing compared to hardwoods. Research efforts have mainly focused on softwoods, leading to limited representation of hardwoods in woody bioresource studies. Softwoods from Scandinavia are favored in Europe and North America for solid biofuels, but indoor use can lead to elevated off-gassing due to fatty and resinous acids. Laboratory experiments show significant emissions of CO, CO_2, and CH_4 from Scandinavian pine products, posing health hazards such as headaches, convulsions, coma, and potential fatalities. Blending Scots pine and Norway spruce for biofuel pellets increases methane generation, raising concerns about occupational safety and incidents.

Decomposition of organic material, like wood, produces CO_2, which can serve as a precursor for CH_4 production during hydrogenation. Softwoods, containing oxidizable hemicelluloses and fatty acid methyl esters (FAMEs), may lead to more CH_4 production. Additionally, CO and VOCs are influenced by wood composition and degradation processes, with higher temperatures accelerating production at 30-40°C

(Porter et al., 1995). To control off-gassing, antioxidants effectively inhibit cyclization reactions and VOC formation by scavenging free radicals. Environmental conditioning, such as lowering temperature and relative humidity, can reduce chemical oxidation and microbial degradation processes, mitigating off-gassing (Soto-Garcia et al., 2015).

The utilization of softwoods, particularly from Canadian and Scandinavian forestry systems, as solid biofuel feedstocks is preferred due to availability and combustion efficiency. However, softwood-based products stored in confined spaces or shipped in bulk can lead to significant emissions of CO, CO_2, and CH_4, posing health risks (Magelli et al., 2009). Future research should focus on investigating hardwood feedstocks, quantifying off-gassing emissions, studying antioxidant effectiveness, controlled storage and shipping conditions, improved safety measures, and environmental impact assessments:

☐ Investigation of hardwood off-gassing: There is a significant gap in understanding the off-gassing emissions of hardwood species commonly used in solid biofuel production. Further research is needed to compare the off-gassing characteristics of hardwoods and softwoods, including differences in chemical composition, degradation processes, and resulting emissions (Castellano et al., 2015). Controlled experiments and advanced analytical techniques can be employed to identify and quantify emitted gases, shedding light on the distinct emission patterns of distinct wood types (Yilmaz et al., 2023);

☐ Impact of feedstock composition: Feedstock composition, particularly resin and fatty acid content, plays a critical role in off-gassing emissions. Systematic studies should analyze the influence of distinct feedstock compositions on off-gassing to optimize feedstock selection and blending strategies for reduced emissions. Detailed analyses of resin and fatty acid content across wood species, along with controlled experiments on off-gassing emissions, can provide valuable insights (Alakoski et al., 2016);

☐ Long-term emissions monitoring: Continuous monitoring of off-gassing emissions over time is essential for understanding emission trends and their potential long-term effects (Alakoski et al., 2016). Long-term monitoring studies, along with ambient air quality and personal exposure data (Soto-Garcia et al., 2015), can inform sustainable emission control strategies and assess health risks associated with prolonged exposure;

- Human health impact assessment: The potential health risks associated with off-gassing and toxic emissions from solid biofuels need thorough investigation. Human health impact assessments through epidemiological studies (Karanasiou et al., 2021), toxicological experiments (Jiang et al., 2019), and exposure modeling (Eichler et al., 2022) can establish dose-response relationships and set exposure limits to protect occupational safety and public health.

4.2. Airborne Fast-Acting Toxic Chemicals: Profile and Implications for Occupational Safety and Human Health

Biomass oxidation produces a diverse range of airborne toxic chemicals, with implications for human health and the environment. A comprehensive analysis has determined the chemical profile of these compounds, emphasizing the importance of occupational safety, industrial hygiene, and environmental protection. Carbon monoxide constitutes 30.3% of the compiled data (**Fig 6**) and is well-known for its role in causing fatalities and injuries. Carbon dioxide, VOCs, and CH_4 account for 24.7%, 23.6%, and 14.6% of the compilation, respectively. Other chemicals, including sulfur oxides (SO_x), nitrogen oxides (NO_x), nitrogen gas (N_2), nitrous oxide (N_2O), and hydrogen gas (H_2), were observed to a lesser extent.

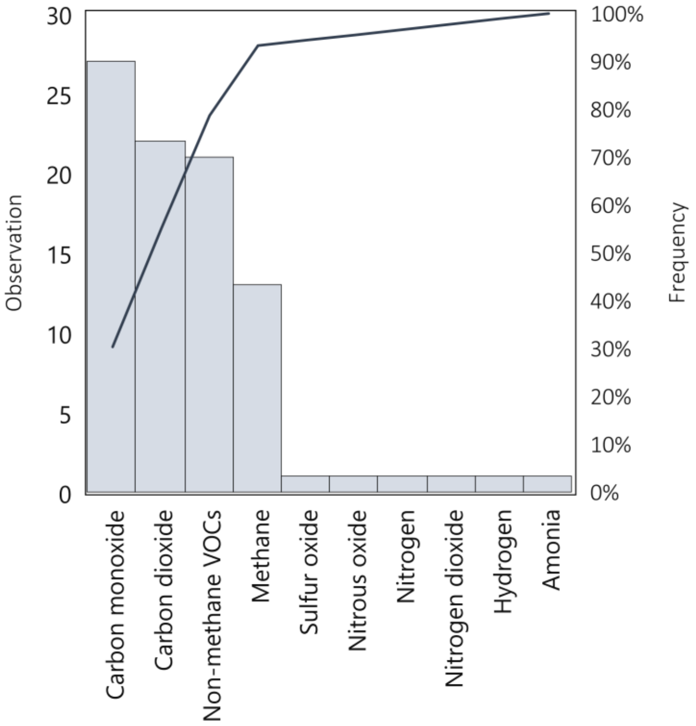

Fig 6. Profile of fast-acting toxic chemicals autogenously generated by biomass. The data reveals that CO is the most significant contributor at 30.3%, known for its lethal effects. CO_2 constitutes 24.7%, posing health risks in confined spaces. VOCs account for 23.6%, leading to air pollution and health problems. CH_4 contributes 14.6% to climate change. Other chemicals like SO_x, NO_x, N_2, N_2O, and H_2 are also present, each with specific toxicological and environmental implications. Stringent safety measures and environmental protection are necessary during biomass oxidation. Continued research is essential to address challenges from airborne toxic compounds during biomass oxidation.

Effective controls and critical limits have been established based on extensive investigations and experiments to address the potential human and environmental toxicity of these chemicals in off-gassing scenarios. For instance, acute fatality can result from exposure to CO concentrations of 12,800 ppm for one minute, while exposure at 6,400 ppm can cause death within 25-30 minutes. Symptoms of CO exposure within concentrations ranging from 40 to 3,200 ppm for 120 to 480 minutes include impaired judgment, drowsiness, and fatigue (Tumuluru et al., 2015). Concerning CO_2, a critical concentration range of 5,000-100,000 ppm has been defined. Prolonged exposure to extreme CO_2 concentrations over 480 minutes can induce convulsions, coma, and, in severe cases, fatality. Even at 30,000 ppm, CO_2 can be hazardous, resulting in headaches, impaired judgment, dizziness, drowsiness, and rapid breathing. Additionally, CH_4 possesses a critical limit of 500,000 ppm, beyond which hazardous conditions can arise. Methane is also prone to explosiveness, and within 480 minutes, it can cause unconsciousness or death due to asphyxiation (Tumuluru et al., 2015).

Off-gassing incidents can indirectly impact human health by depleting the concentration of oxygen (O_2) in enclosed spaces (Svedberg and Johanson, 2017). Oxygen-deficient conditions, ranging from 160,000 to 170,000 ppm, can lead to hypoxia, characterized by rapid and deep breathing as the body compensates for the lack of oxygen delivery. At 60,000 ppm, cardiac arrest occurs, resulting in fatality. Workplace Exposure Limits (WEL) for O_2, which establish the upper limit of acceptable concentration in the workplace, are set at 210,000 ppm. However, more stringent limits, such as the Occupational Safety and Health Administration's (OSHA) specification of 195,000 ppm, are implemented to ensure occupational safety and health in environments where these gases or oxygen-consuming microorganisms may be present (Kuang et al., 2009).

Comprehending the toxicological implications of these chemicals and their critical limits is vital for safeguarding human health in both occupational and environmental settings. This knowledge serves as the foundation for establishing appropriate safety measures and regulations to mitigate the risks associated with off-gassing incidents, ensuring the well-being of workers and minimizing adverse environmental impact. Although significant progress has been made in understanding and addressing the risks associated with biomass off-gassing, further research is needed to explore areas like long-term exposure effects, mixture toxicity, and the impact on ecosystems:

☐ Comprehensive characterization of toxic compounds: There is a need for further research to comprehensively identify and characterize the full spectrum of toxic compounds emitted during biomass oxidation. Advanced analytical techniques such as mass spectrometry (Osman, 2020), gas chromatography

(Huang et al., 2020), and infrared spectroscopy (Bi et al., 2021) can be employed to determine the specific composition and concentrations of these compounds, enabling more targeted control strategies to minimize their release and potential harm to human health and the environment;

- Quantification of exposure levels: Accurate measurement and quantification of actual exposure levels to airborne fast-acting toxic chemicals are necessary in distinct settings, including occupational and residential environments. Personal air sampling (Paris et al., 2023; Škrbić et al., 2020), area monitoring, and biomonitoring (Engelsman et al., 2020) can be utilized to provide data on concentrations of off-gassing chemicals, considering factors such as ventilation rates, proximity to emission sources, and duration of exposure;
- Long-term health effects: Further research is needed to investigate the potential long-term health effects of chronic exposure to off-gassing emissions. Cross-sectional, longitudinal (Manaye et al., 2022) and cohort studies (Zhou et al., 2023) can be conducted to track health outcomes over time, establishing associations between off-gassing exposure and chronic health effects;
- Assessment of environmental impacts: Research should assess the effects of emissions on air quality, climate change, and ecosystem health. Atmospheric modeling techniques (Seigneur and Dennis, 2011) can simulate the dispersion and transport of emitted pollutants, providing insights into their potential effects on the environment;
- Evaluation of safety measures and regulations: Continuous evaluation of safety measures and regulations is vital to ensure their effectiveness and identify areas for improvement (Alakoski et al., 2016). Comparative studies and evaluations can inform the establishment of best practices and guidelines to protect workers and the public.

4.3. The Diverse Universe of VOCs: Chemical Safety and Human Hazards

A diverse range of approximately 150 distinct VOCs has been identified in woody biomass through spectrometric and chromatographic techniques. These VOCs are classified into ten families, with FAMEs comprising 24.2% of the total (**Fig 7**).

However, significant concerns arise due to their corrosive and hazardous nature, posing risks to human health. Terpenes (15.7%) exhibit properties like high flammability, acute toxicity to aquatic life, and potential irritation of the skin, eyes, and respiratory tract. Aldehydes (14.4%), such as hexanal, acetaldehyde, and formaldehyde, are associated with occupational discomfort and explosion risks. Specific aldehydes have established occupational exposure limits (Svedberg et al., 2004).

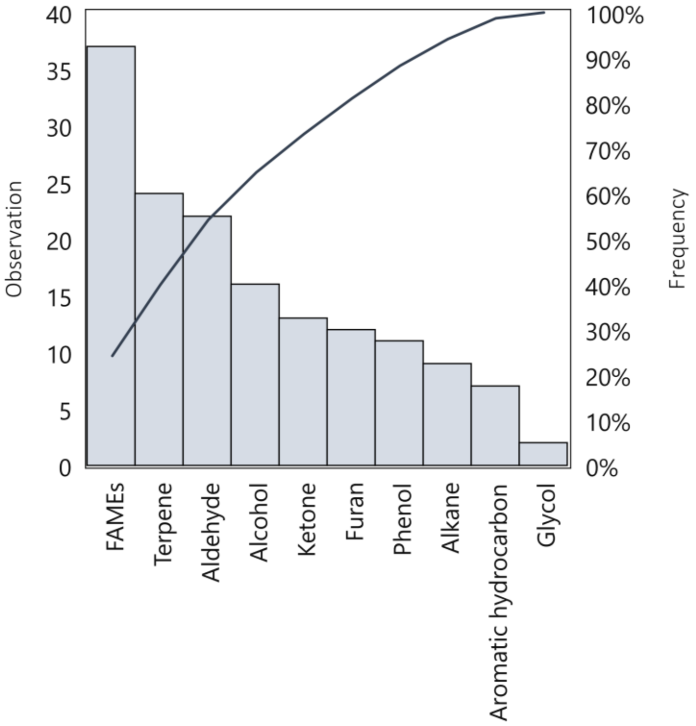

Fig 7. Classification of non-methane volatile organic compounds (VOCs) in woody biomass. The data shows that FAMEs constitute 24.2% of the collection, exhibiting corrosive effects and acute toxicity. Terpenes account for 15.7%, displaying high flammability and potential irritations. Aldehydes make up 14.4%, associated with occupational discomfort and explosion risks. Understanding toxicological implications and specific hazards of these compounds is essential for safety protocols. Continued research and proactive strategies are necessary for effective safety practices in relevant industries.

Chemical hazards include irritants (38.1%), flammables (24.8%), harmful to health (12.9%) and aquatic life (9.9%), acute toxicity (7.7%), corrosives (6.6%), and other effects. Eye irritation (54.25%) is most prevalent, followed by skin (35.1%) and respiratory tract (10.65%). Self-ignition and explosion contribute to 21.4% of risks. Some VOCs cause drowsiness and dizziness. Carcinogenicity (2.7%) and mutagenicity (2.4%) occur at lower frequencies (Svedberg et al., 2004).

Future research should focus on mitigation strategies, toxicity assessments, exposure limits, and monitoring methods to ensure safe woody biomass utilization:

☐ Emissions and exposure assessment: Further studies should quantify and characterize VOC emissions from distinct woody biomass types and throughout the conversion process. This includes evaluating VOC concentrations and compositions during various stages, such as storage, drying, torrefaction, and pellet production (Borén et al., 2018, 2017). Assessing worker exposure levels can provide insights into health risks and inform control strategies (Krigstin et al., 2018). Understanding specific VOCs released at each stage can identify high-risk activities requiring targeted measures. Investigating variations in VOC emissions among biomass types can reveal feedstock influences on VOC profiles. Air sampling techniques can establish exposure limits for worker and environmental protection (Paris et al., 2023; Škrbić et al., 2020);

☐ Toxicological impacts and health risks: Research should investigate the toxicological implications of specific VOCs in woody biomass to determine potential health risks (Singh et al., 2023). Studies should evaluate acute and chronic effects using in vitro and in vivo methods, exploring dose-response relationships and toxicity mechanisms. Effects on respiratory, cardiovascular, and nervous systems should be assessed. Carcinogenicity, mutagenicity, and teratogenicity potential require examination. Interaction studies can assess overall VOC emission risks (Singh et al., 2023);

☐ Impact on indoor air quality: Investigate woody biomass off-gassing impact on indoor air quality in residential and commercial settings (Alakoski et al., 2016). Assess VOC levels and health implications, evaluate ventilation systems, air quality monitoring, and control measures. Conduct long-term monitoring to identify indoor dispersion factors. Establish guidelines for indoor air quality maintenance and effective ventilation systems;

☐ Development of safer and low-emission biomass fuels: Explore alternative biomass-to-fuel technologies and formulations to reduce toxic VOC generation (Moreira et al., 2021). Investigate additives, pretreatment methods, and modified production processes for cleaner combustion and lower VOC emissions. Consider gasification (Akhtar et al., 2018) or pyrolysis (Hu and Gholizadeh, 2019) as low-emission biomass conversion approaches;

☐ Risk communication and awareness: Enhance public and occupational awareness of VOC emission risks from woody biomass (Lehna et al., 2017). Develop educational materials, guidelines, and training programs for workers, policymakers, and the public. Assess perceptions and attitudes towards biomass-related risks to improve communication strategies. Promote best practices, safe handling, and personal protective equipment use in educational efforts.

4.4. Provision of Scientific Information for Research and Development in Safety-Sensitive Strategies

4.4.1. Ventilation

In residential and industrial contexts, proper ventilation is crucial for minimizing off-gassing incidents and maintaining a safe environment. Ventilation mechanisms include passive openings and active mechanical systems, ensuring optimal airflow and reducing harmful compound accumulation (Emhofer et al., 2015). In shipping containers, ventilation plays a pivotal role in maintaining acceptable gas concentrations, protecting workers from toxic atmospheres during handling and inspection (Svedberg and Johanson, 2017).

Research and industrial investigations have supported the efficacy and acceptance of ventilation systems in the biomass and bioenergy sector (Simpson et al., 2016). Implementing appropriate ventilation practices not only fosters safer working environments but also protects individuals from exposure to harmful gases. However, it is essential to consider the environmental impact of ventilation systems. Exhaust processes from ventilation can contribute to greenhouse gas emissions, including CO_2 and CH_4, exacerbating global warming. Addressing this challenge requires developing catalytic and eco-compatible designs that recover and utilize these gases as biofuels and bioproducts, aligning with circular economy principles. Closed-loop facilities optimizing operations while minimizing hazardous substance release can improve safety and energy efficiency in industrial settings like warehouses and distribution centers (Johanson and Svedberg, 2020).

Advancing ventilation systems and addressing safety and environmental concerns requires further investigation in several areas:

☐ Optimization of ventilation system designs: Future research should focus on optimizing ventilation system designs to ensure effective airflow and energy efficiency. Computational fluid dynamics (CFD) simulations can be utilized to study airflow patterns and optimize vent and fan placement (Shen et al., 2020). Factors like vent size, placement, and orientation should be investigated for their impact on fresh air distribution and contaminant removal. Interaction with other building systems (Bournet and Rojano, 2022), such as heating and cooling (Lühr et al., 2021), should be considered to optimize overall building performance;

☐ Development of sustainable ventilation solutions: Deeper exploration is needed to develop sustainable ventilation solutions that minimize environmental impact while ensuring air quality control. Research should explore alternative energy sources, like solar or wind power (Hong et al., 2013), for operating ventilation systems. Integration of energy recovery systems, such as heat exchangers, can reduce energy consumption (Li et al., 2022; Liu et al., 2023). Advanced filtration technologies, like electrostatic precipitators or activated carbon filters (Nandan et al., 2021; Vicente et al., 2022), can enhance pollutant removal and improve indoor air quality (Varshney et al., 2022);

☐ Utilization of captured gases: Further research should investigate the utilization of gases captured by ventilation systems as renewable resources. Advanced conversion technologies, such as biological or chemical processes, can transform captured gases into valuable products. CO_2 can be used for algae cultivation or carbon capture and storage (CCS) (Könst et al., 2017). Methane can be harnessed as a renewable fuel source or converted into chemicals through processes like methanotrophic biorefining. The economic viability, scalability, and environmental benefits of these utilization pathways need to be studied;

☐ Closed-loop facilities and emission reduction strategies: More exploration is required to optimize closed-loop facilities and develop effective emission reduction strategies (Svedberg and Johanson, 2017). Integration of advanced sensing and monitoring technologies can promptly detect and address potential leaks or emissions (Fernandez-Anez et al., 2021). Real-time gas sensors, remote monitoring systems, and predictive analytics can help identify and mitigate potential hazards. Understanding the impact of operational factors, like temperature, humidity, and material handling practices, on off-gassing emissions will aid in developing guidelines and best practices for minimizing emissions in closed-loop facilities (Emhofer et al., 2015);

☐ Assessment of ventilation system performance: In-depth assessment of ventilation system performance is essential to guide improvements. Comprehensive field studies should measure air quality parameters, gas concentrations, and occupant comfort in real-world ventilation systems (Svedberg and Johanson, 2017). Long-term monitoring campaigns in various settings will capture ventilation performance variations over time. Evaluating the impact of ventilation systems on indoor air quality, occupant health, and productivity will establish robust performance metrics and guidelines for system design and operation (Emhofer et al., 2015).

4.4.2. Drying

Back's seminal study in 1981 emphasized the importance of mechanical drying in controlling self-heating and off-gassing in hygroscopic biomass. Using hot air to reduce the feedstock's hygroscopicity decreased its water absorption, enhancing resistance to chemical oxidation and biological degradation.

Subsequent studies by Manninen et al. (2002) and Arshadi et al. (2009) further explored mechanical drying's efficacy in improving hydrophobicity and oxidative stability of solid biofuels from specific wood species. Mechanical drying allowed pellets to withstand harsh storage conditions by eliminating excess moisture acquired during field operations, optimizing industrial processing. Post-pelleting interventions, like in-line blowing units, removed residual surface water, achieving an optimal moisture content range of 10-15% suitable for transportation, storage, and handling. The air stream temperature played a critical role in vaporizing water, aldehydes, and ketones from the biomass, resulting in non-methane VOC emissions at 14.65 ppm and specific aldehyde emissions at 5.2 ppb, both within acceptable limits for occupant comfort and mitigating sensory irritation. Caution should be exercised to avoid overheating, which could lead to increased aldehyde emissions up to 23.25 ppb, creating a potentially hazardous work environment with the potential for eye, skin, and upper respiratory tract disorders (Svedberg et al., 2008; Tumuluru et al., 2015).

To advance the knowledge and understanding of mechanical drying of hygroscopic biomass and address potential hazards associated with this process, the following areas warrant consideration in future research endeavors:

- Optimization of drying parameters: To optimize the drying process, further research can explore the influence of various drying parameters on the quality and stability of biomass. This includes investigating the effects of distinct temperatures, air velocities, and residence times on the reduction of hygroscopicity and the prevention of overheating (Paczkowski et al., 2021; Rojcewicz et al., 2023). Understanding the interactions between these parameters and their impact on moisture content, pellet properties, and VOC emissions will contribute to the development of guidelines for safe and efficient drying practices;
- Evaluation of drying techniques and equipment: While mechanical drying is commonly used, there is a need to explore alternative drying techniques and equipment. Comparative studies can be conducted to assess the performance and efficiency of distinct drying methods, such as convective drying, infrared drying, and microwave drying (Yi et al., 2020). Evaluating the energy

consumption, drying rates, and product quality achieved with these techniques will provide insights into their suitability for hygroscopic biomass and aid in the selection of appropriate drying equipment (EL-Mesery and El-khawaga, 2022; Yi et al., 2020);

- Assessment of product stability and shelf-life: The stability and shelf-life of mechanically dried biomass products, such as pellets, need to be evaluated over extended periods. Long-term studies can assess the impact of storage conditions, such as temperature and humidity, on the quality, degradation, and off-gassing of the dried biomass (Alakoski et al., 2016). This will provide valuable information on the storage requirements and optimal shelf-life of the dried biomass products, enabling better management of inventory and minimizing potential hazards associated with long-term storage;
- Life cycle analysis and environmental impact assessment: Conducting a comprehensive LCA of the mechanical drying process is essential to evaluate its overall environmental impact (Muazu et al., 2017). This includes considering the energy consumption, greenhouse gas emissions, and other environmental burdens associated with the drying equipment, transportation, and waste management. Additionally, assessing the environmental impact of distinct drying methods and comparing them to other biomass drying techniques will provide insights into the sustainability and environmental performance of mechanical drying (Yi et al., 2020);
- Integration of drying with other biomass processing steps: Investigating the integration of mechanical drying with other biomass processing steps can enhance process efficiency and product quality. Research can explore the potential synergies between drying and other processes, such as grinding (Ferreira et al., 2020), torrefaction (Chen et al., 2020), and densification (Cui et al., 2021). Understanding the interactions between these processes and their impact on energy consumption, product characteristics, and emissions will enable the development of integrated biomass processing systems that maximize resource utilization and minimize environmental impact;
- Understanding moisture migration and internal drying mechanisms: Investigating the moisture migration and internal drying mechanisms within

hygroscopic biomass during the drying process is crucial. This involves studying the movement of moisture within the biomass particles, the effects of particle size and structure on moisture distribution, and the impact of drying parameters on moisture removal (Pecha et al., 2021). Advanced imaging techniques, such as X-ray tomography (Boigné et al., 2022) or magnetic resonance imaging (MRI) (Qi et al., 2021), can provide insights into the drying behavior at the microscopic level. Understanding the underlying mechanisms will enable the development of more precise drying models and optimize drying conditions to enhance efficiency and prevent the formation of localized high-moisture regions;

☐ Characterization of VOC emissions: While the emissions of VOCs during biomass drying have been investigated to some extent (Yi et al., 2020), further research is needed to comprehensively characterize the emitted VOCs. This includes identifying and quantifying specific VOCs, studying their formation pathways, and investigating the influence of drying parameters and biomass composition on VOC emissions (Yi et al., 2020). Additionally, understanding the chemical reactions and transformation of VOCs during drying and their potential health and environmental impacts will aid in the development of effective emission control strategies and guidelines;

☐ Assessment of combustion and gasification performance: Evaluating the combustion and gasification performance of mechanically dried biomass is essential to optimize its utilization as a fuel source. Research can focus on assessing the combustion characteristics, such as ignition behavior, burnout efficiency, and pollutant emissions, as well as the gasification reactivity and syngas composition. Investigating the effects of drying conditions, biomass properties, and drying-induced changes in the fuel characteristics on combustion and gasification performance will provide insights into the optimal drying parameters for distinct biomass feedstocks and end-use applications (Yi et al., 2020);

☐ Development of advanced drying technologies: Further research can explore the development of advanced drying technologies tailored for hygroscopic biomass. This includes the application of innovative methods, such as superheated steam drying (Adamski et al., 2021), vacuum drying

(Stramarkou et al., 2021), or combined drying techniques (Meng and Wang, 2020). Investigating the feasibility, energy efficiency, and drying performance of these technologies will contribute to the development of more efficient and sustainable drying processes for hygroscopic biomass, minimizing energy consumption, and improving product quality;

☐ Economic analysis and cost optimization: Conducting economic analyses and cost optimization studies are crucial to assess the viability and competitiveness of mechanical drying processes. This involves evaluating the capital and operating costs of drying equipment, considering the cost of energy consumption, maintenance, and labor (Perazzini et al., 2021). Investigating the potential for process integration, waste heat recovery, and utilization of renewable energy sources can help reduce drying costs and enhance the economic feasibility of biomass drying operations.

4.4.3. Torrefaction

Torrefaction is a thermochemical process that transforms biomass into hydrophobic, stable, and carbon-dense products through controlled pyrolysis in an oxygen-deficient environment at 200 to 320°C (Xi et al., 2021). It effectively mitigates off-gassing issues in biomass by removing moisture and volatile compounds. The technique has been effectively applied to commonly utilized feedstocks in the wood pellet industry, such as Scots pine, Norway spruce, Douglas-fir, and Chinese fir.

The combination of pyrolysis and oxidation has led to high-quality solid biofuels with reduced emissions of CO and non-methane VOCs, enhancing worker safety (Chen et al., 2020). Torrefied pellets have lower CO emissions than conventional pellets (Tumuluru et al., 2015). Oxidative torrefaction lowers VOC emissions compared to untreated biomass (Xi et al., 2021), although it may increase the concentration of hazardous compounds like furans and ketones (Cruz Ceballos et al., 2015; Litwinienko, 2004).

Implementing torrefaction on an industrial scale can be costly, and higher temperatures increase the risk of self-heating, fire, or explosion. Cooling methods like heat exchange or water spraying (Lühr et al., 2021) are used to prevent self-ignition, but alternatives like steam explosion (Borén et al., 2018, 2017), ozonation (Rahman et al., 2017), SFE (Attard et al., 2016), or antioxidants (Arshadi et al., 2018; Sedlmayer et al., 2020; Moreira et al., 2021;) are being explored to develop safer production methods.

To advance the understanding and application of torrefaction as a thermochemical process for biomass transformation and off-gassing control, several areas warrant further investigation:

☐ Process optimization: In-depth research is needed to optimize torrefaction process parameters, including temperature ranges, residence times, and feedstock characteristics. Understanding the effects of these parameters will lead to efficient and consistent torrefaction operations. Exploring distinct pre-treatment methods like steam explosion (Borén et al., 2018, 2017) or chemical additives (Sedlmayer et al., 2020) could enhance process efficiency and product quality;

☐ Emission reduction and control: More research is needed on emission reduction and control strategies. Using catalysts or additives during torrefaction to mitigate hazardous compound formation could further reduce emissions (Ong et al., 2019). Investigating off-gas treatment technologies, like wet, dry, or hybrid scrubbers (Costa et al., 2023), filters (Cornette et al., 2020), or adsorption methods (Kim et al., 2022), will improve air quality during torrefaction. Understanding emission fate and behavior can help develop comprehensive control strategies;

☐ Safety considerations: Safety is critical in torrefaction processes, especially regarding self-heating, fire, and explosion risks (Arriola et al., 2020). Research should focus on cooling methods (Olugbade and Ojo, 2020) to prevent self-ignition and ensure safe storage and handling. Innovative cooling techniques, like heat exchange systems (Liu et al., 2023) or advanced air circulation (Yek et al., 2021), can maintain ambient temperatures and minimize thermal runaway risk. Understanding cooling method effects on torrefied biomass properties ensures product quality and safety;

☐ Scale-up and cost-effectiveness: Research should focus on cost-efficient and scalable torrefaction technologies, optimized process designs, and integration into existing biomass supply chains. Evaluating economic feasibility, energy requirements, and environmental impacts of large-scale torrefaction plants will inform industry stakeholders and policymakers. Exploring synergies with other biomass conversion processes or energy systems, like combined heat and power (CHP) (Cardozo et al., 2014), can enhance economic viability and sustainability.

4.4.4. Steam Explosion

Steam explosion is a thermochemical process that involves subjecting biomass to vapor at specific temperatures and pressures, followed by rapid decompression (Borén et al., 2018, 2017). This process effectively breaks down the lignocellulosic structure of biomass, resulting in the formation of a fibrous liquid. Steam explosion offers versatility and opportunities for upgrading solid biofuels and bioproducts while controlling off-gassing emissions (Borén et al., 2018, 2017).

Researchers have extensively investigated the efficiency of steam explosion in decomposing extractives and hemicelluloses to reduce emissions from solid biofuels. Borén et al. (2017) conducted experiments using pilot-scale batch reactors, focusing on Scots pine and Norway spruce wood. They observed emissions of furfural and alpha-pinene in steam-exploded forest products, particularly in the bark. Emissions varied based on operating temperatures ranging from 180 to 215 °C and pressures of 0.95 to 2 MPa. At temperatures of 180 to 200 °C, emissions of furfural and alpha-pinene were detected, with a subsequent 20% increase observed at higher temperatures. However, further temperature increases to 200 to 215 °C resulted in a significant 75% reduction in emissions, indicating a compensatory effect on thermoreactive hemicelluloses and VOCs.

The introduction of N_2 as an oxidant in the steam explosion process has shown promising results in effectively removing volatiles, comparable to operating at higher temperatures. Borén et al. (2018) investigated the use of N_2 injection in steam explosion of woody biomass, resulting in the production of low-emission solid biofuels. The alternative product emitted lower levels of furfural compared to the reference batch when stored at distinct temperatures. Further temperature increases from 190 to 215

°C led to additional reductions in emissions, highlighting the importance of finding the appropriate operating conditions to optimize the process.

While steam explosion holds promise as a thermochemical process for biomass transformation and emission control, further research is needed to optimize process parameters, characterize the products, control emissions, scale up the process, conduct life cycle assessments, and develop process modeling and simulation tools:

☐ Optimization of process parameters: Research should focus on optimizing steam explosion parameters such as temperature, pressure, and residence time to maximize product yields and minimize volatile compound emissions (Yu et al., 2022). Understanding the influence of biomass types, feedstock characteristics, and moisture content will lead to guidelines for efficient and consistent operations;

☐ Emission control: While steam explosion reduces emissions, further studies should explore techniques to minimize volatile compound release (Borén et al., 2018). Investigating the use of alternative oxidants and developing post-treatment methods (Yu et al., 2022) or purification (Cornette et al., 2020) will contribute to emission control strategies;

☐ Scale-up and process integration: Research should evaluate the feasibility of scaling up steam explosion to larger industrial systems. This involves investigating reactor design, process control, feedstock handling, and integration with downstream processing units to maintain efficiency and emission control;

☐ Life cycle assessment and economic analysis: Conducting life cycle assessments will quantify the environmental impacts of steam explosion (Bilal and Iqbal, 2020), while economic analysis will evaluate its cost-effectiveness (Baral and Shah, 2017). These assessments will provide insights into the overall sustainability and economic viability of the process;

☐ Integration with existing industries and value chains: Exploring the integration of steam explosion with other processes and industries can enhance biomass resource utilization and promote circular economy principles. Identifying synergies with pulp and paper production (Khadraoui et al., 2023), bioenergy generation, or biorefineries (Chandel et al., 2021) will enhance resource utilization and by-product valorization;

☐ Process modeling and simulation: Developing accurate and predictive process models for steam explosion will aid in optimization, scale-up, and control (khan et al., 2023). Computational modeling can provide insights into the effects of process parameters on product yields and emissions, enhancing process efficiency and effectiveness.

4.4.5. Ozonation

Ozonation is a chemical process that utilizes ozone (O_3) to facilitate oxidation and reduction on organic compounds, breaking carbon-carbon double bonds in alkenes and azo compounds (Hassan et al., 2021). The resulting products depend on the reactants and reaction conditions. However, the configuration of the ozonolytic reactor plays a significant role in generating and converting Criegee intermediates, which can lead to the production of VOCs. To mitigate VOC formation, reactor design can be optimized to interrupt intermediate formation or restrict their conversion.

Rahman et al. (2017) conducted a study using an ozone-releasing device to treat feedstock like Scots pine and Norway spruce wood. The device operated at various flow rates and durations, successfully eliminating alkenes, alkynes, and azo compounds. As a result, an alternative product was formed with significantly reduced off-gassing compared to the control. In another study by Rahman and Hopke (2016), ozonolytic cleavage using 6000 ppm O_3 for 7 minutes led to a significant reduction in CO levels within fuel-grade pellets. While ozonolytic cleavage effectively regulates off-gassing from woody biomass by eliminating nucleophilic and electrophilic compounds (Hassan et al., 2021), it is essential to recognize that the process can also yield alcohols, aldehydes, and ketones, which may pose direct hazards to human health. Therefore, strict operational controls and precautions must be in place to ensure the safety of occupational and human health during ozonation techniques.

Further research is needed to optimize the ozonation process, including reactor design and reaction conditions, with the goal of minimizing the formation of hazardous compounds and maximizing off-gassing control in woody biomass. Comprehensive risk assessments should also be conducted to evaluate potential health and environmental impacts from ozonation treatment in the production of solid biofuels:

☐ Optimization of ozonation conditions: Further research should explore the effects of various parameters on off-gassing control and the formation of hazardous compounds. Determining the optimal ozone concentration, reaction time, and flow rate for specific biomass feedstocks is crucial (Rahman et al., 2017). Investigating the interactions among these parameters will help identify the optimal conditions for minimizing off-gassing while ensuring process safety;

☐ Reactor design and engineering: Research can explore innovative reactor designs and configurations to optimize the ozonation process (Rahman et al., 2017). Investigating the use of catalysts or adsorbents in the reactor system can enhance off-gassing control and reduce the formation of harmful by-products. Optimizing the reactor geometry and residence time can influence the reaction kinetics and the distribution of ozonolysis products;

☐ Occupational health and safety considerations: Comprehensive risk assessments and safety protocols should be developed for workers involved in ozonation treatment. Evaluating occupational exposure levels to ozone and other by-products and assessing potential health risks will help ensure worker safety. Guidelines for handling ozonation equipment, managing by-products, and implementing proper ventilation systems are essential (Rahman et al., 2017);

☐ Environmental impact assessment: Assessing the environmental impact of ozonation treatment is critical. Research should focus on evaluating the potential release of ozone and by-products into the environment and their impact on air quality and ecosystems (Rahman et al., 2017). Studying the formation of secondary pollutants will help develop strategies to mitigate adverse environmental effects and ensure the sustainable implementation of ozonation in biomass processing.

4.4.6. Supercritical Fluid Extraction

Supercritical fluid extraction using CO_2 as the solvent has proven effective in controlling off-gassing in woody biomass (Arshadi et al., 2012; Attard et al., 2016). Attard et al. (2016) conducted a study on Scots pine pellets and found that SFE with CO_2 reduced off-gassing by 84.6% to 93.3%. Treated pellets emitted lower concentrations of CO, CO_2, and CH_4 compared to the control, demonstrating the effectiveness of SFE with CO_2. The process was operated at temperatures of 40 to 80 °C and pressures of 35 to 70 MPa, which reduced oxidizable organic compounds in the feedstock.

In a previous investigation by Arshadi et al. (2012), SFE efficiently extracted aldehydes and ketones from woody material, leading to a significant 72.05% reduction in the autogeneration of VOCs. However, the extraction efficiency for some compounds, like oxodehydroabietic and dodecanoic acids, was comparatively lower, indicating a dependence on the chemical characteristics of fatty or resinous compounds. To address this, the use of co-solvolysis with ethanol has been proposed to enhance extraction efficiency. Ethanol, as a polar solvent, can compensate for the limitations of supercritical CO_2 when interacting with non-polar compounds during the extraction process. Further research is needed to fully understand the mechanisms underlying the extraction of fatty and resin acids through SFE with CO_2. Additionally, investigating the potential use of co-solvents and alternative extraction techniques can optimize the SFE process, leading to safer and more effective off-gassing control in solid biofuel production:

☐ Optimization of SFE parameters: Further research is needed to explore the effects of various parameters on extraction efficiency, selectivity, and yield of target compounds (Arshadi et al., 2012; Attard et al., 2016). Parameters such as temperature, pressure, extraction time, and CO_2 flow rate can significantly impact the performance of SFE. Investigating the interactions among these parameters will help identify the optimal operating conditions that maximize the removal of off-gassing precursors while minimizing energy consumption and processing time (Arshadi et al., 2012; Attard et al., 2016);

- Investigation of complex chemical interactions: The extraction of fatty and resinous compounds from woody biomass through SFE with CO_2 involves complex chemical interactions (Attard et al., 2016). Further research is necessary to deepen our understanding of these interactions and the mechanisms underlying the extraction process (Arshadi et al., 2012). Exploring the solvation behavior of nonpolar compounds in supercritical CO_2 and the influence of biomass composition on their extraction efficiency will help optimize the process. Additionally, investigating the factors that affect the selectivity of SFE, such as compound polarity, molecular weight, and functional groups, will contribute to improving off-gassing control (Attard et al., 2016);
- Co-solvent and additive utilization: The addition of co-solvents or additives, such as ethanol, can enhance the extraction efficiency and selectivity of SFE with CO_2. Further research is needed to explore the impact of distinct co-solvents (Radzali et al., 2020), their concentrations, and their interactions with CO_2 on the extraction process (Tzima et al., 2023). Additionally, exploring the potential synergistic effects of additives, such as surfactants or complexing agents (Tzima et al., 2023), can provide valuable insights into improving the efficiency and selectivity of the SFE process;
- Comprehensive compound analysis: Detailed analysis of the compounds extracted through SFE is crucial for evaluating the effectiveness of the process and assessing potential risks associated with the extracted compounds (Hurtado et al., 2023). Further research should focus on comprehensive identification and quantification of VOCs, aldehydes, ketones, and other potentially hazardous compounds in the extracted product. Advanced analytical techniques, such as gas chromatography-mass spectrometry (GC-MS), can help identify and quantify a wide range of compounds present in the extracted biomass (Mathur et al., 2022).

4.4.7. Antioxidant Addition

The degradation of biofuels and biochemicals can result in off-gassing through various oxidation processes, including autoxidation, photooxidation, and enzymatic oxidation (Varatharajan and Pushparani, 2018). To address this issue, researchers are exploring the potential of antioxidants, commonly used in the food sector for preservation, as a solution for controlling off-gassing in biomass.

Several synthetic antioxidants, such as acetylsalicylic acid (ASA) (Sedlmayer et al., 2020), TBHQ, propyl gallate (Arshadi et al., 2018), and tobacco extract (Moreira et al., 2021), have shown promise in scavenging ROS and enhancing the resistance of BTS fuels to oxidation. Research has demonstrated their effectiveness in reducing emissions of CO, CO_2, and VOCs in fuel-grade pellets. However, it is crucial to consider potential hazardous compounds, such as volatile and semi-volatile compounds and heavy metals, that may be present in certain antioxidants like tobacco extract (Moreira et al., 2021).

To utilize antioxidants effectively for off-gassing control in biomass, future research should focus on standardizing application methods and concentrations, optimizing operating conditions, evaluating bifunctional formulations, and exploring waste-to-product pathways for sustainable alternatives. Safety, cost, and potential environmental impacts should be carefully considered in their utilization. Therefore, several areas require improvement and development:

☐ Safety and environmental impact assessment: Further studies are needed to comprehensively evaluate the safety and potential environmental impacts of distinct antioxidants. This includes conducting detailed analyses to assess the presence of hazardous compounds, such as volatile and semi-volatile compounds and heavy metals, in antioxidants (Moreira et al., 2021). It is crucial to understand the potential risks associated with the use of antioxidants and ensure that their inclusion in biomass does not introduce new hazards to human health or the environment. Investigating their fate during biomass processing, combustion, and disposal can provide insights into potential environmental impacts;

☐ Standardization of application methods and concentrations: To establish effective and consistent utilization of antioxidants, it is important to standardize the application methods and concentrations employed. This includes determining the optimal dosage of antioxidants for distinct biomass feedstocks and processing conditions (Arshadi et al., 2018; Moreira et al., 2021; Sedlmayer et al., 2020). Standardization will facilitate the comparison of antioxidant performance across distinct studies, ensure reproducibility, and enable the practical implementation of antioxidants in biomass processing on a larger scale;

☐ Evaluation of bifunctional formulations: Investigating the potential of combining multiple antioxidants or employing bifunctional formulations can enhance the effectiveness of antioxidants in controlling off-gassing. By targeting distinct oxidation pathways simultaneously, bifunctional formulations may exhibit synergistic effects, resulting in improved antioxidant performance (Moreira et al., 2021). Further research is needed to identify compatible combinations of antioxidants, understand their interactions, and optimize their formulations to maximize their efficacy in scavenging reactive species and mitigating off-gassing;

☐ Balancing operating conditions: Achieving the optimal balance of operating conditions, such as temperature, pressure, and residence time, is crucial for maximizing the effectiveness of antioxidants in controlling off-gassing. Research should focus on understanding the influence of these variables on antioxidant performance and identifying the optimal conditions for antioxidant application (Moreira et al., 2021). This includes investigating the kinetics of antioxidant reactions under distinct conditions and assessing the impact of these conditions on antioxidant stability and activity (Moreira et al., 2021);

☐ Waste-to-product pathways: Exploring waste-to-product pathways for antioxidants can contribute to the development of sustainable and cost-effective solutions. This involves investigating the potential utilization of waste or by-products from other industries as a source of antioxidants for biomass processing. Additionally, evaluating the feasibility of recycling or reusing antioxidants extracted from biomass can enhance the overall sustainability of the process, reduce waste generation, and minimize the reliance on synthetic antioxidants (Moreira et al., 2021);

☐ Long-term stability and performance: Assessing the long-term stability and performance of antioxidants in biomass is crucial to ensure their effectiveness over extended periods of storage and use. Long-term studies can provide insights into the durability and shelf life of antioxidants, including their degradation pathways and potential formation of by-products (Moreira et al., 2021). Evaluating the impact of storage conditions, such as temperature and humidity, on antioxidant stability will help determine the optimal storage and handling practices to maintain their effectiveness (Arshadi et al., 2018; Sedlmayer et al., 2020).

5. Conclusion

Our study underscores the significant risks associated with biomass utilization in residential and industrial settings, particularly the generation of hazardous gases. However, through our meta-analysis, we have identified and evaluated a range of technocentric solutions that effectively mitigate these risks. The implementation of preventive and mitigatory practices such as ventilation, drying, thermochemical pre-treatment (torrefaction and steam explosion), ozonation, SFE, and antioxidant addition has demonstrated remarkable results. These strategies enhance the quality and integrity of solid biofuels and storage's suitability, significantly decreasing emissions of CO, CO_2, CH_4, and VOCs. The statistical analyses, including LMM, BFA, and FPA, provide robust evidence supporting the effectiveness of these strategies. They have led to a 25% average decrease in emissions and a strong logarithmic Bayes factor ($\log_e$ BF) estimation of 4.5, indicating significant disparities in off-gassing emissions between treatment and control groups. By prioritizing the adoption of these preventive and mitigatory measures, we can protect occupational safety, human health, and the environment. These strategies contribute to the development of cleaner and safer biomass energy systems, promoting sustainable energy development and a more sustainable future. However, we acknowledge the potential for publication bias in small-sized studies, and further research is needed to strengthen the conclusions and address this limitation.

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Supplementary Material

SM 1. Research Performance and Development: Promoting North-North Collaboration

The literature on biomass off-gassing has experienced remarkable growth, with a substantial increase in publications from 1981 to 2021 (**Fig S1**). Over the years, distinct periods have been dedicated to fundamental studies, accident reports, and technology development in this field. This research has garnered significant attention, as evidenced by approximately 4800 citations and a field-weighted citation impact (FWCI) of 1.15, reflecting its influence compared to similar publications in related areas. Additionally, the literature covers a range of strategies for off-gassing control, with ventilation being the most studied; however, researchers have also explored alternative methods, such as mechanical drying, thermochemical pre-treatment, ozonation, SFE, and antioxidant addition.

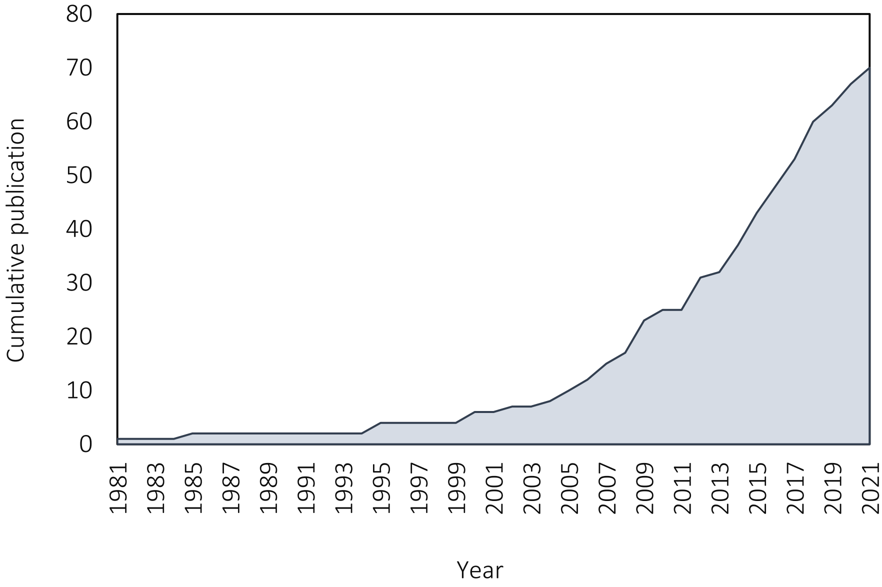

Fig S1. Growth of scientific literature on biomass off-gassing. Publications have grown significantly from one in 1981 to seventy in 2021, reflecting its increasing importance across various fields. The research can be categorized into three periods: 1981-2000 focused on fundamental studies (32.85%), 2001-2010 on accident reports and risks (57.15%), and 2011-2020 on technology development (10%).

The research in biomass off-gassing is supported by various funding sources, with the Natural Sciences and Engineering Research Council of Canada emerging as a leading supporter. This financial backing signifies the recognition of the importance of studying and controlling biomass off-gassing to address environmental challenges. However, collaboration is a vital aspect in this field, and there is a pressing need to focus on North-South collaboration to foster a balanced and inclusive approach.

Including researchers from the Global South in biomass off-gassing research is crucial to generating context-specific solutions and addressing environmental and social justice issues specific to these regions. Researchers from the Global South bring diverse perspectives to the field, enriching the research and promoting a more equitable distribution of knowledge and expertise. Such collaboration empowers researchers in the Global South to actively contribute to addressing this global challenge.

By bridging the North-South divide in biomass off-gassing research, we can achieve a more balanced, inclusive, and sustainable approach to its control. This collaborative effort aligns with global sustainability principles, ensuring that all countries and communities can actively participate in finding effective solutions. By working together, researchers from distinct parts of the world can collectively contribute to a better understanding of biomass off-gassing and develop strategies that minimize its impact on the environment and communities worldwide.

SM 2. Interpretation of Meta-Analysis Findings: Limitations and Directions for Improving Robustness and Reliability

SM 2.1. General

The findings of our meta-analysis should be interpreted considering several limitations. To begin with, potential publication bias exists since we relied solely on published papers, possibly excluding valuable insights from unpublished or grey literature and introducing bias. Future studies should include a broader range of sources to mitigate this bias. Additionally, language bias is a concern as our search was limited to English language papers, potentially omitting relevant studies in other languages. Future research should consider translation services or collaborations to include more diverse studies.

Furthermore, the variability in study designs among selected papers introduces inconsistency and may affect comparability. We must acknowledge these differences and their implications for interpreting results accurately. Moreover, geographic bias is present, with a dominance of research from certain regions, limiting generalizability to other contexts. Caution should be exercised when extrapolating findings to diverse regions with distinct practices and regulations.

Equally relevant is the lacked sufficient bibliometric data to assess the impact of technocentric solutions on off-gassing from solid biofuels other than pellets. Further research is needed to understand their significance for other biomasses. Additionally, while our study focused on protective and mitigatory practices and biomass off-gassing, other factors like material composition, handling, and off-gassing monitoring may influence emissions. Furthermore, our analysis represents the current understanding and may not account for future developments in the field. Researchers should stay updated and incorporate new evidence into their assessments.

Acknowledging these limitations promotes research transparency and aligns with ethical considerations. It encourages further development, improvement, and innovative methodologies in the field. Transparent reporting fosters trust and credibility in scientific research and informs evidence-based decision-making by stakeholders and policymakers.

SM 2.2. Specific

Our meta-analysis utilizes a diverse array of statistical methodologies, including density curve analysis, LLM, BFA, logarithmic data transformation, and FPA. These methodologies effectively address statistical challenges like non-normal data distribution, heterogeneity, nested structures, and complex relationships within the dataset. By incorporating these methodologies, we enhance the validity, reliability, and scientific rigor of our study on preventive and mitigatory biomass off-gassing control techniques.

Density curve analysis helps assess the distributional characteristics of the data and guides the selection of appropriate statistical methods based on normality assumptions (Cacioppo et al., 2013). Linear mixed-effect model analysis addresses heterogeneity and nested structures, capturing variation at distinct levels and improving the reliability of estimates (Luutu et al., 2022). Bayesian factor analysis uncovers latent factors underlying the observed variables (Zhang and Schuster, 2021), enhancing our understanding of relationships within the dataset. Logarithmic data transformation normalizes non-normally distributed data (Rodríguez-Barranco et al., 2017), improving the suitability of statistical models. Funnel plot analysis assesses publication bias and the potential impact of small-study effects (Hariyanto et al., 2021), ensuring the robustness and reliability of our findings.

While our meta-analysis has benefited from the application of these rigorous statistical methodologies, there are still opportunities for further enhancement. To address heterogeneity more comprehensively, advanced methods such as Bayesian hierarchical models or network meta-analysis can be explored. These techniques account for additional sources of variability and incorporate informative prior distributions, yielding more robust estimates and improving the reliability and generalizability of the results:

☐ Handling heterogeneity: Despite using LMM to address heterogeneity, residual variation might persist in our meta-analysis. To enhance robustness, we should consider incorporating advanced techniques such as Bayesian hierarchical models or network meta-analysis (Ma et al., 2018). These methods have the capability to capture additional variability and utilize informative prior distributions, which will ultimately bolster the reliability and generalizability of the results;

☐ Managing missing data: While maximum likelihood estimation in LMM is effective in handling missing data, it is essential to explore alternative methods such as multiple imputation (Kambach et al., 2020) or robust estimation (Pustejovsky and Tipton, 2022). These alternative methods can increase flexibility and robustness in handling missing observations, ultimately strengthening the validity and reliability of the results obtained from the meta-analysis;

☐ Considering time-to-event data: In cases where the studies involve time-to-event outcomes, it is advisable to incorporate survival analysis techniques such as Cox proportional hazards models (Sattar et al., 2022). This type of analysis takes into account time-dependent factors, providing comprehensive insights into the relationship between prevention or mitigation and biomass off-gassing outcomes, thus enhancing the depth of understanding in the meta-analysis;

☐ Assessing sensitivity analysis: To ensure the robustness of our results, conducting critical sensitivity analyses is crucial. We should explore various scenarios, including excluding studies with high bias risk or distinct methodologies (Hariyanto et al., 2021). These sensitivity analyses play a vital role in evaluating the stability and reliability of the findings, thereby reinforcing the credibility of the entire meta-analysis;

☐ Addressing complex interactions: Recognizing the presence of complex intervention-emission interactions is important. To handle these intricacies, we should employ advanced techniques like machine learning or structural equation modeling (Groth et al., 2019). Such methods are capable of capturing the intricate relationships between variables, ultimately enriching the overall analysis and improving its accuracy;

☐ Incorporating individual participant data (IPD): While aggregated data can be sufficient, considering the use of individual participant data (IPD) from included studies can be highly beneficial (Ximenes et al., 2023). IPD meta-analysis provides more detailed information, allowing us to accommodate participant variations and enabling subgroup analyses or exploration of treatment effect modifiers (Ximenes et al., 2023). By incorporating IPD, we can significantly enhance our understanding of the effects of distinct technocentric solutions on biomass off-gassing emissions.

By further exploring and addressing these gaps and potential areas, we can significantly contribute to the advancement of statistical analysis in meta-analysis.

Researchers should give due consideration to these directions to strengthen the rigor, accuracy, and interpretability of their findings, ultimately fostering a more profound understanding of the research field and its implications.

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CHAPTER III – Fuel-Flexible Biomass Off-Gassing: Antioxidant Potential of Agricultural Residues for Biogenic Additives to Low-Emission Wood Pellets

An alternate version of Chapter III is presently accessible as a research article on the web at https://doi.org/10.1007/s13399-023-04869-4

Abstract

Biomass energy is gaining attention as a renewable alternative to fossil fuels due to its potential to mitigate greenhouse gas emissions. However, the combustion of fuel-flexible biomass can lead to the release of pollutants, posing environmental and health concerns. This study aimed to evaluate the antioxidant potential of peanut shells, spent coffee grains, and sugarcane leaves as additives for wood pellets to control off-gassing. Results showcased a sigmoidal nature in the generation of CO_2 and degradation of extractives, indicating autogenous deterioration of the pellets. The Gompertz model effectively captured this behavior, enabling accurate estimation of alpha, beta, and k parameters. The control group exhibited an alpha value of 2995.4 mg kg^{-1}, representing the maximum CO_2 emissions or extractive degradation without additives. Incorporating peanut shells, spent coffee grains, and sugarcane leaves resulted in reduced alpha values of 2732.1, 2405.2, and 2472.4 mg kg^{-1}, respectively, indicating their capacity to decrease specific CO_2 emissions and decelerate extractive degradation. These findings suggest the antioxidant potential of the additives in mitigating CO_2 emissions and extractive degradation processes. However, the higher ash content in pellets containing biogenic additives poses challenges in terms of physical deposits formation, and the presence of nitrogen and sulfur raises concerns about potential emissions of hazardous gases during pellet combustion. Further research and optimization are necessary to address these trade-offs. Enhancing pellet quality, manufacturing processes, and off-gassing control contribute to the viability of biomass energy as a sustainable alternative to fossil fuels.

Keywords: carbon dioxide; extractives; peanut shells; reactive oxygen species; spent coffee grains; sugarcane leaves.

1. Introduction

Biomass energy has emerged as a promising alternative to fossil fuels due to its renewable nature and potential to mitigate greenhouse gas emissions [1]. Biomass pellets, a key form of biomass fuel, offer several advantages such as high energy density, convenient storage and transportation, and efficient combustion. However, the combustion of biomass pellets can result in the release of various pollutants, including volatile organic compounds (VOCs), nitrogen oxides (NO_x), carbon monoxide (CO), particulate matter, and other hazardous substances. These emissions have significant environmental and health implications, contributing to air pollution, smog formation, and adverse effects on occupational safety and human health [2].

The management of off-gassing during biomass pellet combustion has therefore become a crucial consideration in biomass energy systems [3]. Off-gassing refers to the unregulated release of gases and pollutants during the combustion process. Controlling off-gassing is vital to minimize environmental degradation, improve air quality, and ensure the sustainable utilization of biomass energy [4]. To address these challenges, the utilization of additives in the biomass pelletization process has gained attention as a means to modify the chemical composition, physical properties, and combustion behavior of biomass pellets [5].

The incorporation of additives into pellets offers a range of benefits for off-gassing control [6]. These additives encompass natural binders, lubricants, antioxidants, anti-slagging agents, and combustion catalysts, among others [7–9]. By selectively introducing these additives, the structural integrity of biomass pellets can be enhanced, reducing disintegration and dust formation. Additionally, additives with hydrophobic properties can improve moisture resistance, maintaining pellet stability and preventing moisture-related issues. Furthermore, specific additives can influence combustion characteristics, enhancing fuel-air mixing, improving combustion efficiency, and reducing emissions of pollutants [8].

The optimization of additive selection is critical in achieving effective off-gassing control [8]. Distinct agricultural residues, such as peanut shells, spent coffee grains, and sugarcane leaves, offer potential as additives due to their unique properties and compositions. Peanut shells, for instance, possess a high lignin content, which acts as a natural binder, enhancing the durability and structural integrity of biomass pellets.

The hydrophobic nature of lignin also contributes to moisture resistance, reducing the risk of pellet degradation [10]. Spent coffee grains, on the other hand, contain residual oils and compounds that increase the energy content of pellets and exhibit catalytic effects, improving combustion performance [11]. The aromatic profile of spent coffee grains can also help mask or reduce undesirable odors associated with biomass feedstocks. Sugarcane leaves, rich in phenolic compounds and natural waxes [12], can enhance the antioxidant potential and lubricating properties of pellets, while regulating moisture absorption and reducing ash-related issues during combustion.

While the potential of agricultural residues as additives in biomass pelletization is recognized [13], further research is needed to optimize their selection and understand their effects on pellet properties and off-gassing control. Investigating the interactions between distinct agricultural residues, their combinations, and their dosages can provide valuable insights into the most effective additive formulations for specific biomass feedstocks [7]. Furthermore, exploring advanced emission control technologies, assessing health and environmental impacts, and considering policy and regulatory frameworks are essential for the wider adoption of biomass energy systems and the achievement of sustainable and environmentally responsible biomass off-gassing control.

Therefore, we designed research to evaluate the antioxidant potential of peanut shells, spent coffee grains, and sugarcane leaves as additives for wood pellets. By assessing the chemical composition, physical properties, and combustion characteristics of these agricultural residues, we seek to determine their suitability as additives for off-gassing control in biomass pelletization. Our scientific study will contribute to the development of effective biogenic additive strategies, optimizing pellet properties, reducing off-gassing emissions, and advancing the sustainability of biomass energy systems.

2. Materials and Methods

2.1. Acquiring Agricultural and Forestry Residues

In the pre-production step of acquiring agricultural and forestry residues for developing antioxidant additives specifically tailored for high-performance pelletization, a meticulous and comprehensive collection process was undertaken. The targeted residues encompassed peanut shells, spent coffee grains, sugarcane leaves, and pinewood sawdust, which were procured as valuable by-products derived from the mechanical harvesting processes implemented in commercial production systems. To ensure that the collected residues were suitably prepared for subsequent physicochemical characterization, an intricate pre-treatment procedure was carried out. This involved subjecting the residues to the processes of milling and sieving. By employing these techniques, particles within the highly specific size range of 0.25-0.45 mm were thoughtfully selected, as they were deemed most appropriate for the subsequent analytical processes [14]. Once the residues had been suitably prepared, a comprehensive array of physicochemical parameters were evaluated to gain a deeper understanding of their characteristics (**Tab S1, Supplementary material**). This analytical assessment entailed the determination of various key properties, each playing a crucial role in the overall evaluation of the residues. To begin with, the moisture content of the residues was determined in accordance with the ASTM E871-82 standard methodology. This particular method relied on subjecting 0.05 kg samples of the residues to a controlled temperature of 105.1±1.5 °C until a state of constant mass was achieved. The attainment of this constant mass signified the elimination of any residual moisture within the samples, thereby allowing for an accurate assessment of the moisture content. The volatile matter content of the residues was determined using the ASTM E871-82 standard procedure. This involved subjecting 0.05 kg samples to a controlled combustion process within an automated furnace operating at a temperature of 900.05±2.85 °C. By measuring the mass remaining after the combustion process, the volatile matter content could be accurately determined, thereby shedding light on the organic compounds present within the residues. The fixed carbon content of the residues was determined through a stoichiometric comparison of the measured elemental components. This analysis was crucial in completing the proximal analysis, which involved quantifying the key components of moisture, volatile matter, and ash content. By calculating the stoichiometric difference between these components, the fixed carbon content could be accurately determined, further enhancing the understanding of the residues' composition [15].

In addition to these assessments, the ash content of the residues was evaluated utilizing the ASTM D1102-84 standard methodology. This involved subjecting 0.05 kg samples to a controlled combustion process within an automated furnace operating at a temperature of 545.15±2.6 °C. The mass remaining after the combustion process provided valuable insights into the inorganic components present within the residues. Furthermore, to gain a comprehensive understanding of the elemental composition of the residues, an elemental analysis was performed. This involved quantifying the levels of carbon (C), hydrogen (H), oxygen (O), nitrogen (N), and sulfur (S) utilizing a CHNS/O elemental analyzer (PerkinElmer, 2400, Malaysia). By accurately determining the elemental composition, a deeper insight into the chemical makeup of the residues was attained, aiding in their overall characterization. Equally significant, the calorific value of the residues was meticulously quantified using an isothermal calorimeter (IKA, C-200, Germany). This involved the controlled combustion of 0.05 kg samples under standard atmospheric conditions. By carefully measuring the heat released during the combustion process, the calorific value of the residues, expressed in mega Joules per kilogram of matter, could be accurately determined. This particular parameter provided valuable information regarding the energy potential of the residues. Throughout the entire acquisition and characterization process, adherence to the methodologies outlined in Christoforou and Fokaides [15] was of paramount importance. Following these established procedures ensured the reliability and accuracy of the obtained results, providing a robust foundation for further analysis and exploration of the agricultural and forestry residues.

2.2. Developing Effective Antioxidant Additives

In the pre-production step of developing effective antioxidant additives in a liquid form for the purpose of integrating them into pellets, a rigorous and objective solution preparation method was implemented, drawing upon the methodology described by Moreira et al. [9]. This method encompassed a series of steps to ensure the successful creation of potent antioxidant solutions, characterized by optimal efficacy and suitability for the intended application. To initiate the solution preparation process, meticulous care was taken in obtaining precise and accurately weighed powdery aliquots, amounting to 0.1 kg, derived from distinct sources such as peanut shells, spent coffee grains, and sugarcane leaves. These specific residues were deliberately selected based on their well-documented antioxidant properties, which rendered them highly desirable candidates for the envisioned application. Subsequently, the aforementioned powdery aliquots were introduced into a volume of ultrapure water, totaling 2 L. Through this immersion process, a suspension was formed, facilitating the gradual and controlled transfer of the desired antioxidant compounds from the solid phase to the liquid phase of the system. This infusion stage played a pivotal role in maximizing the extraction of the target antioxidant components, thereby enriching the resulting solution with their beneficial properties [9].

To promote an efficient transfer of these compounds, the suspension was subjected to a carefully controlled boiling procedure, maintained at a temperature of 50 °C for a duration of precisely 15 minutes. Such controlled heating conditions were thoughtfully chosen to facilitate the gradual release and dissolution of the antioxidant compounds from the solid residues, ensuring their effective integration into the liquid phase of the solution. Following the infusion process, the prepared suspension was subjected to a refinement step aimed at achieving the desired concentration of the antioxidant solutions. Specifically, a measured volume of 0.05 L from the prepared solutions was diluted with an additional volume of 1 L of ultrapure water. By employing this dilution process, the resulting extract was effectively concentrated at a level of 0.05% $v\ v^{-1}$. This precise concentration ensured compliance with stringent regulatory limits, as advocated by sustainable consumption guidelines. Specifically, the concentration level adhered to the stipulated upper limit of 2% additive content within the pellet composition, as stipulated by Whittaker and Shield [10]. To safeguard the integrity and efficacy of the prepared antioxidant solutions until their utilization in the subsequent pelletization process, appropriate storage measures were employed. The solutions were preserved in a freezer, maintained at a temperature of -5 °C. By subjecting the solutions to controlled freezing conditions, their inherent properties, stability, and functionality were effectively preserved, thereby guaranteeing their optimal performance when incorporated into the subsequent stages of the pelletization process [9].

2.3. Addition and Pelletization

To conduct the pelletization process at the laboratory scale, it was necessary to incorporate the potential antioxidant solutions into 1.5 kg of pinewood sawdust. This pre-production step was carefully executed using a controlled spraying technique to ensure uniform distribution of the solutions throughout the feedstock [9]. A precise volume of 0.1 L of the prepared antioxidant extracts was evenly sprayed onto the pinewood sawdust using an automatic micro-sprayer (Sagyma, ASW-775, Burkard Scientific, Uxbridge, UK), which was pressurized by an airbrush compressor (Sagyma, ASW-775, Burkard Scientific, Uxbridge, UK) operating at a consistent pressure of 155 kPa. This spraying process aimed to facilitate the effective integration of the antioxidant solutions into the feedstock, ensuring their thorough incorporation and subsequent impact on the pelletization process. Subsequently, the treated feedstock, now enriched with the antioxidant solutions, underwent the critical production stage of pelletization. To enable comparative analysis, a control group consisting of the feedstock without any additive was included in the process. The pelletization procedure was performed utilizing an automatic hydraulic presser (**Tab S2, Supplementary material**), which was programmable to apply a compaction pressure of 200 MPa and maintain a temperature of 125 °C for a duration of 90 seconds, following the established technical recommendations by Whittaker and Shield [10].

In practical terms, the feedstock, both with and without the addition of antioxidant solutions, was carefully introduced into the pelletization machine. Within the machine, the feedstock passed through a compressing channel where it encountered pressing rollers that exerted controlled pressure upon it. Under these conditions, the feedstock was effectively transformed into cylindrical pellets, as the applied pressure facilitated the bonding and densification of the material. The pelletizer operated in an automated fashion, promptly ejecting the newly formed pellets from the compressing unit onto a vibratory screener. A simultaneous cooling process prevented the pellets from experiencing autoignition or other undesirable thermal effects. Subsequently, a gravitational conveyor system efficiently transported the pellets to a dedicated storage unit, ensuring their safe and organized collection for further analysis and subsequent use. To ensure the reliability and robustness of the obtained results, the pelletization process was performed in triplicate. This approach involved replicating the entire procedure three times, generating multiple sets of pellets for every experimental condition. Conducting the process in triplicate not only enhanced the statistical validity of the data but also provided a comprehensive dataset that could be subjected to rigorous analysis, enabling thorough evaluation and a more comprehensive understanding of the pelletization outcomes.

2.3.1. Technical Assessment of Pellet’s Standard Qualities

Pellets were assessed, technically, with the primary objective of evaluating their suitability for commercialization and utilization in residential and industrial markets. The assessment focused on key variables such as length, diameter, bulk density, durability, and calorific value. To begin with, the length and diameter of twenty randomly selected pellet specimens were measured using an electronic ruler (FBA-ip54, MrToolz, Brazil) with a resolution of 0.01 mm. This precise measuring tool ensured accurate determination of the pellet's dimensions, providing insights into their uniformity and consistency [16]. In addition, the degree of compactness, or bulk density, of the pellets was assessed by measuring the volume occupied by a unit mass of 0.1 kg. Triplicate samples were placed in a cylinder filled with 2.5 L of ultrapure water. The change in water level allowed for the calculation of bulk density, which provides an indication of the packing density and structural integrity of the pellets [17]. Furthermore, to evaluate the pellets' ability to resist breaking force, a tumble test was conducted. Triplicate samples, each weighing 0.1 kg, were subjected to repetitive free drops from a height of 1.5 m onto the floor, simulating real-world conditions of shock and abrasion [18]. Subsequently, the material was sieved using a stainless wire screener with a 3.15-micron mesh size. The retained material on the sieve represented the pellet's durability, while the material passing through the sieve indicated the production of fines. Accurate weighing was performed using an analytical digital scale (ATX-220, Shimadzu, Brazil) with a resolution of 0.0001 g. This comprehensive test provided insights into the pellets' resistance to mechanical stress and their propensity for generating fines during handling. Moreover, to assess the energy content and efficiency of the pellets for heating purposes, the calorific value was determined. Triplicate samples, weighing 0.1 kg each, were combusted in an adiabatic calorimeter (C-200, IKA, Brazil) to accurately measure the heat released during combustion. The calorific value of the pellets was expressed in megajoules per kilogram (MJ kg^{-1}), providing valuable information about their energy potential and performance in heating systems [15]. By employing rigorous measurement techniques and utilizing appropriate equipment, the quality assessment provided a comprehensive evaluation of the pellets' dimensions, bulk density, durability, and calorific value. These parameters are essential for assessing the pellets' suitability for commercialization and utilization in residential and industrial markets. The findings contribute to informed decision-making regarding the use of biomass energy and help ensure optimal utilization and market acceptance of the pellets, considering the impact of the addition on their standard qualities.

2.4. Autogenous generation of CO2: Quantification and Monitoring

To accurately quantify the phenomenon of off-gassing, a respirometry approach was implemented (**Fig S1, Supplementary material**), building upon the established glass flask method elucidated by Sedlmayer et al. [8]. This methodology, known for its reliability and precision, served as the cornerstone for evaluating the emission of carbon dioxide (CO_2) as a tangible indicator of off-gassing activity. The primary objective was to gain a deeper understanding of the gas generation dynamics during the experimentation. To create an experimental environment conducive to accurate measurements, 0.1 kg samples of pellets were placed within glass flasks. This careful arrangement ensured an optimal quantity of material and ample space to facilitate various oxidation processes inherent to off-gassing phenomena, as advised by Meier et al. [19]. The selection of appropriate storage vessels played a vital role in maintaining the integrity of the samples while allowing for the observation of off-gassing events. To capture and quantify the autogenous generation of CO_2 arising from the autoxidation of organic matter, an adjacent compartment was incorporated into the experimental setup. This compartment, located adjacent to the pellet-containing flasks, played a crucial role in capturing the CO_2 gas as it was released during the oxidation process. To achieve this, a precisely measured quantity of 10 mL of a 0.2 M potassium hydroxide (KOH) solution was introduced into the compartment, as elucidated by Moreira et al. [9].

The introduction of the KOH solution facilitated an interaction between the reactant and the ambient atmosphere, enabling the effective capture and retention of the generated CO_2. This strategic addition ensured that the emitted gas could be accurately quantified and monitored throughout the experimental period. Throughout the experimental duration, control over the environmental conditions was maintained to ensure the validity and reproducibility of the results. The experimental setup was housed within a biochemical chamber, tightly regulated at a temperature of 25±2.5 °C and a relative humidity of 60±5%. Moreover, to minimize any potential confounding effects arising from photooxidation processes, the experiments were conducted under conditions devoid of light. This precautionary measure aimed to maintain the integrity of the samples and preserve the accuracy of the off-gassing observations. To facilitate the systematic monitoring and quantification of CO_2, the samples were subject to regular assessments. Daily observations were made to closely track the progress of off-gassing phenomena, while the quantification of CO_2 was carried out at 5-day intervals throughout a total duration of 120 days [9].

The quantification procedure involved the titration of the analytical solution recovered from the glass flasks. Specifically, an adaptive syringe containing 1 mL of a 0.5 M barium chloride ($BaCl_2$) solution was employed for this purpose. The resulting solution, containing the captured CO_2, was subsequently subjected to precise analysis through the determination of the electroconductivity of the resulting carbonate ions. This analytical measurement, as detailed by Lopes and Bidoia [20], was performed using a conductometer device (Tecnopon, MCA-150, São Paulo, Brazil). To ensure the robustness and reliability of the findings, the experimental tests were executed with a focus on rigorous control measures. Every experimental condition was replicated five times, thereby facilitating the identification and control of systematic errors. This approach played a critical role in ensuring the reproducibility of the methodology and bolstering the overall reliability of the obtained results. The calculation of the autogenous generation of CO_2 (**Eq 1**) involved the utilization of the electrical conductivity of the analytical solution, expressed in mS cm^{-1} at 25 °C, in conjunction with a transformation factor (C). This factor enabled the conversion of the measured quantity of the CO_2 product from millimoles (mmol) to milligrams (mg), as outlined by Lopes and Bidoia [20].

$$\mathrm{G}\ (\mathrm{mg\ kg^{-1}, d.b.}) = 1554.8 - 95.725\ \times\ \mathrm{C}\ \text{(Eq 1)}$$

2.4.1. Autodegradation of Extractives

In conjunction with the investigation of off-gassing phenomena, an additional assay was conducted to delve into the antioxidative potential of the biogenic extracts. This particular assay aimed to assess the ability of the extracts to hinder the auto-degradation of extractive compounds, thereby providing insights into their antioxidative properties. The experimental procedures, as elucidated by Sedlmayer et al. [21], encompassed a series of precise and carefully executed steps to ensure accurate analysis and meaningful results.

To initiate the assay, meticulous processing of samples was undertaken, consisting of 0.05 kg of pellets along with a standard solution composed of petroleum ether (with a boiling point range of 30-60 °C) and acetone. The samples and the standard solution were subjected to a Soxhlet extraction method, whereby a continuous extraction process was employed for a duration of 6 hours. This extraction procedure was repeated for a total of ten cycles, ensuring thorough extraction of the targeted compounds from the pellet matrix. Through this meticulous repetition of cycles, the desired extractive compounds were effectively released and collected. Following the completion of the extraction cycles, the solvent was removed from the solution, while concentrated extractive compounds remained in the system. To facilitate subsequent analysis and standardization, heptanoic acid was introduced into the system. This addition enabled the standardization of the extractive compounds and further preparation for subsequent procedures.

In addition, to examine the extractive compounds in more detail, a critical saponification process was performed. This process involved subjecting the extracted material to an ethanolic solution of potassium hydroxide (KOH) maintained at a carefully regulated pH level of 6.95. Under these controlled conditions, the extractive compounds were saponified, leading to the release of the fraction of extractive matter present in the petroleum ether. This step ensured the efficient liberation of the extractive compounds of interest, which were subsequently recovered for further analysis. To prepare the extractive compounds for subsequent investigations, an essential derivatization procedure was meticulously executed. This involved treating the dried extractive material with bis-(trimethylsilyl)-trifluoro-acetamide and trimethylchlorosilane. Through this derivatization process, the extractive compounds were effectively modified, enhancing their stability and compatibility for subsequent analytical assessments. To evaluate the extent of auto-degradation of the extractives and quantitatively measure their degradation over time, a short-term assay was conducted spanning a duration of one month. This extended monitoring period allowed for a comprehensive understanding of the degradation dynamics of the extractive compounds. Daily measurements were performed to ascertain the degradation levels, providing valuable insights into the antioxidative properties of the investigated extracts. Specifically, the samples were completely dissolved in 1 mL of dichloromethane, facilitating the extraction and subsequent analysis of the compounds [21].

2.5. Specific Antioxidant Activity of Biogenic Extracts

To thoroughly investigate the specific antioxidant activity of biogenic extracts and gain deeper insights into their role in mitigating the oxidation of organic matter within wood pellets, an additional assay was conducted. The purpose of this assay was to unravel the extracts' ability to effectively reduce the autogenous generation of CO_2 by inhibiting the oxidation processes. The methodology employed encompassed a series of systematic steps, carefully designed to provide a comprehensive understanding of the extracts' antioxidant properties, as elucidated by Xie et al. [22]. To commence the assay, precise volumes of 0.5 mL of the pre-pelleting analytical solutions containing the biogenic extracts were combined with 2.5 mL of a 2,2-diphenyl-1-picrylhydrazyl (DPPH•) solution. DPPH•, a well-known stable free radical, served as the electron acceptor in this context. The incorporation of DPPH• facilitated the assessment of the extracts' ability to scavenge free radicals, effectively inhibiting their reactivity. The resulting mixture was subjected to thorough vortexing to ensure complete homogenization, allowing for uniform interaction between the extracts and DPPH•. Subsequently, to maintain the integrity of the samples and ensure consistent incubation conditions, the mixture was stored within a controlled biochemical chamber at a temperature of 25 °C. This temperature was chosen to mimic typical ambient conditions. Furthermore, to prevent potential interference from photooxidation, stringent measures were implemented to ensure the absence of light during the incubation period. This was achieved by storing the samples in opaque containers or using light-blocking materials. By eliminating light exposure, the potential for lightinduced reactions that could influence the results was minimized. To determine the specific antioxidant activity of the extracts, the absorbance of the samples was measured using a UV-Vis spectrometer at a wavelength of 515 nm. Prior to the analysis, the spectrometer was calibrated using pure methanol, ensuring accurate and reliable measurements. Additionally, an oxidative agent was handled as a negative control to establish a baseline for comparison. By comparing the absorbance values of the extracts with those of the control samples, a quantifiable assessment of their antioxidant efficacy could be obtained. The reduction in absorbance indicated the extent to which the extracts neutralized the DPPH• free radicals, shedding light on their antioxidant potential.

In addition to assessing the specific antioxidant activity, a more comprehensive understanding of the extracts' functionality in controlling the specific emission of CO_2 from wood pellets was sought. This involved a detailed characterization process that encompassed the determination of various components, including total polyphenolic compounds, ascorbic acid, carotenoids, and the activity of key enzymes such as superoxide dismutase (SOD), peroxidase (POD), and catalase (CAT). The determination of total polyphenolic compounds, a significant indicator of antioxidant potential, was accomplished using spectrophotometric methods, with the Folin-Ciocalteu assay being a prominent technique [23]. This method relies on the capacity of phenolic compounds to elicit a reduction reaction with the Folin-Ciocalteu reagent, resulting in the formation of a colored complex. The intensity of the color produced is directly proportional to the concentration of phenolic compounds in the analyzed sample. For the determination of ascorbic acid (vitamin C), a compound with antioxidant properties, the iodometric titration method was employed [24]. This method utilizes the redox reaction between ascorbic acid and iodine to quantify ascorbic acid accurately. The determination of carotenoids involved high-performance liquid chromatography (HPLC), a commonly employed technique for the analysis of these pigments [25]. High-performance liquid chromatography offers excellent separation capabilities, allowing for the identification and quantification of individual carotenoid compounds present in the extract.

Furthermore, to gain insights into the enzymatic antioxidant mechanisms, the activity of key enzymes, including superoxide dismutase (SOD), peroxidase (POD), and catalase (CAT), was measured. These enzymes play crucial roles in neutralizing reactive oxygen species (ROS) and protecting against oxidative damage. The determination of SOD activity was based on the inhibition of a reaction involving the reduction of a tetrazolium salt, such as nitroblue tetrazolium (NBT), by superoxide radicals [26]. The reduction of NBT leads to the formation of a colored formazan product, and the rate of inhibition of this reaction is proportional to the SOD activity in the sample. The enzyme activity of POD was determined by measuring the oxidation of suitable electron donors, such as guaiacol or 3,3',5,5'-tetramethylbenzidine (TMB), in the presence of hydrogen peroxide (H_2O_2) [27]. The oxidation of these electron donors leads to the formation of colored products, and the rate of product formation is directly related to the POD activity in the sample. The enzyme activity of CAT was measured by monitoring the decomposition of hydrogen peroxide into water and molecular oxygen. The most commonly used method involved spectrophotometric detection of the oxygen evolved during the reaction [28]. The rate of decrease in hydrogen peroxide concentration was monitored by measuring the decrease in absorbance of a suitable indicator, such as potassium permanganate ($KMnO_4$), at a specific wavelength.

By employing these comprehensive analytical biochemistry methods, the composition of the extracts, as well as the presence and quantities of various bioactive components, could be identified and quantified. This deeper insight into the extracts' composition and the presence of bioactive compounds allowed for a more thorough understanding of their functional properties and their role in effectively controlling the specific emission of CO_2 from wood pellets. The combination of spectrophotometry, titration, high-performance liquid chromatography, and enzyme activity assays provided a multifaceted perspective on the antioxidant capabilities and underlying mechanisms of the biogenic extracts, paving the way for further exploration and potential applications in the realm of sustainable biomass utilization.

2.6. Statistical Data Analysis

The Gompertz model (**Eq 2**) was employed to analyze the experimental data and characterize the kinetics of autogenous CO_2 emissions from wood pellets. This mathematical model provides a robust framework for understanding the emission behavior over time [29].

$f_{(t)} = \alpha e^{-\beta^{-kt}}$(Eq 2)

In Eq 2, the dependent variable f represents the autogenous generation of CO_2 in units of mg kg^{-1} (dry basis) or the degradation of extractive matter in units of % kg^{-1} (dry basis) over time (t). The parameter alpha (α) corresponds to the asymptote, which signifies either the maximum emission or the minimum degradation achieved during the process. The parameter beta (β) represents the halftime of the sigmoid model, indicating the point at which the emission rate reaches half of its maximum or minimum value. The parameter k denotes the specific growth rate of the curve, determining the steepness or rate of change of the emission or degradation. The variable t denotes time, and e represents the Euler constant.

To assess the appropriateness of the Gompertz model and validate its application to the CO_2 emission and extractive degradation data, several statistical criteria were utilized. The Akaike Information Criterion (AIC) and Bayesian Information Criterion (BIC) were employed to compare the goodness of fit of the model among experimental conditions. Lower values of AIC and BIC indicate a superior fit of the Gompertz model to the data. Furthermore, the coefficient of determination (r^2) was calculated to quantify the proportion of variability in the data that is accounted for by the model. In addition to the time-dependent analysis of emission and degradation kinetics, explanatory relationships between materials, additives, and products were established through principal component analysis (PCA). This multivariate statistical technique enabled the extraction of insights into the control of off-gassing. By identifying patterns and correlations among variables, PCA provided valuable information about the interrelationships and influences within the system. To conduct the necessary analyses and design illustrative graphs for communicating the results, statistical computing and graphic tools available in the R software were utilized. R, a widely used programming language and environment for statistical computing, provided a robust and reliable platform for data analysis, model fitting, and visualization.

3. Results and Discussion

3.1. Autogenous Generation of CO_2 and Degradation of extractives

We conducted a meticulous and comprehensive investigation into the dynamics of CO_2 generation and extractive degradation in pellets, employing the Gompertz model to establish functional kinetic relationships between materials, products, and processes. Our objective was to thoroughly analyze and characterize these phenomena and assess the influence of biogenic additives, including peanut shells, spent coffee grains, and sugarcane leaves, on their modulation. The understanding of these dynamics holds significant importance in the development of sustainable and environmentally friendly pellet manufacturing lines.

Our findings revealed a sigmoidal nature in the generation of CO_2 (**Fig 1A**) and degradation of extractives (**Fig 1B**), which indicates the autogenous deterioration of the pellets. The application of the Gompertz model effectively captured this behavior, allowing us to accurately estimate alpha, beta, and k parameters. Specifically, the alpha (α) parameter signifies the asymptotic value of CO_2 emissions or extractive degradation. The control group, serving as the baseline, exhibited an alpha value of 2995.4 mg kg^{-1} (**Tab S3, Supplementary material**), representing the maximum attainable level without the presence of additives. However, the inclusion of peanut shells, spent coffee grains, and sugarcane leaves resulted in notable reductions in alpha values to 2732.1, 2405.2, and 2472.4 mg kg^{-1}, respectively. These diminished alpha values indicate the additives' capacity to decrease specific CO_2 emissions and decelerate extractive degradation. Moreover, the fact that these values are lower than those of the control group suggests the antioxidant potential of these additives in mitigating CO_2 emissions and extractive degradation processes.

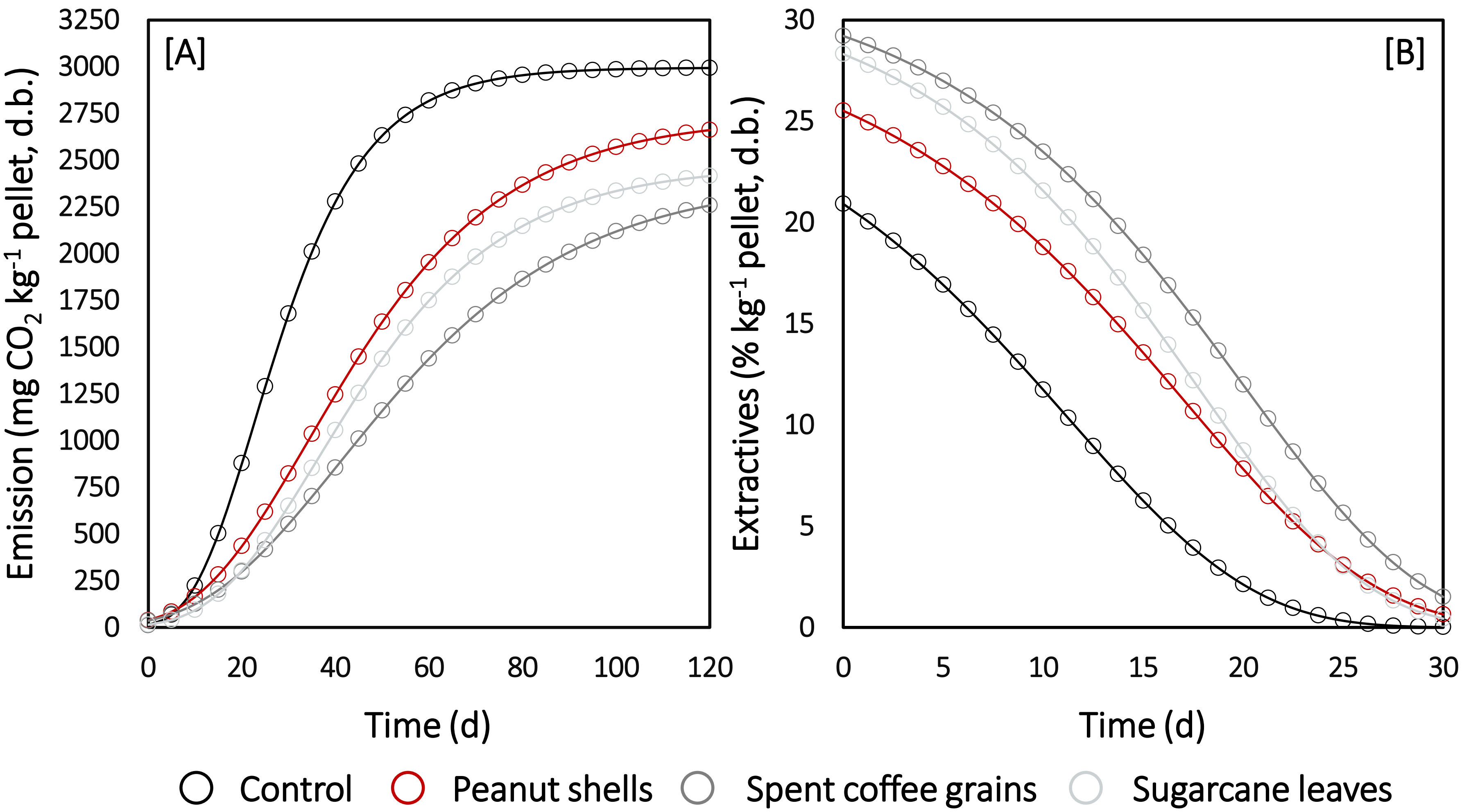

Fig 1. Autogenous generation of CO_2 [A] and degradation of extractives [B] in pellets with addition of peanut shells, spent coffee grains, and sugarcane leaves as potential biogenic antioxidants.

In addition, the beta (β) parameter represents the growth rate constant, indicating the rate at which the processes accelerate or decelerate. All experimental groups exhibited beta values greater than one, indicating an acceleration of the processes as they progressed. The control group demonstrated a relatively fast acceleration with a beta estimate of 5.5 (**Tab S3, Supplementary material**). However, spent coffee grains exhibited a lower beta estimate of 4.2, suggesting a comparatively slower acceleration compared to the control group. Similarly, sugarcane leaves and peanut shells had beta estimates of 5.15 and 4.3, respectively. Although all additives demonstrated an acceleration of the processes, the lower beta estimate for spent coffee grains suggests its superior ability to decelerate CO_2 generation by effectively reducing the degradation of extractives.

Moreover, the k parameter represents the specific-growth rate or degradation rate, quantifying the rate at which the variable changes over time. The control group displayed a relatively higher k value of $7.5e^{-2}$, indicating a faster specific-growth rate (**Tab S3, Supplementary material**). In contrast, spent coffee grains exhibited the lowest estimate of k at $3.5e^{-2}$, indicating a slower and more controlled emission of CO_2. Peanut shells and sugarcane leaves had relatively higher k values of $4.25e^{-2}$ and $4.5e^{-2}$, respectively, indicating a faster specific-growth rate compared to spent coffee grains; however, still slower than the control group. These findings suggest that the addition of these biogenic additives leads to a more manageable and controlled emission of CO_2 and degradation of extractives.

Furthermore, in the reference pellets containing 29.2% extractives, we observed a significant reduction in extractive content after 30 days of storage at a specific degradation rate (k) of $-1.25e^{-2}$ (**Tab S3, Supplementary material**). For pellets with spent coffee grains, particularly, the extractive content decreased to approximately 3.35%, while the control group exhibited a final extractive content of only 0.015%. The estimated k values for these experimental conditions further support the efficacy of the biogenic additives, as the degradation-specific rates were lower for the pellets with additives compared to the control group. Specifically, the addition of spent coffee grains demonstrated the highest efficacy in preserving extractive content, while sugarcane leaves demonstrated the potential for an increased degradation-specific rate. These results highlight the importance of developing suitable additives for high-performance pelletization.

In summary, our findings emphasize the effectiveness of biogenic additives, such as peanut shells, spent coffee grains, and sugarcane leaves, in reducing specific CO_2 emissions and decelerating extractive degradation in pellets. The lower alpha values indicate the additives' ability to decrease CO_2 emissions and extractive degradation, underscoring their antioxidant potential. The beta values reveal the distinct acceleration rates of the processes, with spent coffee grains exhibiting superior capabilities for decelerating CO_2 generation. The k values reflect the specific-growth rates, indicating a more controlled emission of CO_2 and degradation of extractives in the presence of biogenic additives. Moreover, the incorporation of these additives into pinewood sawdust for pelletization resulted in a more gradual and lower reduction in extractive content during storage, further highlighting their potential for promoting sustainable and environmentally friendly sold biofuels.

3.1.1. Antioxidant Potential and Functionality of Biogenic Extracts

The term "autogenous generation of CO_2" refers to the internal production of CO_2 within the pellets themselves. This phenomenon arises through various mechanisms, including the decomposition of organic matter and the release of gases during specific chemical reactions. Conversely, the degradation of extractives pertains to the breakdown or deterioration of specific non-structural constituents of biomass, such as oils, waxes, resins, and tannins. The deterioration of these extractives can result in a decline in the overall integrity and quality of the pellets. Nevertheless, the antioxidant capabilities of extracts derived from peanut shells, spent coffee grains, and sugarcane leaves (**Tab 1**) play a significant role in reducing CO_2 emissions by mitigating extractive degradation when introduced as biogenic additives in the pelletization process. This incorporation enhances the reactivity and stability of the product, significantly reducing off-gassing.

Peanut shells contain a diverse array of bioactive compounds [30], including phenolic compounds, flavonoids, and lignans, which possess antioxidant properties, enabling them to scavenge ROS and inhibit oxidative reactions [31]. In the context of analytical biochemistry of our study, the biogenic extract derived from peanut shells exhibited notable quantities of total polyphenols (54.9 mg GAE g^{-1}), ascorbic acid (285.7 µg mL^{-1}), and carotenoids (8.2 µg mL^{-1}). Moreover, the extract demonstrated substantial cumulative enzymatic activity of 244.6 U g^{-1}. Notably, it also exhibited a reducing power of 3.85 µg g^{-1} and inhibited DPPH• free radical activity by 78.3%. The incorporation of peanut shell extracts into the pellets effectively neutralizes ROS generated during the degradation of extractives, thus impeding their oxidation and degradation.

Similarly, spent coffee grains display noteworthy antioxidant activity owing to their elevated content of phenolic compounds, particularly chlorogenic acids [32]. These compounds possess robust free radical scavenging abilities, effectively suppressing oxidative reactions and inhibiting the breakdown of extractives within the pellets. The biogenic extract derived from spent coffee grains exhibited considerable quantities of total polyphenols (78.4 mg GAE g^{-1}), ascorbic acid (352.5 µg mL^{-1}), and carotenoids (9.45 µg mL^{-1}). Notably, it showcased cumulative enzymatic activity of 258.75 U g^{-1}, surpassing that of peanut shells and sugarcane leaves. Additionally, it demonstrated a reducing power of 2.75 µg g^{-1} and a remarkably high DPPH-scavenging capability of 89.5%. By incorporating spent coffee ground extracts as biogenic antioxidants, the oxidative degradation of extractives can be effectively curtailed, leading to a decrease in CO_2 emissions during pellet storage.

Tab 1. Antioxidant potential and functionality of biogenic extracts

Variable	Peanut shells	Spent coffee grains	Sugarcane leaves
DPPH• radical scavenging activity, %	78.3	89.5	56.3
Reducing power, µg g^{-1}	3.85	2.75	10.25
Total polyphenols, mg GAE g^{-1}	53.9	78.4	61.75
Ascorbic acid, µg mL^{-1}	285.7	352.5	298.4
Carotenoids, µg mL^{-1}	8.2	9.45	3.85
SOD activity, U g^{-1}	158.4	127.4	121.5
CAT activity, U g^{-1}	54.1	84.5	62.4
POD activity, U g^{-1}	32.1	46.85	29.3

Additionally, sugarcane leaves encompass various bioactive compounds, including phenolics and flavonoids, which possess antioxidant properties and provide protection against ROS [12]. Upon incorporation into the pellets, the biogenic extract derived from sugarcane leaves, containing non-enzymatic and enzymatic antioxidants, such as polyphenols (61.75 mg GAE g^{-1}), ascorbic acid (298.4 µg mL^{-1}), carotenoids (3.85 µg mL^{-1}), SOD (121.5 U g^{-1}), CAT (62.4 U g^{-1}), and POD (29.3 U g^{-1}), effectively inhibits the degradation of extractives by neutralizing ROS and preventing oxidative reactions. This antioxidant activity aids in reducing CO_2 emissions by preserving the integrity of the extractives and minimizing the release of gases during incubation. However, it is important to note that a higher quantity of addition may be required, as the reducing power (10.25 $\mu g\ g^{-1}$) and scavenging capability (56.3%) are relatively inferior compared to spent coffee grains and peanut shells.

The incorporation of biogenic extracts with antioxidant properties into the pelletization process offers a promising avenue for controlling off-gassing. By effectively mitigating extractive degradation, these extracts help preserve the integrity of the pellets and minimize the release of CO_2. The antioxidant components present in the biogenic extracts, such as phenolic compounds, flavonoids, and lignans in peanut shells [30, 31], chlorogenic acids in spent coffee grains [32], and phenolics, flavonoids, and tannins in sugarcane leaves [12], play a crucial role in neutralizing ROS and inhibiting oxidative reactions. The scavenging of ROS by these antioxidant compounds prevents the oxidation and breakdown of extractives, thereby reducing the generation of CO_2 during pellet storage. By protecting the extractives from degradation, the biogenic extracts contribute to the overall stability and reactivity of the product, while minimizing off-gassing. In addition to their antioxidant capabilities, these biogenic extracts also exhibit enzymatic activities, such as superoxide dismutase (SOD), catalase (CAT), and peroxidase (POD), which further enhance their off-gassing control potential. These enzymes catalyze the decomposition of harmful ROS, minimizing their damaging effects on the extractives and reducing the release of CO_2. Furthermore, the quantification of antioxidant components, such as total polyphenols, ascorbic acid, carotenoids, and enzymatic activities, provides a scientific basis for assessing the off-gassing control potential of the biogenic extracts. The higher reducing power, DPPH-scavenging capability, and enzymatic activities observed in the extracts derived from spent coffee grains and peanut shells highlight their stronger antioxidant potential, which correlates with their effectiveness in reducing the emission of CO_2 (**Fig 1A**) and deterioration of extractive matter (**Fig 1B**).

By incorporating these biogenic extracts as additives, the pellet industry can adopt a more sustainable and environmentally friendly approach to off-gassing control. This has significant implications for improving air quality, promoting occupational safety and human health, reducing environmental pollution, and promoting the adoption of greener pelletization processes.

3.2. Functional Relationships between Product's Emission Activity and Additive's Antioxidant Capability/Functionality

The autogenous generation of CO_2 and the deterioration of extractives in wood pellets were successfully mapped to the antioxidant capabilities and functionalities of biogenic additives using PCA (**Fig 2**). Specifically, through factorial mapping, we were able to extract explanatory information from experimental data and represent it in the orthogonal latent hits, namely PC_I and PC_{II} (**Tab S4, Supplementary material**). The primary component accounted for 67.5% of the interpretable and understandable variance, while the secondary component captured the remaining portion, thus completely explaining the variations in CO_2 emissions and extractive degradation upon the incorporation of biogenic additives derived from peanut shells, spent coffee grains, and sugarcane leaves in wood pellets.

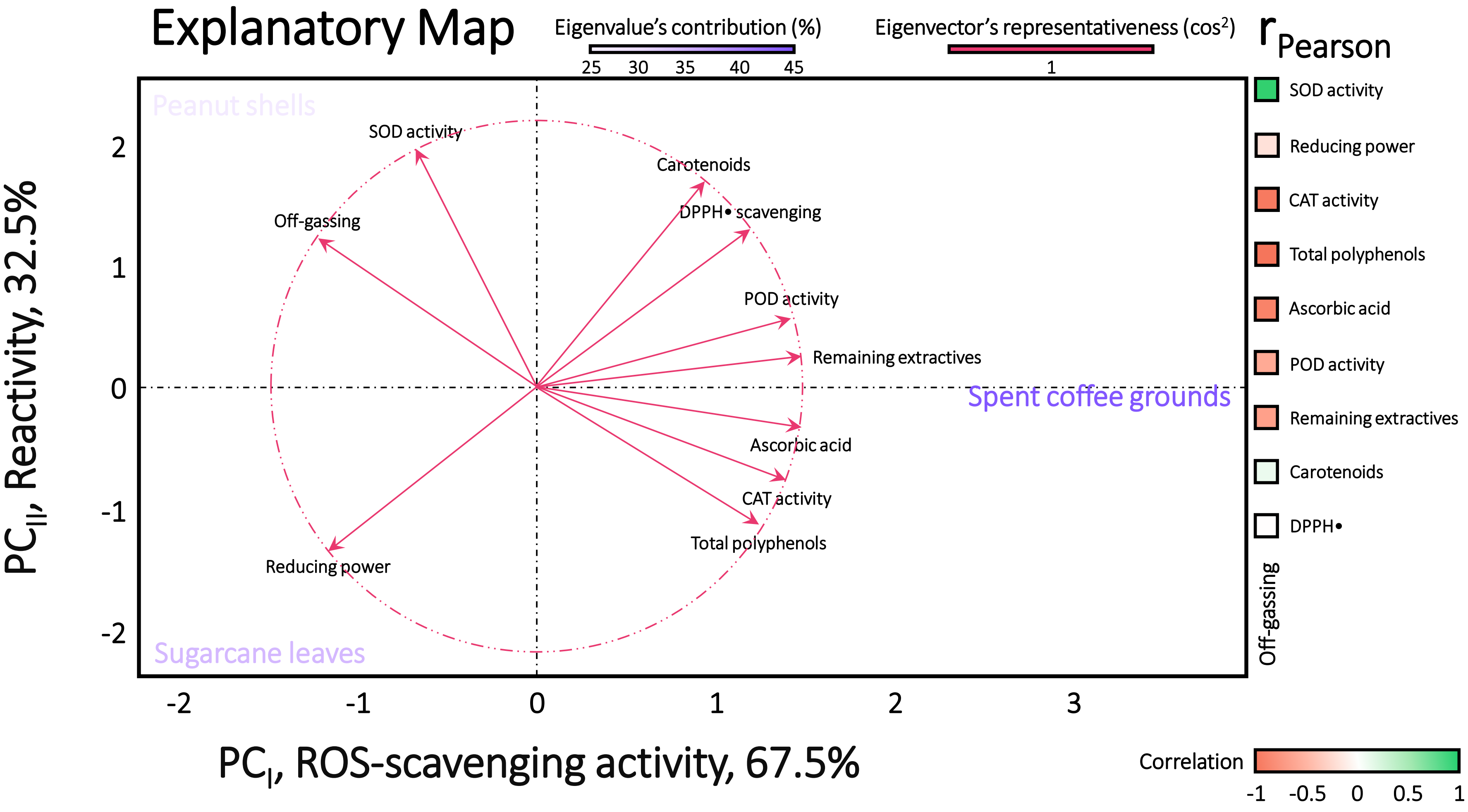

Fig 2. Factorial map for the autogenous generation of CO_2 and deterioration of extractives to antioxidant capabilities of biogenic additives derived from peanut shells, spent coffee grains, and sugarcane leaves.

Upon in-depth analysis and interpretation of the explanatory mapping, positive correlations were established between PC_I and various factors, including remaining extractives, DPPH• radical scavenging activity, total polyphenols, ascorbic acid, carotenoids, CAT activity, and POD activity. These linear associations were quantified by correlation coefficients (r) of 0.65, 0.8, 0.95, 0.975, 0.7, 0.95, and 1, respectively. In contrast, PC_I exhibited negative linear associations with reducing power, SOD activity, and off-gassing, with correlation coefficients of -0.65, -0.35, and -0.65, respectively. These findings signify the role of the biogenic additives' ROS-scavenging activity in preventing extractive degradation and subsequent CO_2 generation. Thus, the more effective the biogenic extracts derived from peanut shells, spent coffee grains, and sugarcane leaves are in inhibiting organic matter-damaging reactive oxygen species (ROS) such as hydrogen peroxide (H_2O_2) or superoxide anion radical ($O_2^{\bullet-}$), the lower the deterioration of non-structural components in the material, such as oils, waxes, resins, and tannins, leading to reduced CO_2 emissions into the environment.

Furthermore, the factorial map indicated that spent coffee grains exhibited the highest ROS-scavenging activity, as they progressed farthest from the origin along the analytical dimension of the primary component. This outperformance of spent coffee grains in limiting extractive deterioration and CO_2 generation was supported by the convergence of eigenvectors, including carotenoids, DPPH• radical scavenging activity, POD activity, ascorbic acid, CAT activity, and total polyphenols. Thus, these components provided reliable insights into their antioxidant capabilities and functionalities, contributing to the control of off-gassing and improvement of pellet integrity and stability. The biogenic extracts derived from peanut shells and sugarcane leaves, on the other hand, made lesser contributions to the characterization and interpretation of PC_I, emphasizing the superior representation of spent coffee grains' ROS-scavenging activity.

Moving on to the secondary component, it exhibited positive correlations with off-gassing (r = 0.8) and negative correlations with reducing power (r = 0.75). While spent coffee grains did not significantly contribute to its variance representation, peanut shells and sugarcane leaves played substantial roles, contributing 52.2% and 47.7%, respectively, to the interpretation and attribution of pellet reactivity and integrity. The extracts derived from peanut shells and sugarcane leaves contained lower concentrations of polyphenols, ascorbic acid, and carotenoids compared to spent coffee grains. Additionally, they exhibited lower cumulative enzymatic activities, including SOD, CAT, and POD. Consequently, wood pellets containing peanut shell or sugarcane leaf extracts as substitutes in their compositions displayed greater reactivity to ROS, leading to more rapid degradation and increased CO_2 release during storage compared to pellets with the addition of spent coffee grains. This trend was captured in the second dimension of the factorial map, representing the significance of the biogenic extracts' reducing power in relation to pellet reactivity and the autogenous formation and release of gases due to extractive degradation by ROS.

Upon conducting a thorough analysis and interpretation of the data, our study has delved deeper into the explanation of the relationships between the antioxidant capabilities and functionalities of biogenic additives and the autogenous generation of CO_2 and deterioration of extractives in wood pellets. The positive correlations established between the primary component (PC_I) and various factors shed light on the underlying mechanisms driving the observed outcomes. For instance, the positive correlation between PC_I and remaining extractives (r = 0.65) suggests that the presence of higher levels of remaining extractives is associated with a higher PC_I value, indicating better preservation of these non-structural components. This implies that the biogenic additives with strong antioxidant capabilities are effective in protecting and preserving the extractive matter within the wood pellets.

Moreover, the positive correlations between PC_I and DPPH• radical scavenging activity (r = 0.8), total polyphenols (r = 0.95), ascorbic acid (r = 0.975), carotenoids (r = 0.7), CAT activity (r = 0.95), and POD activity (r = 1) provide further evidence of the antioxidant properties of the biogenic additives. These correlations suggest that higher levels of these antioxidant compounds and enzymatic activities are associated with a higher PC_I, indicating improved protection against the autogenous generation of CO_2 and degradation of extractives. This reinforces the notion that the ROS-scavenging activity of the biogenic extracts, including their ability to neutralize harmful reactive oxygen species such as hydrogen peroxide (H_2O_2) or superoxide anion radical ($O_2^{\bullet-}$), plays a vital role in preventing extractive deterioration and subsequent CO_2 emissions. Conversely, the negative correlations between PC_I and reducing power (r = -0.65), SOD activity (r = -0.35), and off-gassing (r = -0.65) reveal the inverse relationship between these factors and the antioxidant capabilities of the biogenic additives. A lower PC_I value is associated with higher reducing power, SOD activity, and off-gassing, indicating a reduced ability of the additives to scavenge ROS and protect against extractive degradation. These findings reemphasize the importance of the ROS-scavenging activity of the biogenic extracts in mitigating CO_2 emissions and preserving the integrity of the wood pellets.

Furthermore, the factorial mapping derived from PCA provided valuable insights into the antioxidant capabilities and functionalities of the biogenic extracts, particularly highlighting the superiority of spent coffee grains in terms of ROS-scavenging activity. The convergence of eigenvectors, including carotenoids, DPPH radical scavenging activity, POD activity, ascorbic acid, CAT activity, and total polyphenols, towards spent coffee grains in the factorial map suggests that these components contribute significantly to the control of off-gassing and improvement of pellet integrity and stability. This implies that spent coffee ground extracts possess a higher potential for ROS-scavenging activity compared to extracts derived from peanut shells and sugarcane leaves. On the other hand, peanut shells and sugarcane leaves made relatively lesser contributions to the characterization and interpretation of PC_I, indicating their lower representation of antioxidant capabilities compared to spent coffee grains. The extracts derived from peanut shells and sugarcane leaves contained lower concentrations of polyphenols, ascorbic acid, and carotenoids, as well as exhibited lower cumulative enzymatic activities (SOD, CAT, and POD). Consequently, the wood pellets containing these extracts as substitutes displayed greater reactivity to ROS, leading to faster degradation and increased CO_2 release during storage. This reinforces the importance of selecting and optimizing the biogenic extracts to ensure their antioxidant capacities align with the desired outcomes.

In summary, our study's in-depth exploration of the explanatory mapping derived from PCA enhanced our understanding of the relationships between the antioxidant capabilities/functionality of biogenic additives and the autogenous generation of CO_2 and extractive deterioration in wood pellets. The positive correlations with various factors highlighted the protective role of the biogenic additives in preserving the extractive matter and mitigating CO_2 emissions. Conversely, negative correlations with reducing power, SOD activity, and off-gassing underscored the importance of ROS-scavenging activity in inhibiting CO_2 generation. The factorial mapping emphasized the superior antioxidant capabilities of spent coffee grains compared to peanut shells and sugarcane leaves, providing valuable insights for the selection and optimization of biogenic extracts to effectively control off-gassing in wood pellets.

3.3. The Impact of Addition on the Technical Quality of Pellets

The successful incorporation of additives in the manufacturing of functional pellets for heating and power is contingent upon various factors that require the improvement of their stability and reactivity while preserving their suitable qualities for commercialization and utilization in residential and industrial biomass conversion equipment and devices. Biogenic extracts derived from peanut shells, spent coffee grains, and sugarcane leaves have the potential to modify the technical quality of wood pellets, albeit with some compromises in their potential applications in renewable and sustainable energy production systems (**Tab 2**). This poses challenges in promoting them as additives for commercial manufacturing lines.

Notably, pellets containing these extracts as substitutes in their compositions demonstrate the ability to meet stringent requirements of international standards concerning parameters like length, diameter, bulk density, heating value, durability, and moisture content. For example, the inclusion of spent coffee grains in the products leads to significant enhancements in bulk density, heating value, durability, and moisture content, measuring at 695.1 kg m^{-3}, 25.3 MJ kg^{-1}, 99.5%, and 9.85%, respectively. Consequently, these modified pellets exhibit superior qualities in terms of compactness, mechanical resistance to shocking and abrasive forces, and concentration of isothermally available energy per unit mass, surpassing the reference materials. Nevertheless, it is essential for customers to exercise caution regarding the utilization of such pellets in residential and commercial niches due to certain considerations.

For instance, pellets containing biogenic extracts from peanut shells, spent coffee grains, and sugarcane leaves exhibit higher ash contents of 3.7, 2.4, and 3.4%, respectively, surpassing critical limits that give rise to the formation of physical deposits within furnaces and boilers, notably slagging and fouling [33]. Furthermore, these pellets contain nitrogen (N) and sulfur (S) at alarming levels of 0.4-1.1% and 0.1-0.6%, respectively, which typically contribute to the emission of hazardous gases, including nitrous oxides (NO_x) and sulfur oxides (SO_x), during the combustion process [34]. These factors underline the limitations associated with their utilization and emphasize the importance of enhancing their incorporation during the pelletization process. This enhancement is necessary not only to ensure occupational safety and safeguard human health but also to uphold industrial hygiene and promote environmental protection. These endeavors align closely with the desirable aspects of sustainable solid biofuel markets.

Tab 2. Technical quality of pellets with addition of peanut shells (PS), spent coffee grains (SCG), and sugarcane leaves (SL) as potential biogenic antioxidants

Property	Addition				Standard														
	PS	SCG	SL	Control	ONORM M 7135	SS 187120			DIN 51731	DIN EN 15270	DINPlus/ENPlus			CTI-R 04/05			IWPB		
					Austria	Sweden			Germany		Europe			Italy			Canada (ind.)		
						G_1	G_2	G_3	Pellet/briquette	High-quality pellet	A_1	A_2	B	A_1	A_2	A_3	G_1	G_2	G_3
Length, mm	28.85	29.4	30.1	28.4	<5	<4	<5	<5	<50	<50	3.15-40	3.15-40	3.15-40		<50		≤40	≤40	≤40
Diameter, mm	6.9	6.85	6.9	6.8	4-10	<25	<25	<25		6-8	6-8	6-8	6-8	6-8	6-8	10-25	6-8	6-8	6-10
Bulk density, kg m^{-3}	685.1	695.1	644.5	682.2	<1120	<1120	>600	>500	<1200	<1200	≥600	≥600	≥600	620-720	600-720	≥500	>600	>600	>600
HHV, MJ kg^{-1}	24.8	25.3	19.8	23.4	>17.5	>16.5	>16.5	>15	15.5-19.5	>17.5	≥16.5	≥16.5	≥16.5	≥16.5	≥16		≥16.5	≥16.5	≥16.5
Durability, %	98.15	99.5	97.1	99.2	>97.7	>99.2	>98.5	>98.5		>97.7	≥97.7	≥97.7	≥96.5	≥99	≥99		≥97.5	≥97	≥96.5
Moisture, %	10.4	9.85	11.15	9.9	<10	<10	<10	<10	<12	<10	≤10	≤10	≤10	≤10	<10	≤15	≤10	≤10	≤10
Ash, %	3.7	2.4	3.4	0.3	<0.5	<0.7	<1.5	<1.5	<1.5	<0.5	≤0.7	≤1.5	≤3	≤0.7	<1.5		≤1	≤1.5	≤3
N, %	0.4	0.8	1.1	0.45	<0.3				<0.3	<0.03				≤0.3	≤0.3				
S, %	0.1	0.15	0.6	0.5	<0.04				<0.08	<0.04				≤0.5	≤0.5				

Upon in-depth analysis and interpretation of biogenic extracts' advantages and disadvantages for pelleting, their utilization in the manufacturing process leads to notable improvements in several technical aspects. The modified pellets demonstrate superior qualities in terms of bulk density, heating value, durability, and moisture content, surpassing those of the reference materials. These enhancements contribute to enhanced efficiency and performance in biomass conversion equipment, facilitating effective utilization for heating and power generation purposes [13]. In addition, it aligns with the principles of renewable and sustainable energy production. Specifically, by utilizing residual agricultural and forestry materials, such as peanut shells, spent coffee grains, sugarcane leaves, and pinewood sawdust, these pellets contribute to waste reduction and effective utilization of biomass resources that would otherwise go unutilized. This aspect is crucial for achieving a more environmentally friendly and sustainable energy landscape. Furthermore, the pellets incorporating biogenic extracts meet stringent requirements outlined by international standards governing parameters such as length, diameter, bulk density, heating value, durability, and moisture content. This adherence ensures that the pellets adhere to high quality standards and can be reliably employed in diverse residential and industrial biomass conversion systems [10].

In contrast, one of the primary drawbacks of the pellets incorporating biogenic extracts is their higher ash content in comparison to traditional wood pellets. The ash content, measuring at 2.4-3.7%, surpasses critical limits associated with the formation of physical deposits, such as slagging and fouling, within furnaces and boilers. Consequently, the utilization of these pellets may necessitate more frequent maintenance and cleaning of the combustion systems, which can increase operational costs and efforts [33]. Additionally, the presence of excess nitrogen (N) and sulfur (S) in the biogenic extracts may result in the release of hazardous gases, including nitrous oxides (NO_x) and sulfur oxides (SO_x), during the combustion process [34]. These emissions contribute to air pollution and can have adverse effects on human health and the environment. As a result, effective measures need to be implemented to mitigate these emissions and minimize their impact. Therefore, the utilization of pellets incorporating biogenic extracts derived from peanut shells, spent coffee grains, and sugarcane leaves may encounter challenges in achieving widespread market acceptance. Concerns regarding the higher ash content and potential emissions of hazardous gases can influence customer perceptions and their willingness to adopt these pellets as a sustainable fuel source [33]. Addressing these concerns through comprehensive research, effective communication, and continual improvement in pellet characteristics is crucial to expand the market acceptance of these innovative biomass fuel products [35].

In synthesis, the incorporation of biogenic extracts in pellet manufacturing presents notable advantages such as enhanced technical quality, contribution to renewable energy production, and compliance with international standards. However, it is imperative to acknowledge the limitations associated with higher ash content, potential emissions of hazardous gases, and limited market acceptance. By conducting further research and development, optimizing the pelletization process, reducing ash content, and implementing emission mitigation strategies, the drawbacks can be addressed, leading to wider adoption and market penetration of these pellets within the context of renewable and sustainable energy production.

3.4. Advancements, Trade-offs, and Implications to Advance the Control of Biomass Off-Gassing by Antioxidant Addition

Our study has made significant advancements in understanding and controlling off-gassing in wood pellets through the incorporation of biogenic additives derived from peanut shells, spent coffee grains, and sugarcane leaves. By investigating the autogenous generation of CO_2 and degradation of extractives, as well as the antioxidant potential of these additives, we have shed light on their effects on pellet quality and off-gassing control.

One of the key advancements of our study is the establishment of functional kinetic relationships between materials, products, and processes using the Gompertz model. This model allows for accurate estimation of alpha, beta, and k parameters, providing insights into the behavior of CO_2 generation and extractive degradation in pellets. By analyzing these parameters, we have gained a deeper understanding of the impact of biogenic additives on these processes, including their capacity to decrease specific CO_2 emissions and decelerate extractive degradation. This knowledge is crucial for optimizing pellet manufacturing processes and improving the overall quality of pellets. Another advancement lies in the characterization of the antioxidant potential and functionality of the biogenic extracts. By quantifying parameters such as total polyphenols, ascorbic acid, carotenoids, and enzymatic activities, we have provided a scientific basis for assessing the off-gassing control potential of these additives. The findings highlight the antioxidant capabilities of the biogenic extracts, their ability to scavenge reactive oxygen species (ROS), and their role in inhibiting oxidative reactions and extractive degradation. This understanding opens up new possibilities for utilizing these extracts as effective off-gassing control agents in pellet production.

However, along with these advancements, our study also reveals trade-offs and implications that need to be considered. One trade-off is the higher ash content observed in the pellets incorporating biogenic additives. This elevated ash content can lead to the formation of physical deposits, such as slagging and fouling, within furnaces and boilers. The presence of these deposits necessitates more frequent maintenance and cleaning, potentially increasing operational costs and efforts. Addressing this trade-off requires further research and optimization to reduce the ash content while maintaining the desired pellet qualities and off-gassing control. Additionally, the presence of nitrogen (N) and sulfur (S) in the biogenic extracts raises concerns about potential emissions of hazardous gases, including nitrous oxides (NO_x) and sulfur oxides (SO_x), during pellet combustion. These emissions can contribute to air pollution and have adverse effects on human health and the environment. Mitigating these emissions is crucial for ensuring the prominence of pellet off-gassing control and promoting the adoption of these pellets as a sustainable fuel source. Future studies should focus on developing strategies to minimize NO_x and SO_x emissions, such as optimizing the pellet formulation or incorporating additional emission control technologies.

The implications of our study are significant for the prominence of off-gassing control in pellet production. By providing insights into the effectiveness of biogenic additives in reducing specific CO_2 emissions and preserving extractive integrity, our findings contribute to the development of more sustainable and environmentally friendly pellet manufacturing processes. These advancements have implications for improving air quality, promoting occupational safety and human health, reducing environmental pollution, and fostering the adoption of greener pelletization methods.

Furthermore, our study has broader implications for the biomass energy industry and the transition to renewable and sustainable energy sources. Wood pellets are increasingly recognized as a viable alternative to fossil fuels, and controlling off-gassing is a crucial aspect for their acceptance and utilization. The use of biogenic additives derived from agricultural and forestry residues aligns with the principles of waste reduction and effective biomass resource utilization. By incorporating these additives, the industry can enhance the technical quality of pellets, improve their performance in biomass conversion equipment, and contribute to a more sustainable energy landscape.

To recapitulate, our study has advanced the understanding and control of off-gassing in wood pellets through the incorporation of biogenic additives. While there are trade-offs and implications to be considered, such as higher ash content and potential emissions of hazardous gases, our findings provide valuable insights for optimizing pellet production processes, reducing off-gassing, and promoting the prominence of sustainable and environmentally friendly wood pellets. Further research and development in this area are necessary to overcome challenges and fully realize the potential of these additives in the biomass energy industry.

4. Conclusion

We investigated the incorporation of biogenic additives derived from peanut shells, spent coffee grains, and sugarcane leaves in wood pellet manufacturing, with a focus on controlling off-gassing. Through comprehensive analysis and characterization, we have made significant advancements in understanding the dynamics of CO_2 generation and extractive degradation in pellets, as well as the antioxidant potential of these additives. Our findings demonstrate that the inclusion of biogenic additives in pellet compositions effectively reduces specific CO_2 emissions and decelerates extractive degradation. The Gompertz model provided accurate estimations of alpha, beta, and k parameters, elucidating the behavior of these processes and highlighting the role of the additives in mitigating off-gassing. Furthermore, the biogenic extracts exhibited notable antioxidant capabilities, with significant quantities of total polyphenols, ascorbic acid, carotenoids, and enzymatic activities, thereby contributing to the preservation of extractive integrity and minimizing off-gassing during pellet storage. While these advancements offer promising prospects for off-gassing control, trade-offs and implications need to be addressed. The higher ash content quantified in pellets containing biogenic additives poses challenges in terms of physical deposits formation within combustion systems. Additionally, the presence of nitrogen and sulfur in the additives raises concerns about potential emissions of hazardous gases during pellet combustion. Overcoming these trade-offs requires further research and optimization to reduce ash content and mitigate emissions, ensuring the environmental and occupational safety of pellet utilization. By enhancing the technical quality of pellets, optimizing manufacturing processes, and reducing off-gassing, our findings contribute to the promotion of biomass energy as a viable and environmentally friendly alternative. Additionally, the utilization of biogenic additives derived from agricultural and forestry residues aligns with waste reduction and effective biomass resource utilization. This aspect highlights the potential of our study in the context of sustainable energy production. Overall, our study provides scientific evidence and insights into the incorporation of biogenic additives for controlling off-gassing in wood pellet production. It highlights the potential to reduce specific CO_2 emissions, preserve extractive integrity, and enhance the overall quality of pellets. The trade-offs and implications identified underscore the need for further research and optimization to address challenges related to ash content and emissions. By advancing off-gassing control, our study contributes to the development of sustainable and environmentally friendly solid biofuel markets and the transition to renewable energy sources.

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Supplementary Material

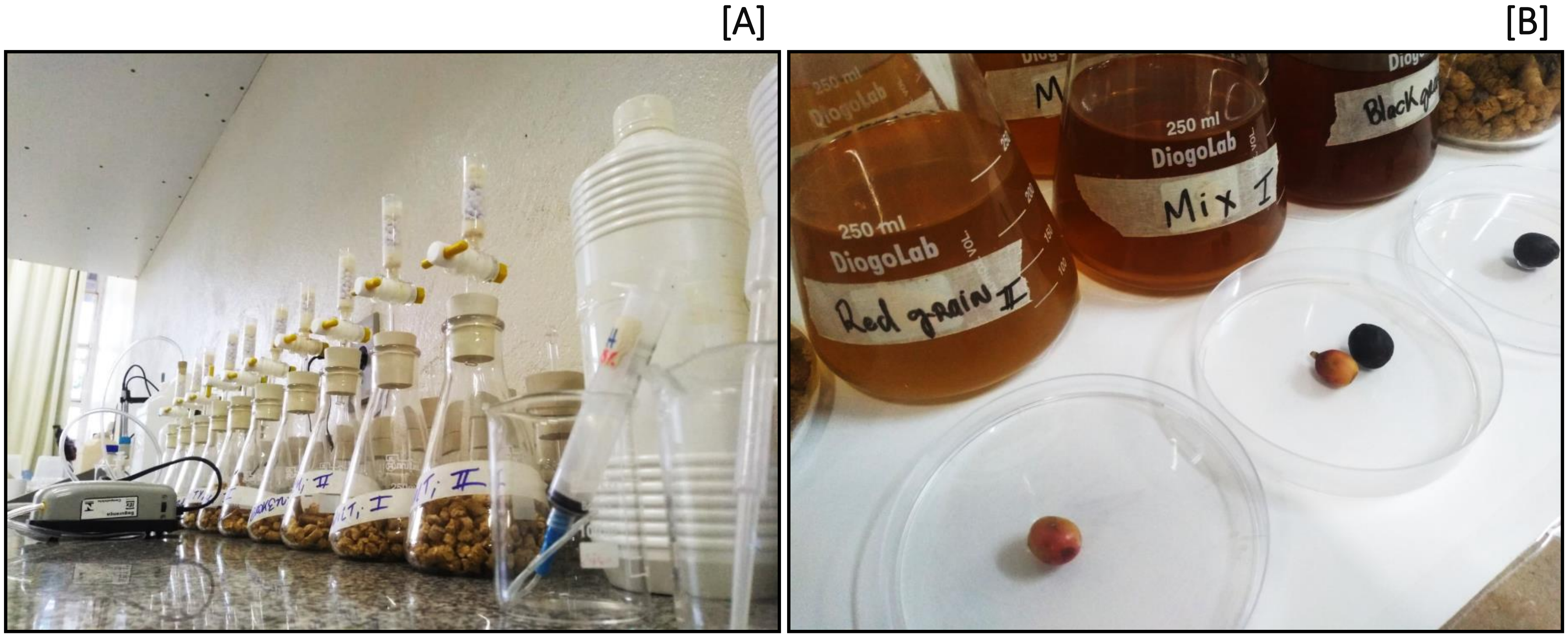

Fig S1. Respirometric experiment [A] for the quantification of specific emission of CO_2 from wood pellets with and without the addition of biogenic extracts [B] from peanut shells, spent coffee grains, or sugarcane leaves as potential antioxidants to control off-gassing.

Tab S1. Standards and instruments for the physicochemical characterization of materials

Norm/Method	Property	Instrument
ASTM D3173-87	Moisture	Drying-oven (Marconi MA035/5)
ASTM D120-30	Volatile matter	Muffle furnace (SPlabor 1200DM/B)
ASTM D3172-07	Fixed carbon	This is not a process of analysis
ASTM D1762-84	Ash	Muffle furnace
CEN's EN 15104	C, H, O, and N	Elemental analyzer (Flash Smart CHNS/O)
CEN's EN 15289	S	Elemental analyzer (Perkin CHNS/0 2400 II)
ASTM D2015-96	Heating value	Isothermal digital calorimeter (IKA C200)

ASTM, American Society for Testing and Materials

Tab S2. Technical specifications of the pelleting system

Key	Unit
Load capacity of the hoper	250 kg
Feeding rate	75 kg h^{-1}
Engine potency	20 hp
Production capacity	250 kg h^{-1}
Nominal diameter of compressing channel	200 mm
Nominal diameter of tungsten pressing rollers	2 × 100 mm
Maximum nominal pressure in hydraulic system	300 MPa
Maximum nominal temperature of flat die	150 °C
Nominal diameter of the pellet	6-8 mm
Bulk density of the pellet	1000-1400 kg m^{-3}
Mass	850 kg
Dimension of the pelletizer machine	4200 mm × 2450 mm × 1750 mm

Tab S3. Parametrization and appropriateness of Gompertz model for the specific emission of CO_2 from wood pellets with and without the addition of biogenic extracts from peanut shells, spent coffee grains, and sugarcane leaves as potential antioxidants to control off-gassing

Source	alpha	beta	k	AIC	BIC	r^2
	Emission					
Peanut shells	2732.1	4.3	$4.25 \times e^{-2}$	264.4	271.8	0.7
Spent coffee grains	2405.2	4.2	$3.5 \times e^{-2}$	258.5	262.1	0.75
Sugarcane leaves	2472.4	5.15	$4.5 \times e^{-2}$	278.2	280.9	0.6
Control	2995.4	5.5	$7.5 \times e^{-2}$	243.5	248.7	0.8
	Extractive					
Peanut shells	30.1	$1.65 \times e^{-1}$	$-1.05 \times e^{-1}$	12.3	13.4	0.6
Spent coffee grains	32.45	$1.05 \times e^{-1}$	$-1 \times e^{-1}$	10.9	11.2	0.6
Sugarcane leaves	31.85	$1.2 \times e^{-1}$	$-1.2 \times e^{-1}$	16.7	118.2	0.7
Control	28.1	$2.95 \times e^{-1}$	$-1.1 \times e^{-1}$	11.9	13.4	0.75

Tab S4. Outcome of principal component analysis for the specific emission of CO_2 from wood pellets with and without the addition of biogenic extracts from peanut shells, spent coffee grains, and sugarcane leaves as potential antioxidants to control off-gassing

	Bartlett's test of sphericity	
X-square	-629.6	
Degree of freedom	45	
p-value	2.15e-05	
	Component	
	I	II
Eigenvalue	6.75	3.25
Percentage of variance	67.5	32.5
Cumulative percentage of variance	67.5	100
	Loading	
Off-gassing	-0.65	0.8*
Remaining extractives	1*	0.05
DPPH• radical scavenging activity	0.8*	0.6
Reducing power	-0.65	-0.75*
Total polyphenols	0.95*	-0.35
Ascorbic acid	0.975*	-0.2
Carotenoids	0.7*	0.7*
SOD activity	-0.35	0.95*
CAT activity	0.95*	-0.3
POD activity	1*	0.1
	Contribution, %	
Peanut shells	14.5	52.2*
Spent coffee grains	66.6*	0.1
Sugarcane leaves	18.9	47.7*

Significance code: * p-value < 0.05.

CHAPTER IV – Fuel-Flexible Biomass Off-Gassing: The Impact of Antioxidant Spent Coffee Grains on Emissions of CO_2, CO, CH_4, And VOCs, Physical Deposits, and Combustion in Wood Pellets

An alternate version of Chapter IV is presently accessible as a research article on the web at https://doi.org/10.1016/j.indcrop.2023.117748

Highlights

Introduces biogenic antioxidants from residues to reduce emissions during storage.
Demonstrates superior performance of spent coffee grains.
Insights for crop professionals, enhancing pellet properties.
Reduces off-gassing, mitigating emissions and volatile compounds.
Explores areas for optimizing additive's properties and antioxidant capabilities.

Abstract

The increasing demand for sustainable energy sources has led to the growth of the solid biofuel industry, particularly in the form of pellets. While pellets offer numerous benefits for residential and industrial heating systems, there are inherent risks associated with their utilization, including the generation of toxic chemicals during storage and transportation. This study aims to explore the potential of using biogenic antioxidant additives derived from agricultural residues to control off-gassing in pinewood pellets. Comparative experiments were conducted using distinct agricultural residues, including spent coffee grains (SCG), peanut shells, and sugarcane leaves. The emissions of CO, CO_2, CH_4, and VOCs were measured during storage conditions resembling long-term incubation. The technical quality of the pellets, including bulk density, heating value, and durability, was also assessed. Among the agricultural residues tested, SCG demonstrated superior performance in reducing emissions of CO_2, CO, CH_4, and VOCs. The addition of SCG as a biogenic antioxidant additive resulted in a significant reduction in total off-gassing compared to the control group. Furthermore, pellets containing SCG exhibited improved technical quality, with higher bulk density, heating value, and durability. The results highlight the effectiveness of

SCG in preserving essential components and reducing emissions during storage. However, the utilization of SCG may lead to elevated concentrations of ash, nitrogen, and sulfur, which can pose limitations and environmental risks. Mitigating these concerns is essential to ensure compliance with regulations and minimize adverse impacts. The utilization of SCG's biogenic extract as an additive in pellets demonstrates promise for enhancing off-gassing control and advancing sustainable solid biofuel production. Further research is needed to optimize the additive concentration, explore encapsulation methods, and address the limitations associated with nitrogen, sulfur, and ash content. By overcoming these challenges, the industry can benefit from improved pellet properties, reduced emissions, and enhanced sustainability in biofuel production and utilization.

Keywords: carbon dioxide; carbon monoxide; extractives; methane; reactive oxygen species; volatile organic compounds.

1. Introduction

The global demand for sustainable and renewable energy sources has led to the growth of the solid biofuel industry, with pellets emerging as a prominent carrier of such energy (Gunnarsdottir et al., 2021). These pellets are extensively used in residential and industrial heating and power generation systems, including household stoves, electric heaters, furnaces, boilers, and combustors. Their usage has the potential to significantly contribute to sustainable energy development in both developed and emerging economies, particularly in rural areas where access to energy is a significant challenge. However, despite the numerous benefits of solid biofuels, there are inherent risks associated with their utilization, especially when derived from forestry resources such as pinewood sawdust (Alakoski et al., 2016). One critical issue is the autogenous generation of toxic chemicals, which can occur indoors and pose hazards to workers and customers. The off-gassing of pellets during transportation and storage gives rise to various fast-acting toxic compounds, including carbon monoxide (CO), carbon dioxide (CO_2), methane (CH_4), and volatile organic compounds (VOCs) (Siwale et al., 2022). These compounds not only deteriorate occupational safety and human health but also disrupt environmental protection efforts, thereby undermining the sustainability of solid biofuel value chains.

Instances of severe incidents related to off-gassing have been reported in both residential and industrial settings (Svedberg et al., 2008). Poor storage conditions, such as inadequate ventilation, can lead to the accumulation of acutely toxic concentrations of CO in the ambient atmosphere (Svedberg and Johanson, 2017). Such incidents have resulted in cases of poisoning and, tragically, even deaths (Gauthier et al., 2012). Consequently, these incidents have raised awareness and prompted society and relevant authorities to address the risks associated with off-gassing in the solid biofuel industry. To mitigate these risks, researchers have been actively exploring strategies to control off-gassing in wood solid biofuels. The focus has been on improving environmental conditions during storage or transportation, such as conditioning temperature, relative humidity of the air, and aeration (Svedberg and Johanson, 2017). Another approach involves enhancing the stability and integrity of the product. Studies have investigated the effectiveness of techniques like supercritical fluid extraction (Arshadi et al., 2012; Attard et al., 2016), which removes fatty and resinous acids from the feedstock before pellet formation. Additionally, the incorporation of antioxidants like tert-butylhydroquinone (TBHQ), propyl gallate (Arshadi et al., 2018), and acetylsalicylic acid (ASA) (Sedlmayer et al., 2020) has demonstrated promise in reducing specific emissions of CO, CO_2, and VOCs. While these studies have yielded encouraging results, the development of sustainable antioxidants for controlling off-gassing in wood pellets remains a challenge. This presents an opportunity for further research and innovation. It is within this context that our study proposes the application of a biogenic extract derived from spent coffee grains (SCG) as a potential solution. Spent coffee grains, being a by-product of crop harvesting, contains a range of antioxidant compounds such as polyphenols, ascorbic acid, and carotenoids (Chatzimitakos et al., 2023). Furthermore, its enzymatic components, including superoxide dismutase (SOD), catalase (CAT), and peroxidase (POD), contribute to its ROS-scavenging capabilities. These combined properties make SCG a compelling candidate for inhibiting the oxidation of extractives and the subsequent generation of off-gassing (Chatzimitakos et al., 2023).

In our exploratory study (data not published), we aimed to select agricultural residues from crop harvesting to develop biogenic antioxidant additives specifically for controlling off-gassing in fuel-grade pinewood pellets. Comparative experiments involving SCG, peanut shells, and sugarcane leaves revealed that SCG outperformed the other residues in reducing the specific emission of CO_2. By inhibiting the degradation of essential components like oils, waxes, resins, and tannins by ROS under controlled storage conditions, SCG demonstrated its ability to preserve more extractive matter, resulting in lower CO_2 emissions during short-to-medium-term incubation. Furthermore, products containing SCG exhibited superior technical quality, as indicated by higher bulk density, heating value, and durability compared to reference pellets. However, it is crucial to consider the potential limitations associated with SCG utilization. Products incorporating SCG may contain higher concentrations of ash, nitrogen (N), and sulfur (S) compared to critical limits for safe biomass conversion equipment utilization. This may restrict their applications and acceptance, as they can lead to the formation of undesirable physical deposits in furnaces and boilers (Smith et al., 2016), consequently reducing cost-effectiveness. Moreover, the combustion of these deposits can generate hazardous compounds such as nitrous oxides (NO_x) and sulfur oxides (SO_x), posing risks to both society and the environment (Sommersacher et al., 2012).

Understanding the trade-offs associated with incorporating SCG into pellets for off-gassing control, alongside a focused investigation on CO_2 emissions, presents an opportunity for further research and development. Hence, our in-depth study seeks to assess the potential of SCG's biogenic extract in controlling emissions of CO, CH_4, and VOCs under various storage conditions. Additionally, we aim to characterize the impact of SCG on fouling and slagging formation propensity, as well as combustion efficiency. Through these investigations, we aim to expand our understanding of the significance and implications of SCG in developing safer and more sustainable solid biofuels.

2. Materials and Methods

2.1. Origination of spent coffee grains’ biogenic extract

The SGC's biogenic extract was derived from initial research conducted to address the issue of off-gassing in pinewood pellets (**Supplementary material**). Among various potential sources of antioxidant addition, such as peanut shells and sugarcane leaves, the biogenic extract was chosen due to its distinctive ability to retard the deterioration of extractives and minimize the specific emission of CO_2 during short-to-medium-term storage at the flask level (**Fig 1, Fig S1, Supplementary material**). After confirming its technical superiority over competing biogenic extracts, the extract was stored in airtight glass containers within a freezer established at -5°C. This storage approach aimed to preserve the extract's antioxidant capabilities (**Tab S2, Supplementary material**) until the pellet manufacturing processes could be initiated. To ensure the extract's efficacy and suitability for its intended applications, comprehensive high-throughput characterizations were conducted. These characterizations included evaluating its DPPH• radical scavenging activity, reducing power (Xie et al., 2015), total polyphenol content (Singleton and Rossi, 1965), ascorbic acid content (Roe and Kuether, 1943), carotenoid content (Rodriguez-Amaya, 2001), and enzymatic activity encompassing superoxide dismutase (SOD), catalase (CAT), and peroxidase (POD) (Beauchamp and Fridovich, 1971). By reproducing these characterizations, we aimed to validate the extract's capabilities, functionality, and the efficacy of freezing-storage in preserving these properties.

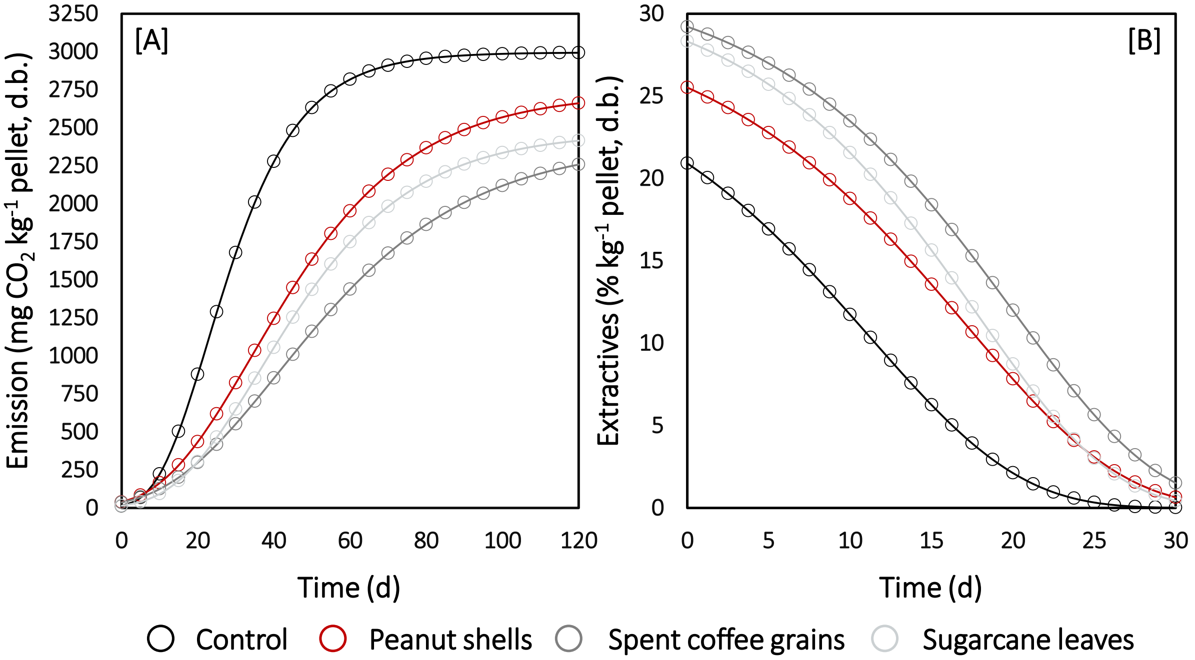

Fig 1. Autogenous generation of CO_2 [A] and degradation of extractives [B] in wood pellets with addition of biogenic extracts derived from peanut shells, spent coffee grains, and sugarcane leaves in the initial research on potential antioxidants to control off-gassing.

Furthermore, we characterized the extract's solubility and analytical purity. The determination of solubility involved measuring the absorbance or transmission of light through a solution of the material in water using spectrophotometry (Yan et al., 2022). A 10% (v/v) solution of the material was prepared by adding 1 mL of the material to 10 mL of ultrapure water, ensuring complete dissolution. A spectrophotometer was then utilized to measure the absorbance or transmission of light through the solution at a specific wavelength (515 nm). A blank solution containing only the solvent (water) was prepared and used as a reference for baseline correction. The spectrophotometer was adjusted to zero absorbance or 100% transmission using the blank solution. Subsequently, the solution containing the material was placed in the sample holder, and the spectrophotometer was programmed to measure the absorbance or transmission of light. By comparing the absorbance of the solution to a calibration curve constructed using a standard solution of known concentrations, the concentration of the material in the original solution was determined, representing its water solubility. In addition, the determination of analytical purity involved separating and quantifying the individual components present in the material using high-performance liquid chromatography (HPLC) (Shehata et al., 2016). A 10% (v/v) solution of the material was prepared by dissolving 1 mL of the material in ultrapure water. The solution was then filtered through a nitrate-cellulose membrane to remove any particulate matter or impurities that could interfere with the HPLC analysis. An aliquot of the filtered solution was injected into the HPLC system using a sample injector. The sample was separated as it passed through a chromatographic column, which contained a stationary phase designed to interact with the components based on their physicochemical properties. The components of the material were eluted from the column at distinct retention times, influenced by their specific interactions with the stationary phase. The UV-Vis detector measured the absorbance or response of the eluted compounds at 515 nm. By comparing the chromatographic peak areas of the individual components of interest to the total area of all peaks in the chromatogram, the percentage or quantitative composition of each component in the material was determined, providing an assessment of its analytical purity. These thorough characterizations of solubility and analytical purity added valuable information about the physiochemical and hydraulic properties of the extract, further confirming its suitability for pelletization.

2.2. Addition, Pelletization, and Technical Assessment of Product's Standard Qualities

A precise experimental protocol was employed to investigate the effects of the biogenic antioxidant extract on pinewood sawdust pellets. The application of the extract involved a careful and controlled process, where a volume of 0.1 L was applied at various concentrations (0.05%, 0.1%, 0.2%, and 0.4%) using an airbrush compressor (Sagyma, ASW-775, Burkard Scientific, Uxbridge, UK) operated at a consistent pressure of 155 kPa (Moreira et al., 2021). This method ensured uniform and controlled application of the extract onto the sawdust particles. Following the application stage, the compaction process was carried out using an automatic hydraulic presser machine (**Tab S3, Supplementary material**). The feedstock, both with and without the addition of the extract, was compacted at a pressure of 200 MPa and a temperature of 150 °C for a duration of 90 seconds. This specific methodology for compaction was based on the comprehensive critical review of solid biofuels by

Whittaker and Shield (2017), ensuring consistency and comparability with prior studies. The aim of this compaction process was to effectively bind the sawdust particles together by applying sufficient pressure and heat, enhancing the formation of the pellets. To ensure standardization and reproducibility, each batch of pelleting consisted of precisely 1.5 kg of feedstock. The resulting pellets were carefully recovered from the pelletizer and allowed to cool to ambient temperature. Subsequently, they were hermetically stored in plastic bags to maintain their integrity and prevent any external contamination or moisture ingress until further assessments were conducted.

To evaluate the standard qualities of the pellets, several measurements were performed. The length and diameter of the pellets were determined following the methodology established by Azargohar et al. (2019). This involved precise measurement of the dimensions of a representative number of pellets using appropriate measuring tools to ensure statistical significance and representative sample analysis. The bulk density of the pellets, which indicates their packing density and structural characteristics, was measured using the approach described by Park et al. (2020). This method involved determining the mass and volume of a representative number of pellets, enabling the calculation of bulk density. The heating value of the pellets, representing their energy content, was determined using a calorimetric combustion system (C-200, IKA, Brazil). This method, as outlined by Christoforou and Fokaides (2019), measured the heat released during the complete combustion of the samples, providing valuable information about the energy potential of the pellets. Durability testing was conducted according to the methodology outlined by (Abdulmumini et al., 2020) to assess the resistance of the pellets to mechanical stress and abrasion. This involved subjecting the pellets to controlled impact or compression forces, followed by measuring any particle breakage or degradation. The durability of the pellets provided insights into their ability to withstand handling, transportation, and storage without significant damage.

In addition to the standard quality assessments, further tests were conducted to investigate the mechanical resistivity and hygroscopicity of the pellets. The tensile strength of the pellets was determined using **Eq 1**, which involved downsizing twenty randomly selected pellets to a size of 2 mm and subjecting them to a controlled pulling force using a programmable universal testing machine (6800 Series, Instron, US). The force applied to the pellets was precisely controlled at a rate of 1 mm min^{-1} until they broke. This testing methodology, inspired by Chew et al. (2018), allowed for the measurement of tensile strength, providing valuable information about the mechanical integrity and structural stability of the pellets. Hygroscopicity, representing the ability of the pellets to attract and retain environmental vapor, was determined by subjecting the samples to a humidity chamber (KBF 115, Binder Inc., US) established at a temperature of 25°C and a relative humidity of 90% for a duration of 72 hours. The weight of the samples was carefully measured before and after the testing period, allowing for the calculation of weight changes due to water absorption or adsorption. The methodology for hygroscopicity assessment was based on the procedure described by Shojaeiarani et al. (2019), providing insights into the interaction of the pellets with moisture and their potential moisture management characteristics.

$$\sigma = \frac{2F}{\pi dL} \text{ (Eq 1)}$$

In Eq. 1, F, d, and L represent breaking force (N), diameter (m), and length (m), respectively.

All tests and assessments were conducted meticulously and in triplicate to ensure the reliability, accuracy, and reproducibility of the obtained results. By following these methodologies, the experimental procedures aimed to provide comprehensive insights into the properties and performance of the pellets with the addition of the biogenic antioxidant extract.

2.3. Off-gassing Monitoring and Quantification: CO_2, CO, CH_4, and VOCs

In accordance with Attard et al. (2016), triplicate samples weighing 0.1 kg each were prepared for the experiment. These samples were carefully transferred to chambers with controllable temperature and relative humidity conditions. The chambers provided an enclosed environment where the samples could undergo incubation under controlled conditions. By using triplicate samples, we aimed to ensure the reliability and reproducibility of the experimental results. The system was programmed to operate at distinct temperature conditions: 25, 35, and 50 °C. These temperature settings simulated a range of environmental conditions, allowing us to investigate the effects of temperature on the emissions of gases from the samples. Additionally, distinct relative humidity levels were applied: 30, 60, and 90%. These humidity settings reflected particular moisture conditions that can influence the oxidation processes of organic matter.

To measure the concentrations of CO_2, CO, CH_4, and VOCs, as well as the depletion of O_2, we utilized a portable multi-gas monitor, specifically the Radius® BZ1 from Area Monitor. This instrument employs advanced photoionization and infrared sensing technology, enabling accurate and sensitive detection of gases. The multi-gas monitor offered the capability to measure gases over a wide range of temperatures, spanning from -20 to 55 °C, and relative humidity levels ranging from 15 to 95%. This wide operating range allowed us to capture gas emissions in diverse environmental conditions. Throughout the six-month incubation period, gas concentrations were monitored at regular intervals of every five days. The multi-gas monitor was employed to measure the concentrations of CO_2, CO, CH_4, and VOCs autogenously generated during the incubation process. Additionally, the depletion of O_2 was recorded, providing insights into the ongoing oxidation processes within the samples. The repeated measurements over an extended period allowed us to observe the temporal dynamics of gas emissions and oxidation reactions.

By employing this comprehensive methodology, we aimed to gain a deeper understanding of the emissions of CO_2, CO, CH_4, and VOCs under varying temperature and humidity conditions. The incorporation of triplicate samples, controlled incubation environments, and advanced gas monitoring technology provided a robust framework for accurate and reliable data collection. Through the meticulous implementation of these methodologies, our study sought to contribute valuable insights into the complex processes of organic matter oxidation and gas emissions.

2.4. Combustion Performance

The combustion performance of pellets with the addition of SCG's biogenic extract was characterized using thermogravimetry. Triplicate samples weighing 0.05

kg each were subjected to thermogravimetric analysis using a thermogravimetric analyzer (PGA-8000, PerkinElmer, Brazil). The temperature was increased from 25 to 1000 °C at a heating rate of 10 °C min^{-1}. During the analysis, an inert gaseous mixture of nitrogen and oxygen (N_2/O_2, 4:1 v v^{-1}) was injected into the reactor at a flow rate of 50 mL min^{-1}. This gas mixture facilitated the oxidative kinetics of the samples (Chen et al., 2021), allowing for the measurement of heat flow through a series of chemical reactions that occur during combustion. These reactions include processes such as water vaporization or dewatering, devolatilization, and carbonization. To evaluate indicators of combustion performance, we estimated DTGc, DTGi, DTGf, and DTGt using equations (**Eqs 2-5**) that involve critical temperatures and rates of thermal conversion of organic matter to carbon-dense charcoal. These equations are commonly observed in the coalification of biomass and provide insights into the combustion characteristics of the samples.

$$\mathrm{DTG_c} = \frac{\mathrm{R_p} \times \mathrm{R_v}}{\mathrm{T_i}^2 \times \mathrm{T_b}} \text{(Eq 2)}$$

$$\mathrm{DTG_i} = \frac{\mathrm{R_v}}{\mathrm{T_i} \times \mathrm{T_p}} \text{(Eq 3)}$$

$$\mathrm{DTG_f} = \frac{\mathrm{R_p}}{\mathrm{T_i}^2} \text{(Eq 4)}$$

$$\mathrm{DTG_t} = \frac{8.5875 \times 10^7 \times \mathrm{R_v}}{\mathrm{T_i} \times \mathrm{T_p}} \text{(Eq 5)}$$

In the series of thermogravimetric equations, DTGc, DTGi, DTGf, and DTGt represent combustibility, ignitability, flammability, and thermostability, Rp and Rv denote maximum and average loss of matter (% min^{-1}), and Ti, Tb, and Tp signify crucial temperatures (°C) of ignition, burnout, and peak, respectively.

By applying these equations and analyzing the thermogravimetric data, we aimed to gain a comprehensive understanding of the combustion performance of the pellets with the addition of SCG's biogenic extract. These calculations and assessments provided valuable insights into the combustibility, ignitability, flammability, and thermostability of the samples, contributing to the evaluation of their overall combustion characteristics.

2.5. Profile of Meltable Oxides, Slagging, and Fouling

To assess the profile of meltable oxides, slagging, and fouling tendencies in the pellets, we employed EDXRF spectroscopy (Sigvardsen and Ottosen, 2019). This spectroscopic technique allowed us to determine the presence and concentration of metal oxides in the samples. To further evaluate the propensity of the pellets to slag and foul in biomass conversion equipment, such as furnaces and boilers, we utilized stoichiometric equations (Smith et al., 2016). These equations were solved to estimate the slagging index and fouling index, providing insights into the potential for meltable ashes that can cause operational issues. The slagging index (**Eq 6**) was determined by calculating the ratio of meltable (CaO, Fe_2O_3, K_2O) to refractory (SiO_2, Al_2O3, TiO_2) oxides, multiplied by the concentration of SO_3. This index served as an indicator of the pellet's propensity to form slag, which can lead to the accumulation of molten ash and can impact the efficiency and performance of biomass conversion equipment. The fouling index (**Eq 7**) was calculated by dividing the sum of meltable oxides (CaO, MgO, K_2O) by the product of refractory oxides and the concentration of K_2O. This index provided insights into the potential for fouling, which refers to the deposition and accumulation of ash on heat transfer surfaces, affecting heat transfer efficiency.

$$\mathrm{Slagging_{index}} = \left(\frac{\mathrm{CaO + Fe_2O_3 + K_2O}}{\mathrm{SiO_2 + Al_2O_3 + TiO_2}}\right) \times \mathrm{SO_3}\ (\mathrm{Eq\ 6})$$

$$\mathrm{Fouling_{index}} = \frac{\mathrm{CaO + MgO + K_2O}}{\mathrm{(SiO_2 + Al_2O_3 + TiO_2) \times K_2O}}\,(\mathrm{Eq\ 7})$$

By employing these stoichiometric equations and spectroscopic analysis, we aimed to gain a comprehensive understanding of the profile of meltable oxides, slagging, and fouling tendencies in the pellets. These assessments were crucial in evaluating the suitability of the pellets for biomass conversion processes and determining their potential impact on equipment performance and operation.

2.6. Statistical Data Analysis

We employed statistical data analysis techniques to examine the emissions of CO, CO_2, CH_4, and VOCs, as well as the simultaneous depletion of O_2, in relation to varying concentrations of the additive in the product. Specifically, Gompertz model, encompassing kinetic parameters (**Eq 8**) (Tjørve and Tjørve, 2017), was utilized to analyze the relationship between the additive concentration and the emissions and O_2 depletion. This allowed us to determine the dynamic impact of the additive on these gas emissions and the oxygen levels.

$$f_{(t)} = \alpha e^{-\beta^{-kt}} (\text{Eq } 8)$$

In Eq. 7, the dependent variable f represents the autogenous generation of CO_2, CO, CH_4, or VOCs or the O_2 depletion in units of part per million (ppm) over time (t). The parameter alpha (α) corresponds to the asymptote, which signifies either the maximum emission or the minimum depletion achieved during the process. The parameter beta (β) represents the halftime of the sigmoid model, indicating the point at which the emission rate reaches half of its maximum or minimum value. The parameter k denotes the specific growth rate of the curve, determining the steepness or rate of change of the emission or depletion. The variable t denotes time, and e represents the Euler constant.

Furthermore, we employed contour plot approach and the confidential inference tree (CIT) methodology as multivariate statistical methodologies to gain insights into the relationships between the variables of interest. The contour plot approach is a visualization technique that allows for the examination of how continuous variables, temperature and relative humidity, collectively influence the emissions of CO, CO_2, CH_4, and VOCs. By plotting these variables on the x and y axes and representing the emissions as contours on the plot, the contour plot provides a visual representation of the interactions and trends between the variables. This method enables researchers to observe patterns, identify regions of high emissions, and assess the overall impact of changing storage conditions on the emissions of interest. Conditional inference tree is a statistical modeling technique that helps analyze and interpret the relationships between variables. It operates by creating a tree-like structure that partitions the data based on distinct conditions or rules. In this study, the CIT methodology was used to explore the interactions between storage conditions and the collective activity of the chemicals under investigation. By splitting the data based on various conditions and evaluating the statistical significance of every split, the CIT methodology provided insights into the interplay between storage conditions and chemical emissions. Additionally, within every level of additive concentration, the contour plot and CIT methodologies were applied to assess the importance of availability in stabilizing the product under standard and challenging environments. This approach allowed us to investigate how the availability of the additive influenced the stability of the product under distinct storage conditions at varying concentrations. By systematically analyzing a range of concentrations, we were able to evaluate the effectiveness of the additive in preserving the product across distinct scenarios and make conclusions about its stability-enhancing capabilities.

To conduct these statistical analyses, the widely recognized R software was used. It offers a comprehensive suite of statistical tools and functions that facilitated the implementation of the Gompertz sigmoid, contour plot, and CIT modeling. Additionally, R was used to conduct multiple comparison analyses, such as the post-hoc Tukey's HSD test, which provided a statistical evaluation of the impact of adding the specific additive to the product’s qualities encompassing length, diameter, bulk density, heating value, durability, moisture, ash, N, and S, tensile strength, and hygroscopicity. Moreover, R was used to generate visual representations, such as graphs and figures, which effectively communicate our findings to the readers.

3. Results and Discussion

3.1. Emissions of CO, CO_2, CH_4, and VOCs

3.1.1. Performance of SCG's Biogenic Extract under Original Experimental Conditions

The presence of the antioxidant additive (94.25% purity and 1.9 g L^{-1} solubility) in the pellets demonstrated a notable effect on the emissions of CO_2, CO, CH_4, and VOCs (**Fig 2**). Specifically, pellets without the antioxidant additive accumulated approximately 21039.4 ppm of these gases, whereas the pellets containing the additive accumulated 18268.9 ppm. Therefore, it was evident that the incorporation of the antioxidant additive during the manufacturing process led to a significant reduction of 13.2% in the total off-gassing. Upon closer analysis and examination of the specific emissions, it was found that the SCG's biogenic extract acted as an effective antioxidant, resulting in reduced emissions of CO_2, CO, CH_4, and VOCs. The concentrations of CO_2 in the pellets without and with the additive were quantified at 14487.95 ppm and 12987.1 ppm, respectively. Similarly, lower values were observed for CO, CH_4, and VOCs, with concentrations of 5011.9 ppm and 3794.65 ppm, 448.1 ppm and 361.4 ppm, and 40.15 ppm and 37.95 ppm, respectively. Consequently, the use of the biogenic extract demonstrated reductions of 12.95%, 24.3%, 19.35%, and 5.45% in the specific emissions of CO_2, CO, CH_4, and VOCs, respectively. It is noteworthy that CO_2 exhibited the highest concentration among the gases, potentially limiting the effectiveness of the additive in controlling its specific emission, thus resulting in a lower percentage reduction compared to CO and CH_4. Conversely, the SCG's biogenic extract showcased its highest efficacy in reducing the specific emission of CO, which accounted for approximately 25.4% of the total off-gassing from the pellets containing the additive. Furthermore, CO_2, CH_4, and VOCs represented 72.2%, 2.25%, and 0.15% of the total off-gassing, respectively.

As biomass undergoes degradation, the organic matter present within it is broken down by microbial activity and environmental factors (Cutz et al., 2021). This breakdown leads to the release of distinct gases, including carbon monoxide (CO), carbon dioxide (CO_2), methane (CH_4), and volatile organic compounds (VOCs). Understanding the mechanisms behind their formation is crucial for comprehending the off-gassing phenomena observed in our study. To being with, CO_2 is a byproduct of the oxidative degradation of organic carbon compounds. As biomass deteriorates, the organic carbon undergoes oxidation reactions, resulting in the production of CO_2. This process is primarily driven by aerobic microbial activity, where microorganisms metabolize organic matter in the presence of oxygen. Additionally, abiotic reactions, such as chemical decomposition and combustion, can also contribute to CO_2 formation. CO_2 is a major greenhouse gas and its emissions have significant implications for climate change. Additionally, CO is formed through incomplete combustion and oxidative processes. During biomass deterioration, incomplete combustion can occur due to limited oxygen availability or suboptimal conditions. This leads to the production of CO instead of CO_2 (Cutz et al., 2021).

Furthermore, CO can also be generated through the oxidative breakdown of carbonaceous compounds. This process involves the removal of oxygen atoms from organic molecules, resulting in the release of CO. Carbon monoxide is a toxic gas that can have adverse effects on human health and the environment (Guo et al., 2022). Moreover, CH_4 is a byproduct of anaerobic microbial activity during biomass degradation. In environments with limited oxygen, such as waterlogged or oxygen-depleted conditions, certain microorganisms called methanogens thrive and break down organic matter through anaerobic respiration (Alakoski et al., 2016). This process results in the production of CH_4 as a metabolic byproduct. Methane is a potent greenhouse gas and plays a significant role in global warming. Equally relevant is the process of VOCs, which encompass a wide range of organic compounds that have low boiling points and high vapor pressures. They are released during the deterioration of biomass as a result of various biochemical and chemical processes. Volatile organic compounds can be produced by microbial metabolism, enzymatic reactions, and chemical degradation of organic matter. These compounds include alcohols, aldehydes, ketones, organic acids, and aromatic compounds. Their emissions can have implications for air quality and human health, as some VOCs can be toxic or contribute to the formation of air pollutants, such as ozone and particulate matter (Borén et al., 2017).

To better comprehend the dynamics and kinetics of these gases and the effectiveness of the antioxidant additive, a Gompertz sigmoid function was employed to model and predict their behavior (**Fig 2**). Through this stochastic modeling approach, alpha values for the total off-gassing were estimated to be 21050.4 and 18300.5 ppm for the treatment and control groups, respectively (**Tab S4, Supplementary material**). Additionally, beta and k values were determined, representing the retardation of effective off-gassing commencement and the specific growth rate, respectively. The estimated beta values were 14.3 and 27.5, while the k values were 9.15e^{-2} and 9.75e^{-2} for the treatment and control groups, respectively. Similar trends were observed when individual gases were analyzed. For instance, the modeling process yielded alpha, beta, and k values of 14500 ppm, 12.3, and 8.5e^{-2}, respectively, for CO_2. In the case of CO, the estimated values were 5100 ppm, 14.9, and 7.5e^{-2}, respectively. It is worth mentioning that these predictions exhibited coefficients of determination ranging from 0.65 to 0.8, thereby reinforcing the consistency and reproducibility of our experimental approach and stochastic modeling. Furthermore, the modeling provided valuable insights into the depletion of oxygen (O_2) as off-gassing occurred and gases such as CO_2, CO, CH_4, and VOCs were released into the ambient atmosphere. The k values for the treatment and control groups were found to be negative at -8.75e^{-3} and -9.5e^{-3}, respectively, highlighting the declining relative concentration of O_2 over time.

The utilization of the Gompertz sigmoid function in our study holds significant importance for assessing the robustness and reliability of the experimental findings. The parameters derived from the Gompertz model provide valuable insights into the behavior and kinetics of the gases emitted from the pellets, as well as the efficacy of the antioxidant additive. To begin with, the alpha values estimated from the Gompertz model represent the maximum asymptotic level of off-gassing. In our study, we obtained alpha values of 21050.4 and 18300.5 ppm for the treatment and control groups, respectively. These values indicate the maximum concentration of emitted gases that can be achieved under the given experimental conditions. The disparity between the alpha values of the treatment and control groups suggests that the presence of the antioxidant additive effectively reduced the overall off-gassing level. Additionally, the beta parameter in the Gompertz model signifies the time at which off-gassing commences. By estimating the beta values of 27.5 and 14.3 for the treatment and control groups, respectively, we gain insights into the retardation of off-gassing initiation. The higher beta value in the treatment group indicates that off-gassing began at a later stage compared to the treatment group. This observation reinforces the effectiveness of the antioxidant additive in delaying the onset of off-gassing. Furthermore, the k parameter in the Gompertz model represents the specific growth rate of off-gassing over time. In our study, the estimated k values were $9.15e^{-2}$ and $9.75e^{-2}$ for the treatment and control groups, respectively. These values provide an indication of how rapidly the gases are emitted and accumulated. The lower k value in the treatment group suggests a slower specific growth rate, indicating that the antioxidant additive effectively reduced the rate of gas emission.

In summary, our study's findings evidenced the emission characteristics of permanent gases and VOCs from pellets during a six-month storage period. The incorporation of SCG's biogenic extract as an antioxidant additive demonstrated a significant reduction in total off-gassing. Furthermore, the additive showcased its effectiveness in reducing the specific emissions of CO, CO_2, CH_4, and VOCs, albeit with varying percentages. By incorporating the Gompertz model into our analytical approach, we not only gain a better understanding of the gas emission dynamics but also enhance the reliability of our study. The model provides a mathematical framework to describe the kinetics of off-gassing and allows for predictions beyond the experimental timeframe. Their parameters provide insights into the maximum asymptotic level of off-gassing (alpha), the retardation of off-gassing commencement (beta), and the specific growth rate of off-gassing (k). These parameters, combined with the accurate coefficients of determination, ranging from 0.65 to 0.8, enhance our understanding of gas emission dynamics and contribute to the overall credibility and validity of our experimental findings.

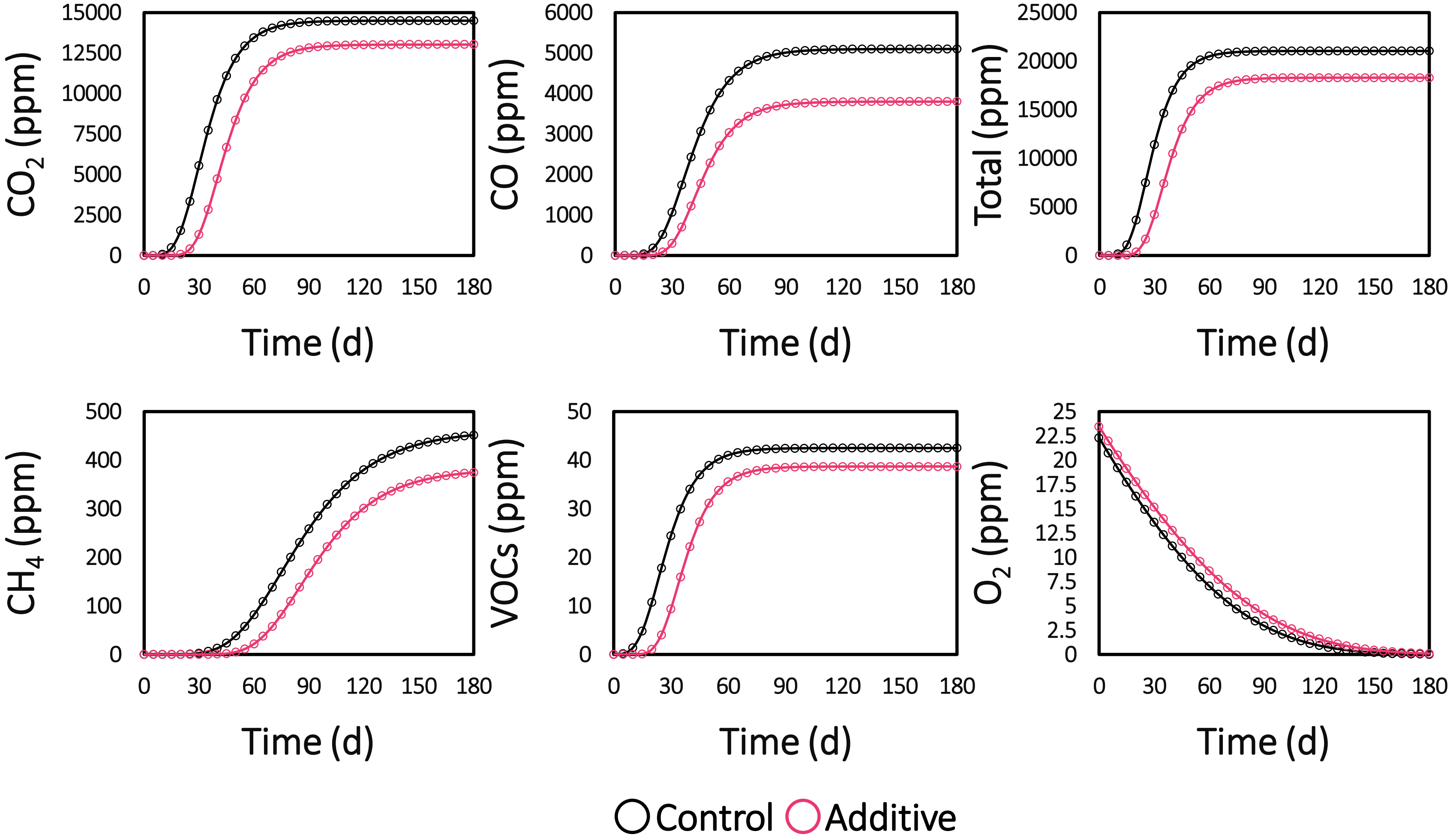

Fig 2. Gompertz sigmoid modeling of the autogenous generation of CO_2, CO, CH_4, and VOCs in wood pellets with SCG's biogenic extract at 0.05% under standard storage conditions of 25 °C of temperature and 60% of relative humidity of the air.

3.1.2. The Impact of Varying Additive Concentration and Environmental Temperature and Relative Humidity

We conducted a study to investigate the impact of increasing additive concentration on off-gassing emissions in pellets. However, our findings did not support our initial hypothesis of diminished total off-gassing with escalated additive concentrations, as visually depicted by the contour plot graphs (**Fig 3**), which exhibited a striking similarity across distinct additive concentrations. Conversely, it became apparent that the phenomenon was significantly influenced by alterations in environmental conditions, specifically by combining variations in temperature and relative humidity to create standard and challenging atmospheres for the organic matter's deterioration. For instance, in the absence of the additive, we observed a substantial increase in total off-gassing from approximately 20,000 ppm as the temperature and relative humidity levels rose, reaching approximately 50,000 ppm. In contrast, samples containing the biogenic extract derived from SCG (the additive) demonstrated disparate outcomes. The quantification of off-gassing in these samples remained stable at around 20,000 ppm at a temperature of 25 °C and relative humidity of 30%, but increased to approximately 45,000 ppm when exposed to a temperature of 50 °C and relative humidity of 90%. These findings provide support for the protective role of the additive in mitigating the environmental deterioration of the product's stability and integrity.

By examining contour plot, we gained insights into the behavior of off-gassing emissions at various additive concentrations, temperatures, and relative humidity levels. Although we did not observe a substantial variation in off-gassing emissions with increasing additive concentration, the contour plot helped us visualize this lack of significant impact. The contour lines appeared similar across distinct additive concentrations, indicating that increasing additive concentration did not lead to a significant reduction in off-gassing emissions. This finding contradicted our initial hypothesis and underscored the limited influence of additive concentration alone on off-gassing control. In contrast, the contour plot analysis highlighted the significant impact of environmental conditions on off-gassing behavior. As the temperature and relative humidity levels increased, the contour lines exhibited a clear upward trend, indicating an increase in off-gassing emissions. This observation aligned with our findings that higher temperature and humidity levels resulted in elevated off-gassing. The contour plot allowed us to visually compare the emission patterns under distinct temperature and humidity conditions, providing a clear representation of the influence of these variables on off-gassing. The CIT model further substantiated these trends by establishing humidity as the earliest node in its decision structure, indicating its primary influence over temperature in determining off-gassing propensity (**Fig 4**).

The CIT provided valuable insights into the hierarchical decision structure of factors influencing off-gassing emissions in pellets. It employed a series of splits and nodes to partition the data based on specific criteria, allowing for the identification of distinct subgroups and patterns. One of the key splits was based on humidity, categorizing it into two segments: >60% and £60%. Emissions within the >60% humidity segment ranged from 38,000 to 50,700 ppm, while the £60% segment exhibited emissions ranging from 12,000 to 46,000 ppm. This split emphasized the influential role of humidity in determining off-gassing behavior, suggesting that higher humidity levels contribute to increased emissions. Further division within the £60% humidity segment was based on temperature, resulting in the identification of two nodes: >35 °C and £35 °C. These nodes represented distinct ranges within the subset of samples characterized by lower humidity levels. The emissions within these nodes demonstrated variation. For temperatures exceeding 35 °C, emissions ranged from 32,600 to 46,000 ppm. In contrast, temperatures below or equal to 35 °C exhibited emissions ranging from 12,000 to 27,000 ppm. This split indicated that temperature also plays a significant role in off-gassing, particularly within the context of lower humidity levels. Additionally, the CIT model established a node specifically related to storage temperature, differentiating conditions exceeding 25 °C from those below or equal to 25 °C. This split further emphasized the influence of temperature on off-gassing behavior. Samples stored at temperatures between 35-50 °C emitted higher quantities of CO_2, CO, CH_4, and VOCs compared to those stored at 25 °C. This finding highlights the importance of controlling and managing storage temperature to mitigate off-gassing and preserve pellet stability.

The lack of significant impact of increasing additive concentration on off-gassing emissions is an essential finding with implications for optimal pellet off-gassing control. It suggests that simply increasing the additive concentration may not be an effective approach for reducing emissions of CO_2, CO, CH_4, and VOCs. Consequently, it is imperative to explore alternative strategies or factors that can better influence off-gassing control in pellets. In contrast, the significant impact of changing environmental conditions, specifically temperature and relative humidity, emphasizes their critical role in optimal pellet off-gassing control. The observed increase in total off-gassing as temperature and relative humidity levels rose underscores the importance of considering and controlling these factors in pellet storage and handling to minimize off-gassing and enhance pellet stability and integrity.

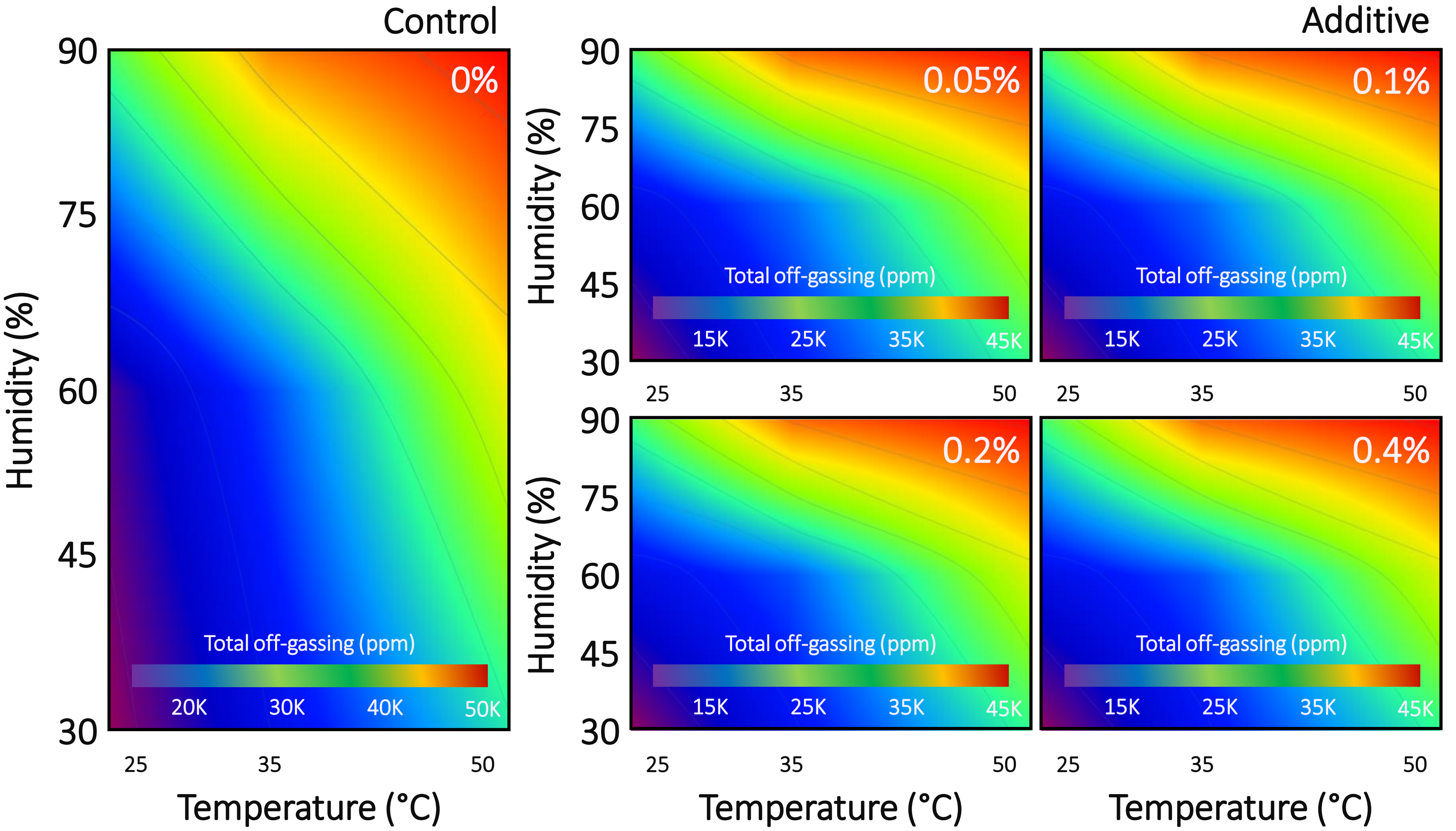

Fig 3. Contour plot modeling of the autogenous generation of CO_2, CO, CH_4, and VOCs in wood pellets with SCG's biogenic extract at 0.05-0.4% under standard storage conditions of 25-50 °C of temperature and 30-90% of relative humidity of the air.

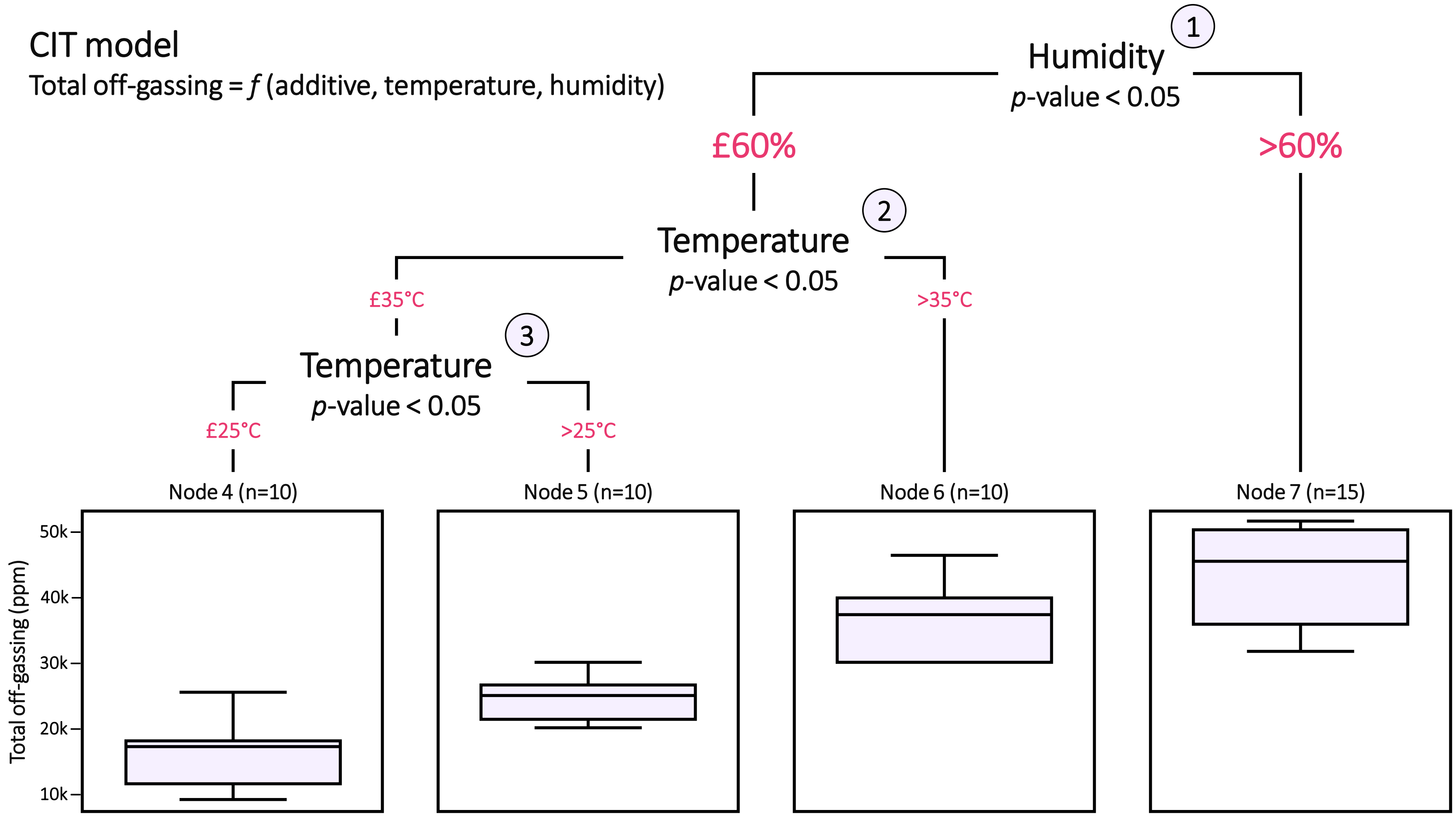

Fig 4. Conditional inference tree (CIT) modeling of the impact of changing storage's conditions on the total off-gassing in wood pellets with SCG's biogenic extract as an antioxidant additive.

Additionally, the finding that samples containing the SCG's biogenic extract exhibited relatively stable off-gassing levels across distinct temperature and humidity conditions highlights the potential of the additive for optimal pellet off-gassing control. The additive's ability to maintain consistent off-gassing levels under challenging environmental conditions suggests its protective role in mitigating the deterioration of pellets and minimizing emissions. This finding emphasizes the importance of considering additives or treatments that can enhance the stability and integrity of pellets in off-gassing control strategies. Furthermore, the identification of humidity as the most influential factor in off-gassing, with temperature amplifying its effect, provides valuable insights for optimizing pellet off-gassing control. Higher humidity levels were associated with increased emissions, underscoring the need to maintain lower humidity conditions during pellet storage. Moreover, the interaction between temperature and humidity reinforces the importance of considering both factors together to better understand and control off-gassing phenomena (Alakoski et al., 2016). By carefully managing humidity and temperature levels, it is possible to mitigate off-gassing and promote a more stable and controlled pellet storage environment.

In summary, the findings suggest that optimizing pellet off-gassing control requires considering and managing environmental conditions, particularly humidity and temperature. It highlights the need to explore alternative strategies beyond additive concentration and emphasizes the potential of additives like the SCG's biogenic extract in enhancing pellet stability and integrity. This includes maintaining lower humidity levels, preferably below 60%, and temperature ranges below 35 °C. By understanding the role of humidity and temperature and establishing optimal storage conditions, it is possible to mitigate off-gassing and promote better control over pellet off-gassing, leading to improved product quality and reduced emissions. Additionally, by controlling these environmental factors, it is possible to minimize off-gassing and preserve pellet stability, integrity, and quality. Furthermore, considering the protective role of the additive, incorporating it into the pellets can further enhance their resistance to environmental deterioration and contribute to more optimal storage conditions.

3.2. The Impact of SCG’s Biogenic Extract on the Technical Quality of Pellets

The utilization of SCG's biogenic extract as an additive in pellets has demonstrated a range of notable benefits, specifically in terms of controlling off-gassing and reducing emissions of CO_2, CO, CH_4, and VOCs. Furthermore, through a comprehensive six-month storage evaluation under varying environmental conditions, including standard and challenging temperatures and humidities, the pellets enriched with the biogenic extract exhibited exceptional protection against physical deterioration due to aging (**Graphical abstract**), thereby indicating significantly enhanced properties. Understanding the significance of these qualities in the context of sustainable biofuel production and utilization is crucial in comprehending the impact of SCG's biogenic extract as an additive. By delving deeper into these qualities and elucidating how the additive influences them (**Fig 5**), we can gain a comprehensive understanding of the potential benefits and implications.

To begin with, the durability of pellets plays a pivotal role in their ability to withstand the rigors of transportation, storage, and combustion processes (Whittaker and Shield, 2017). The incorporation of SCG's biogenic extract led to a remarkable increase in durability, with the durability percentage rising from 98.4% (control group) to an impressive 99.2%. This substantial improvement signifies that the pellets fortified with the biogenic extract are better equipped to withstand the abrasive forces typically encountered during these stages. Enhanced durability contributes to cost-effective and efficient handling, minimizing pellet breakage and degradation. This, in turn, results in reduced biomass loss and improved overall system performance, thus promoting sustainable solid biofuel production by minimizing waste and enhancing operational efficiency (Whittaker and Shield, 2017).

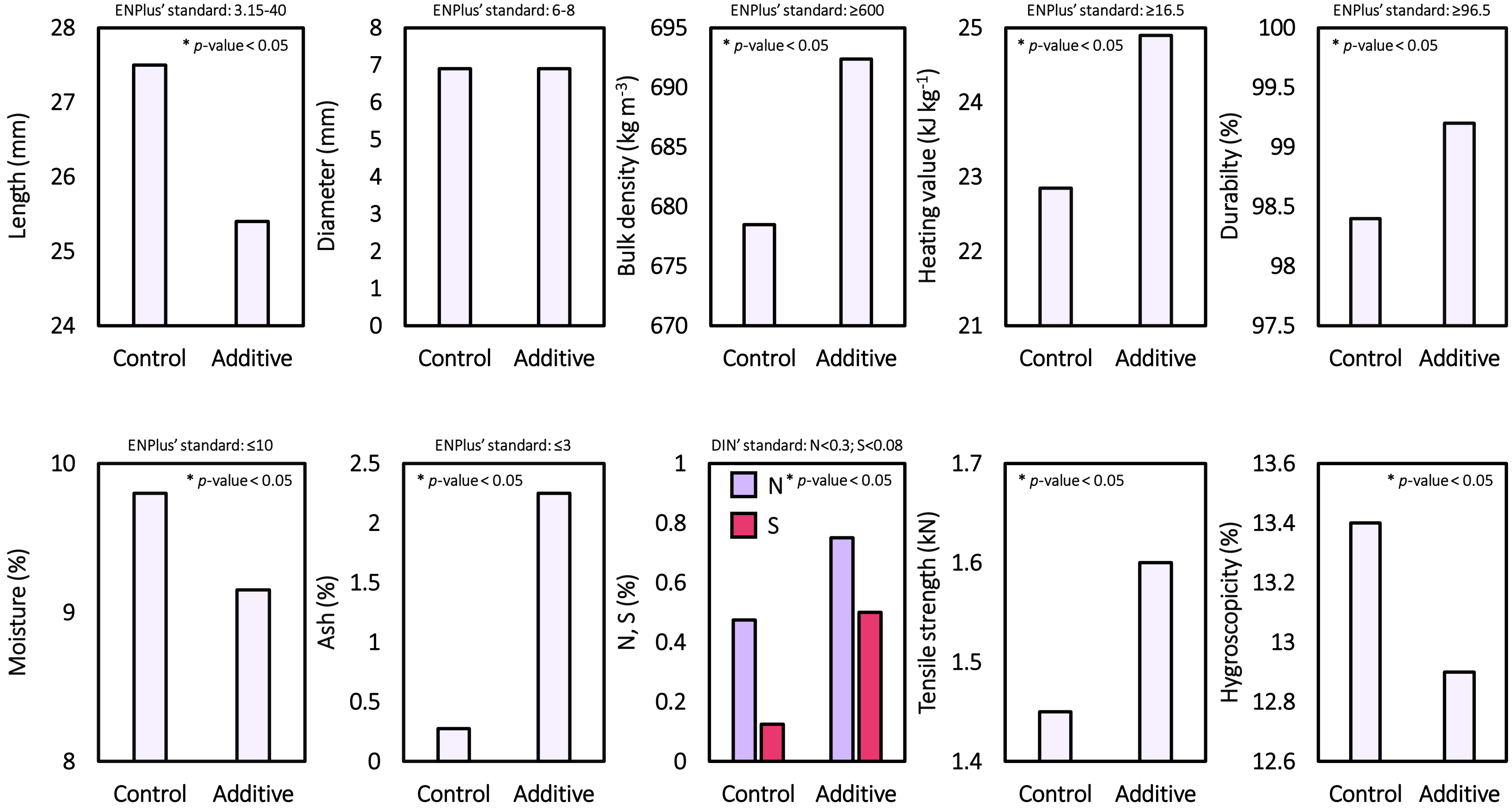

Fig 5. Comparative analysis of the technical quality of pellets with and without addition of SCG's biogenic extract at 0.05%.

In addition, hygroscopicity, which refers to the moisture absorption capacity of pellets, assumes significant importance. Excessive water absorption in pellets can adversely affect the combustion process by diminishing heating efficiency and encouraging the release of pollutants (Shojaeiarani et al., 2019). The incorporation of SCG's biogenic extract led to lower hygroscopicity in the pellets, with a water absorption rate of 12.9% compared to the control group's 13.4%. This reduced hygroscopicity enables the pellets to maintain the desired moisture content, effectively preventing excessive water absorption. By mitigating water absorption, the pellets can uphold optimal combustion conditions, resulting in improved energy conversion efficiency and reduced emissions (Shojaeiarani et al., 2019). Consequently, this aspect contributes substantially to sustainable solid biofuel utilization by enhancing overall combustion performance and minimizing environmental impacts.

Moreover, bulk density assumes a critical role in pellet quality, as it directly impacts the energy content per unit volume (Park et al., 2020). The addition of SCG's biogenic extract significantly increased the bulk density from 678.5 to 692.4 kg m^{-3}. This augmented bulk density facilitates efficient storage, transportation, and handling of the pellets. Higher bulk density optimizes storage space, reduces logistical costs, and promotes the effective utilization of biomass resources. As a result, improved bulk density significantly contributes to sustainable solid biofuel production and utilization by enhancing logistical efficiency, reducing carbon emissions associated with transportation, and maximizing the utilization of available storage facilities (Park et al., 2020). Furthermore, heating value represents a fundamental parameter that denotes the energy output during combustion (Christoforou and Fokaides, 2019). Pellets incorporating SCG's biogenic extract demonstrated a noteworthy increase in heating value, elevating it from 22.85 to 24.9 kJ kg^{-1} compared to the control group. This higher heating value makes the pellets more efficient as a source of heat and power generation. By offering enhanced heating values, the pellets contribute to sustainable bioenergy practices by maximizing energy conversion efficiency and reducing overall fuel consumption. Consequently, this can lead to a diminished reliance on fossil fuels, mitigating greenhouse gas emissions, and promoting the establishment of sustainable energy systems (Christoforou and Fokaides, 2019). Equally significant is the tensile strength of pellets, which directly impacts their structural integrity and resistance to breakage during handling and combustion processes. Incorporating SCG's biogenic extract resulted in a notable increase in tensile strength, rising from 1.45 to 1.6 kN relative to the control group. This enhancement indicates improved resistance to breakage and fragmentation, ensuring that the pellets retain their physical form even under demanding conditions. Pellets with enhanced tensile strength are less prone to degradation, effectively minimizing fines generation, combustion inefficiencies, and emissions (Chew et al., 2018). Therefore, pellets exhibiting improved tensile strength significantly contribute to sustainable solid biofuel production and utilization by reducing pellet degradation and enhancing combustion performance.

While the findings highlight the positive impact of SCG's biogenic extract as an additive, it is crucial to address the limitations associated with the elevated concentrations of N, S, and ash in the pellets. The elevated ash content of 2.25% surpasses the critical limit of 0.7% specified by the ENPlus certification scheme for highest-class pellets in residential applications. Excessive ash content can result in severe slagging and fouling in residential and industrial heating and power generation systems, diminishing their efficiency and necessitating more frequent maintenance (Míguez et al., 2021; Smith et al., 2016). Furthermore, elevated levels of N and S can lead to the formation of harmful gases, such as nitrous (NO_x) and sulfur (SO_x) oxides, during combustion, thus posing adverse environmental and health impacts (Sommersacher et al., 2012). To ensure sustainable solid biofuel production and utilization, it is imperative to address these limitations through optimization strategies that aim to reduce ash, nitrogen, and sulfur concentrations in the pellets. By mitigating these limitations, the full potential of SCG's biogenic extract as an additive can be realized, fostering sustainable solid biofuel practices.

3.2.1. Heat flow and Thermal Decomposition of Volatile Organic Matter

The combustion of pellets resulted in characteristic thermogravimetric curves commonly observed in biomass burning experiments (**Fig 6**). These curves represent the critical stages of water vaporization or dewatering, devolatilization, and carbonization. The thermogravimetric characterization of heat flow (**Fig 6A**) and the thermal decomposition of volatile organic matter (**Fig 6B**) provide insights into the material's behavior during the combustion process.

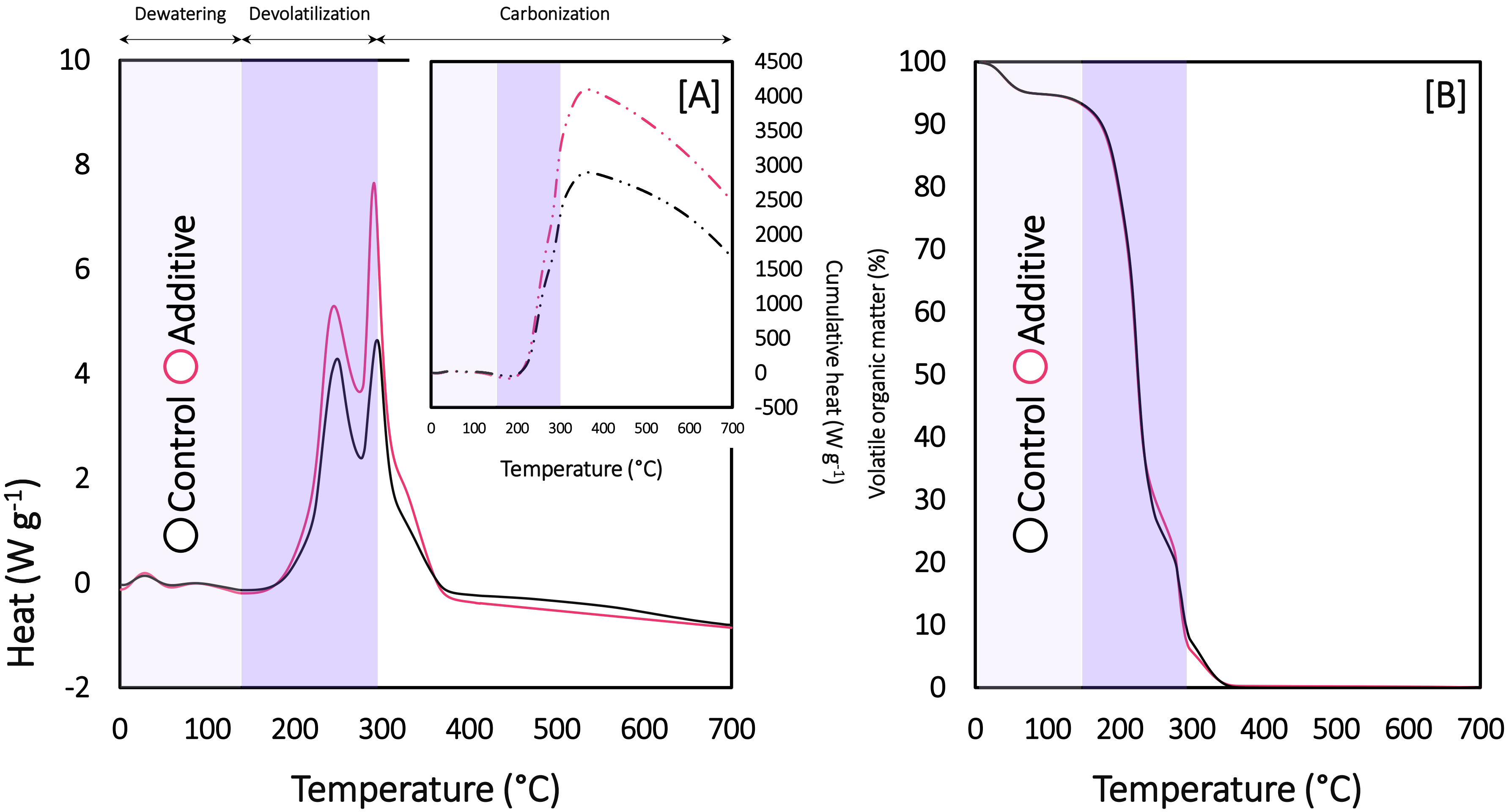

Fig 6. Heat flow [A] and thermal decomposition of volatile organic matter [B] in wood pellets with SCG's biogenic extract at 0.05%.

Pellets containing SCG's biogenic extract as a substitute in their composition exhibited notable advantages. They consumed a lower quantity of energy for dewatering due to their reduced water content compared to reference pellets. Additionally, these pellets initiated self-sustained combustion earlier and released higher quantities of heat, leading to sharper peaks in devolatilization and carbonization. The presence of volatile components in the extract may have contributed to the accelerated decomposition rate, resulting in more vigorous burning and increased energy transfer compared to the control pellets. These characteristics were reflected in higher estimates of combustibility, ignitability, and flammability (**Tab 1**), indicating their potential application in systems requiring rapid and intensive heat flow for cost-effectiveness.

Tab 1. Indicators of combustion performance of wood pellets with SCG’s biogenic extract at 0.05%.

Indicator	Unit	Additive	Control
Temperature of ignition	°C	332.4	324.9
Temperature at peak		416.95	388
Temperature of burnout		500	575
Loss of matter at peak	% min^{-1}	5.55	4.5
Average loss of matter		1.6	1.4
Combustibility	DTGc × e^{-7}	1.6	1.05
Ignitability	DTGi × e^{-5}	1.15	1.1
Flammability	DTGf × e^{-5}	5	4.3
Thermostability	DTGt × e^{-3}	1	0.95
Solid residue	%	15.4	13.1

The combustion process of biomass or fuel involves several stages, including dewatering, devolatilization, and carbonization (Akhtar et al., 2018). These stages are critical in understanding the behavior of the material during combustion. Dewatering is an essential stage in the combustion process of pellets, involving the removal of moisture or water content. As the pellets are heated, the water within them undergoes vaporization. This stage is crucial as it allows the pellets to progress to subsequent stages of combustion. In the case of pellets containing SCG's biogenic extract, the reduced water content compared to reference pellets results in a lower energy requirement for dewatering. This reduction in moisture content facilitates a more efficient combustion process by allowing the pellets to advance more rapidly to subsequent stages.

In addition, devolatilization is the stage characterized by the release of volatile organic compounds (VOCs) from the pellets as they undergo thermal decomposition (Akhtar et al., 2018). During this stage, the complex organic compounds present in the pellets are transformed into gaseous products, including carbon monoxide, methane, and other volatile hydrocarbons. The presence of SCG's biogenic extract in the pellet composition contributes to the velocity of devolatilization, as evident from the sharper peaks observed in the thermogravimetric curves. The volatile components present in the extract act as additional fuel sources, facilitating the decomposition process and promoting more vigorous burning.

Furthermore, carbonization, the final stage of the combustion process, involves the conversion of solid carbonaceous material into char (Akhtar et al., 2018). This stage is characterized by the formation of stable carbon structures through the pyrolysis of the remaining solid residue. The sharper peaks observed in the carbonization stage of the thermogravimetric curves for pellets containing SCG's biogenic extract indicate a more pronounced carbonization process. This can be attributed to the increased release of volatile matter during devolatilization, leading to a higher proportion of solid carbonaceous material available for carbonization.

Moving on to the material's reactivity, ignitability refers to the ability of a biomass or fuel to initiate combustion and sustain a self-sustained flame (Akhtar et al., 2018). In the case of pellets with SCG's biogenic extract, their enhanced ignitability compared to reference pellets can be attributed to the presence of volatile components within the extract, such as polyphenols. These volatile compounds possess lower ignition temperatures, making it easier for the pellets to ignite spontaneously. As a result, pellets with the extract exhibit an earlier commencement of self-sustained combustion, ensuring a prompt and efficient start to the combustion process. Flammability pertains to the ability of a material to sustain a flame and propagate combustion. The pellets with SCG's biogenic extract demonstrate heightened flammability compared to the reference pellets. The additional volatile components in the extract contribute to the release of a greater quantity of flammable gases during the devolatilization stage. These gases, including carbon monoxide and hydrocarbons, act as fuel sources, sustaining the flame and promoting more vigorous burning. The higher flammability observed in the pellets with the extract results in increased heat release and a more intense flame, facilitating the efficient transfer of energy. Combustibility encompasses the overall capability of a material to undergo complete combustion, releasing a substantial amount of heat. The pellets with SCG's biogenic extract exhibit enhanced overall combustibility compared to the reference pellets. The presence of volatile components in the extract accelerates the decomposition rate, resulting in more efficient combustion. This leads to the release of higher quantities of heat and increased energy transfer to the system. As a result, the pellets with the extract display higher estimates of combustibility, indicating their potential suitability for applications where rapid and intensive heat flow is desired for enhanced cost-effectiveness (Akhtar et al., 2018).

By understanding the mechanisms and characteristics of dewatering, devolatilization, and carbonization, as well as the material's reactivity in terms of ignitability, flammability, and combustibility, we can gain deeper insights into the combustion behavior of pellets containing SCG's biogenic extract. These insights are crucial for assessing the feasibility and potential applications of such pellets in various heating and power generation systems. However, it is important to consider the implications of the increased formation of solid residue resulting from the use of SCG's biogenic extract. The addition of the extract led to a higher percentage of solid residue formation in the thermogravimetric analyzer, confirming its propensity for increased ash content. This raises caution in promoting it as a bioresource for high-performance pellet manufacturing lines. The higher ash content poses challenges in terms of maintenance, reduced efficiency, and potential emissions concerns, particularly in heating and power generation systems. Regular cleaning and maintenance may be required to prevent blockages and ensure optimal performance, while reduced efficiency and potential emissions may necessitate additional measures for emissions control.

In summary, while the inclusion of SCG's biogenic extract in pellet composition offers advantages in terms of combustion characteristics, the increased formation of solid residue must be carefully considered. The potential benefits in terms of combustion performance and heat flow should be weighed against the challenges associated with increased ash content in heating and power generation systems.

Thorough assessment is necessary to determine the suitability and feasibility of using pellets with SCG's biogenic extract in residential and industrial-scale applications.

3.2.2. Potential Fouling and Slagging Formation

The inclusion of SCG's biogenic extract in wood pellets has led to notable effects on their composition, particularly concerning nitrogen (N), sulfur (S), and ash concentration. Consequently, a thorough examination of their inorganic composition becomes crucial for understanding the potential for slagging and fouling. To achieve this, samples with and without the antioxidant additive underwent comprehensive characterization using EDXRF spectroscopy, with a focus on meltable (CaO, MgO, Fe_2O_3, K_2O) and refractory (SiO_2, Al_2O_3, TiO_2) oxides. The obtained results revealed a significant similarity in the overall mineral profiles of the treatment and control groups, except for the presence of SO_3 (**Tab 2**).

The cumulative proportion of meltable oxides in the treatment and control groups was measured at 25.6% and 26.1%, respectively. Similarly, the cumulative proportion of refractory oxides in their respective compositions was found to be 56.6% and 57%. However, it is worth noting that the treatment group exhibited a higher SO_3 concentration of 7.7%, compared to the slightly lower concentration of 6.7% observed in the control group. Despite the elevated SO_3 content in the pellets with SCG's biogenic extract, their propensity for slagging remains comparable to that of the control group. This finding is further supported by the calculated indices of 3.45 and 3 for the treatment and control groups, respectively, indicating a high likelihood of slagging (Smith et al., 2016). In contrast, the propensities for fouling were relatively low, with indices of 5.75 and $5.725e^{-2}$ for the treatment and control groups, respectively.

Meltable oxides, such as CaO, MgO, Fe_2O_3, and K_2O, exhibit a characteristic molten phase at high temperatures (Míguez et al., 2021; Smith et al., 2016). These oxides can combine with other elements present in the biomass or fuel during combustion, forming liquid slag. The molten slag has the potential to deposit and adhere to the internal surfaces of the equipment, leading to slagging issues. Slagging occurs when the molten slag deposits on the heat transfer equipment, such as boiler tubes or gasification reactors, impeding heat transfer efficiency and causing operational problems. The presence of meltable oxides, especially in excessive quantities, can contribute to the formation of sticky and adherent deposits, exacerbating the slagging problem. In contrast, refractory oxides, including SiO_2, Al_2O_3, and TiO_2, possess high melting points and do not readily liquefy under typical biomass conversion conditions. These oxides are associated with the formation of solid, non-molten ash particles. Unlike molten slag, these solid particles may not strongly adhere to the equipment surfaces and can be carried away with the flue gas or gasification product stream. Of particular significance, SO_3 is considered a critical element in slagging behavior. Higher concentrations of SO_3 in the biomass or fuel can increase the likelihood of slag formation due to its ability to combine with other oxides, forming compounds with lower melting points. However, it is important to note that the presence of SO_3 alone does not guarantee severe slagging issues. The overall composition of the ash, including the concentrations of other meltable and refractory oxides, along with the operational conditions of the equipment, can influence the propensity for slagging.

Tab 2. Profile of meltable oxides and potential fouling and slagging in wood pellets with addition of SCG's biogenic extract at 0.05%

Indicator	Unit	Additive	Control
SiO_2	%	40.5	40.7
Al_2O_3		15.3	15.7
Fe_2O_3		2.5	2.6
Na_2O		10.1	10.2
CaO		15.6	15.9
MgO		0.4	0.4
K_2O		7.1	7.2
TiO_2		0.8	0.6
SO_3		7.7	6.7
Slagging	Index (dimensionless)	3.45	3
Fouling		$5.75e^{-2}$	$5.725e^{-2}$

$Slagging_{index}$: low < 0.6; 0.6 ≤ moderate ≤ 2; high > 2;

$Fouling_{index}$: low < 0.6; 0.6 ≤ moderate ≤ 40; high > 40 (Smith et al., 2016).

The slagging and fouling indices, as well as the critical limits, provide a systematic framework for categorizing the severity of deposit formation encountered in biomass conversion equipment. These indices and critical limits offer valuable tools for operators to assess the likelihood of slagging and fouling based on quantifiable values obtained from scientific studies, as outlined by Smith et al. (2016). For instance, slagging index values below 0.6 indicate a low probability of slag formation. This suggests that the deposition of materials on equipment surfaces is minimal and does not significantly impede heat transfer or cause operational disruptions. In the range of 0.6 to 2, the intermediate category, there is a moderate potential for slagging, indicating more notable deposits that are not severe enough to cause critical issues. In such cases, careful monitoring and mitigation strategies may be required to manage deposit accumulation and maintain optimal equipment performance. Values exceeding 2 indicate a pronounced propensity for slag formation, reflecting considerably severe deposits that can lead to operational complications such as reduced heat transfer efficiency, heightened pressure drop, or equipment degradation. Robust and comprehensive mitigation measures are typically necessary to effectively address significant slagging challenges. In terms of the fouling index, values below 0.6 signify a low likelihood of fouling. Deposits formed in this category are minimal and do not significantly compromise equipment performance or require extensive cleaning or maintenance interventions. The moderate range, between 0.6 and 40, indicates a moderate potential for fouling, suggesting that deposits may accumulate to a certain extent but can be managed through regular cleaning or maintenance practices. Values exceeding 40 indicate a notable propensity for fouling, where deposits are substantial and can cause significant operational challenges such as reduced heat transfer, escalated pressure drop, or equipment malfunction. Rigorous cleaning or maintenance protocols may be necessary to effectively address severe fouling issues (Míguez et al., 2021; Smith et al., 2016)

The implications of using SCG's biogenic extract as an additive in pellet-burning equipment should be considered in light of its potential to increase the slagging propensity (Míguez et al., 2021; Smith et al., 2016). The findings suggest that the addition of the biogenic extract has resulted in a higher concentration of SO_3, a critical element for slagging. However, despite the elevated SO_3 content, the overall slagging propensity remains comparable to that of the control group. To address the high slagging propensity associated with the additive, several strategies can be employed to reduce or mitigate its impact, such as optimizing additive composition, fuel blending, ash management, combustion process enhancement, equipment design and maintenance, and continuous monitoring and control. Specifically, the composition of the biogenic extract can be optimized to reduce the SO_3 content while maintaining its desired antioxidant properties. This can help minimize the contribution of SO_3 to the overall slagging propensity. Blending the pellets containing the biogenic extract with other fuels or additives that have lower slagging propensities can help dilute the concentration of SO_3 and mitigate the overall slagging tendency.

Implementing effective ash management strategies, such as regular ash removal or ash agglomeration techniques, can prevent the occurrence of ash and slag deposits on equipment surfaces. This can help maintain optimal heat transfer efficiency and reduce the risk of slag-related issues. In parallel with managing ash, optimizing the combustion process, including factors such as temperature, residence time, and air-to-fuel ratio, can help minimize slagging. Fine-tuning these parameters can promote efficient combustion and reduce the formation of molten slag. Furthermore, ensuring that the pellet-burning equipment is designed to minimize slag formation/accumulation and facilitate easy maintenance is crucial. Features such as slag removal systems, enhanced heat exchange surfaces, and regular cleaning and inspection routines can help mitigate slag-related issues. Moreover, implementing a robust monitoring and control system that can detect and respond to changes in slagging propensity in real-time can be beneficial. This allows for proactive adjustments in operational parameters to minimize slag formation and optimize equipment performance. It is important to note that these strategies should be implemented in a comprehensive and integrated manner, taking into account the specific characteristics of the additive, the solid biofuel, the equipment, and the combustion process. Regular monitoring and assessment of the slagging propensity, coupled with ongoing research and development efforts, can further contribute to the optimization and refinement of strategies to reduce the high slagging propensity associated with the use of SCG's biogenic extract in pellet-burning equipment (Míguez et al., 2021; Smith et al., 2016).

In summary, by characterizing, analyzing, and comprehending the composition and behavior of both meltable and refractory oxides, operators can assess the potential for slagging and fouling in biomass conversion equipment. By quantifying the concentrations of these oxides and analyzing their interactions, operators can gain insights into the risk of deposit formation and implement appropriate mitigation strategies. These strategies may involve optimizing operating conditions, implementing cleaning mechanisms, or modifying fuel formulations to minimize slagging and maintain equipment efficiency and reliability. Moreover, the quantitative assessment of the slagging and fouling indices within their respective critical limits enables operators to determine the severity of deposit formation, prioritize mitigation efforts, and implement suitable strategies to mitigate the adverse consequences of slagging and fouling in biomass conversion equipment.

3.3. Advancements, Trade-Offs, and Implications to Advance the Control of Off-Gassing by Biogenic Additive

Researchers can further investigate the composition and concentration of SCG's biogenic extract to optimize its properties (e.g., analytical purity) and effectiveness in controlling off-gassing. By understanding the specific antioxidant compounds present in the extract and their reactivity, scientists can fine-tune the formulation to enhance its anti-degradation properties. This could involve identifying the most active antioxidant compounds or exploring distinct extraction methods to obtain a more potent extract. Additionally, combining SCG's biogenic extract with other additives or compounds may lead to synergistic effects and improved off-gassing control. Researchers can explore the compatibility and interactions between the extract and other antioxidants, stabilizers, or additives commonly used in pellet manufacturing. By combining distinct compounds, it may be possible to enhance the overall antioxidant activity, stability, and performance of the pellets. Furthermore, encapsulation of SCG's biogenic extract can provide controlled release and prolonged activity of the antioxidant compounds. Researchers can investigate various encapsulation methods, such as microencapsulation or nanoparticle encapsulation, to protect the extract from degradation and optimize its delivery. Encapsulation can also improve the compatibility of the extract with the pellet matrix, ensuring its effective distribution and long-term functionality.

However, the production, extraction, and incorporation of SCG's biogenic extract as an additive may introduce additional costs to the pellet manufacturing process. Scaling up the production of the extract to meet commercial demand, ensuring consistent quality, and investing in specialized equipment for extraction and formulation may incur expenses. Manufacturers need to carefully assess the cost-effectiveness of using the extract and evaluate its impact on the overall economics of pellet production. Moreover, the elevated concentrations of nitrogen, sulfur, and ash resulting from the addition of SCG's biogenic extract may raise concerns regarding regulatory compliance. Certification standards for pellet quality often impose limits on these elements. Manufacturers may need to explore strategies to reduce nitrogen, sulfur, and ash content in the pellets while maintaining the desired off-gassing control. Compliance with environmental regulations is crucial for ensuring market acceptance and sustainable biofuel production.

The effective control of off-gassing through the use of SCG's biogenic extract has positive environmental implications. By minimizing emissions of greenhouse gases and volatile organic compounds during pellet production, storage, and combustion, the extract contributes to mitigating climate change and improving air quality. This aligns with the goals of sustainable bioenergy production and environmental stewardship. Additionally, optimal control of off-gassing enhances the energy efficiency of pellet combustion. When off-gassing is minimized, combustion processes can operate more efficiently, leading to improved energy conversion and reduced fuel consumption. By promoting efficient energy use, SCG's biogenic extract supports the transition to sustainable and renewable energy sources, reducing reliance on fossil fuels and lowering overall greenhouse gas emissions. Furthermore, the development and application of SCG's biogenic extract in off-gassing control can create market opportunities for pellet manufacturers. By producing pellets with enhanced stability, reduced off-gassing, and improved properties, manufacturers can meet the demands of environmentally conscious consumers, bioenergy producers, and regulatory requirements. This can lead to increased market share, improved competitiveness, and the potential for expansion into new markets that prioritize sustainable and low-emission biofuels.

In summary, advancements in SCG's biogenic extract involve optimizing its formulation, exploring synergistic combinations, and employing encapsulation techniques. However, trade-offs such as cost considerations and regulatory compliance need to be addressed. The implications of using the extract include positive environmental impact, improved energy efficiency, and market opportunities. By further advancing off-gassing control, SCG's biogenic extract can contribute to the sustainability and viability of solid biofuel production and utilization, driving the transition to a cleaner and more sustainable energy future.

4. Conclusion

The utilization of SCG's biogenic extract as an additive in pellets has demonstrated significant benefits in terms of controlling off-gassing emissions and improving pellet properties. The additive effectively reduced total off-gassing and specific emissions of CO_2, CO, CH_4, and VOCs. However, increasing additive concentration alone did not have a substantial impact on off-gassing control, highlighting the importance of considering other factors such as temperature and relative humidity. Environmental conditions, particularly humidity and temperature, played a significant role in off-gassing behavior, with higher levels leading to increased emissions. The additive showed promise in maintaining stable off-gassing levels under challenging conditions, indicating its protective role in preserving pellet stability and integrity. Optimizing pellet off-gassing control requires managing humidity and temperature levels to mitigate off-gassing and enhance pellet quality. The biogenic extract also had positive effects on pellet properties. Pellets with the additive exhibited increased durability, reduced hygroscopicity, improved bulk density, higher heating value, enhanced tensile strength, and tuned combustibility. These properties contribute to cost-effective handling, efficient storage and transportation, optimal combustion performance, and enhanced energy conversion efficiency. However, it is important to address the elevated concentrations of nitrogen, sulfur, and ash in the pellets to ensure compliance with certification standards and mitigate potential environmental and health impacts.

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Declarations

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Supplementary Material

SM 1. Acquiring Agricultural and Forestry Residues

In the pre-production step of acquiring agricultural and forestry residues for developing antioxidant additives specifically tailored for high-performance pelletization, a meticulous and comprehensive collection process was undertaken. The targeted residues encompassed peanut shells, spent coffee grains, sugarcane leaves, and pinewood sawdust, which were procured as valuable by-products derived from the mechanical harvesting processes implemented in commercial production systems. To ensure that the collected residues were suitably prepared for subsequent physicochemical characterization, an intricate pre-treatment procedure was carried out. This involved subjecting the residues to the processes of milling and sieving. By employing these techniques, particles within the highly specific size range of 0.25-0.45 mm were thoughtfully selected, as they were deemed most appropriate for the subsequent analytical processes (García et al., 2021). Once the residues had been suitably prepared, a comprehensive array of physicochemical parameters were evaluated to gain a deeper understanding of their characteristics (**Tab S1**). This analytical assessment entailed the determination of various key properties, each playing a crucial role in the overall evaluation of the residues. To begin with, the moisture content of the residues was determined in accordance with the ASTM E871-82 standard methodology. This particular method relied on subjecting 0.05 kg samples of the residues to a controlled temperature of 105.1±1.5 °C until a state of constant mass was achieved. The attainment of this constant mass signified the elimination of any residual moisture within the samples, thereby allowing for an accurate assessment of the moisture content. The volatile matter content of the residues was determined using the ASTM E871-82 standard procedure. This involved subjecting 0.05 kg samples to a controlled combustion process within an automated furnace operating at a temperature of 900.05±2.85 °C. By measuring the mass remaining after the combustion process, the volatile matter content could be accurately determined, thereby shedding light on the organic compounds present within the residues. The fixed carbon content of the residues was determined through a stoichiometric comparison of the measured elemental components. This analysis was crucial in completing the proximal analysis, which involved quantifying the key components of moisture, volatile matter, and ash content. By calculating the stoichiometric difference between these components, the fixed carbon content could be accurately determined, further enhancing the understanding of the residues' composition (Christoforou and Fokaides, 2019).

In addition to these assessments, the ash content of the residues was evaluated utilizing the ASTM D1102-84 standard methodology. This involved subjecting 0.05 kg samples to a controlled combustion process within an automated furnace operating at a temperature of 545.15±2.6 °C. The mass remaining after the combustion process provided valuable insights into the inorganic components present within the residues. Furthermore, to gain a comprehensive understanding of the elemental composition of the residues, an elemental analysis was performed. This involved quantifying the levels of carbon (C), hydrogen (H), oxygen (O), nitrogen (N), and sulfur (S) utilizing a CHNS/O elemental analyzer (PerkinElmer, 2400, Malaysia). By accurately determining the elemental composition, a deeper insight into the chemical makeup of the residues was attained, aiding in their overall characterization. Equally significant, the calorific value of the residues was meticulously quantified using an isothermal calorimeter (IKA, C-200, Germany). This involved the controlled combustion of 0.05 kg samples under standard atmospheric conditions. By carefully measuring the heat released during the combustion process, the calorific value of the residues, expressed in mega Joules per kilogram of matter, could be accurately determined. This particular parameter provided valuable information regarding the energy potential of the residues. Throughout the entire acquisition and characterization process, adherence to the methodologies outlined in Christoforou and Fokaides (2019) was of paramount importance. Following these established procedures ensured the reliability and accuracy of the obtained results, providing a robust foundation for further analysis and exploration of the agricultural and forestry residues.

SM 2. Developing Effective Antioxidant Additives

In the pre-production step of developing effective antioxidant additives in a liquid form for the purpose of integrating them into pellets, a rigorous and objective solution preparation method was implemented, drawing upon the methodology described by Moreira et al. (2021). This method encompassed a series of steps to ensure the successful creation of potent antioxidant solutions, characterized by optimal efficacy and suitability for the intended application. To initiate the solution preparation process, meticulous care was taken in obtaining precise and accurately weighed powdery aliquots, amounting to 0.1 kg, derived from distinct sources such as peanut shells, spent coffee grains, and sugarcane leaves. These specific residues were deliberately selected based on their well-documented antioxidant properties, which rendered them highly desirable candidates for the envisioned application. Subsequently, the aforementioned powdery aliquots were introduced into a volume of ultrapure water, totaling 2 L. Through this immersion process, a suspension was formed, facilitating the gradual and controlled transfer of the desired antioxidant compounds from the solid phase to the liquid phase of the system. This infusion stage played a pivotal role in maximizing the extraction of the target antioxidant components, thereby enriching the resulting solution with their beneficial properties (Moreira et al., 2021).

To promote an efficient transfer of these compounds, the suspension was subjected to a carefully controlled boiling procedure, maintained at a temperature of 50 °C for a duration of precisely 15 minutes. Following the infusion process, the prepared suspension was subjected to a refinement step aimed at achieving the desired concentration of the antioxidant solutions. Specifically, a measured volume of 0.05 L from the prepared solutions was diluted with an additional volume of 1 L of ultrapure water. By employing this dilution process, the resulting extract was effectively concentrated at a level of 0.05% $v\ v^{-1}$. This precise concentration ensured compliance with stringent regulatory limits, as advocated by sustainable consumption guidelines. Specifically, the concentration level adhered to the stipulated upper limit of 2% additive content within the pellet composition, as stipulated by Whittaker and Shield (2017). To safeguard the integrity and efficacy of the prepared antioxidant solutions until their utilization in the subsequent pelletization process, appropriate storage measures were employed. The solutions were preserved in a freezer, maintained at a temperature of -5 °C. By subjecting the solutions to controlled freezing conditions, their inherent properties, stability, and functionality were effectively preserved (Moreira et al., 2021).

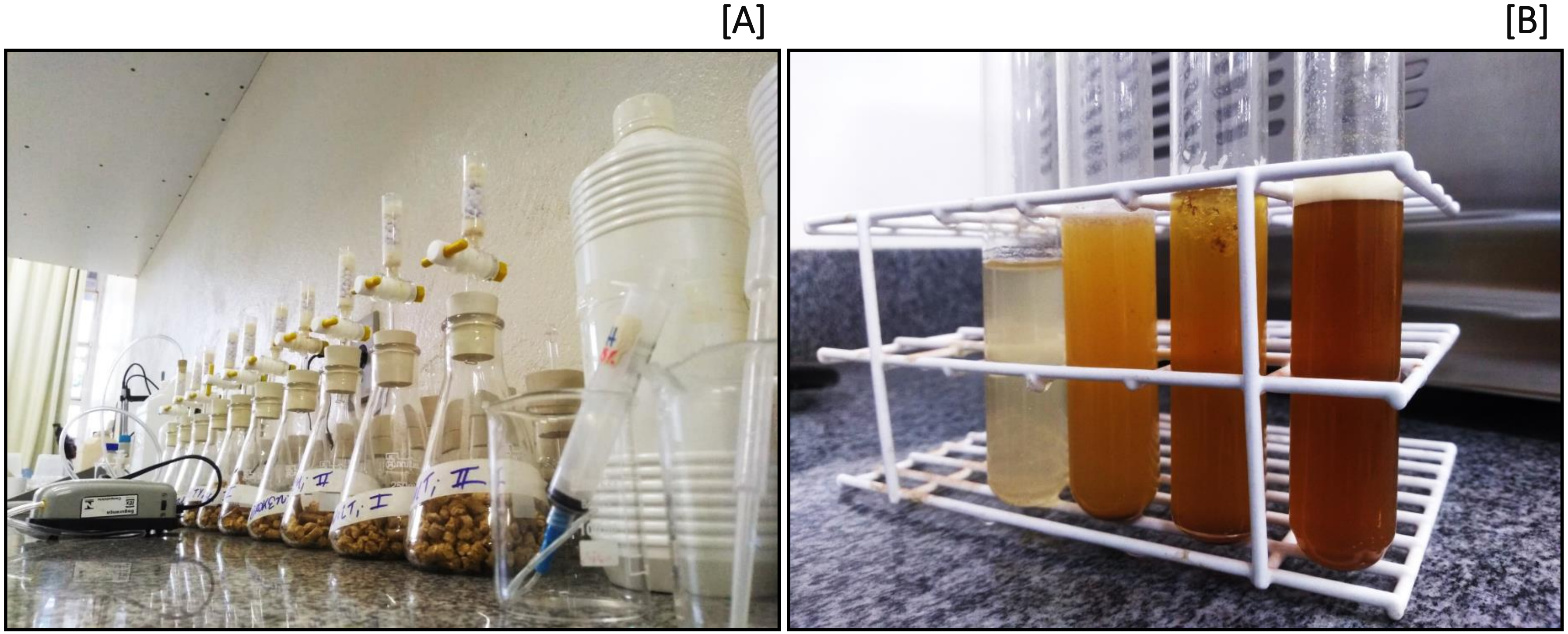

Fig S1. Respirometric experiment [A] for the quantification of specific emission of CO_2 from wood pellets with and without the addition of biogenic extracts [B] from peanut shells, spent coffee grains, or sugarcane leaves as potential antioxidants to control off-gassing.

Tab S1. Standards and instruments for the physicochemical characterization of materials

Norm/Method	Property	Instrument
ASTM D3173-87	Moisture	Drying-oven (Marconi MA035/5)
ASTM D120-30	Volatile matter	Muffle furnace (SPlabor 1200DM/B)
ASTM D3172-07	Fixed carbon	This is not a process of analysis
ASTM D1762-84	Ash	Muffle furnace
CEN’s EN 15104	C, H, O, and N	Elemental analyzer (Flash Smart CHNS/O)
CEN’s EN 15289	S	Elemental analyzer (Perkin CHNS/0 2400 II)
ASTM D2015-96	Heating value	Isothermal digital calorimeter (IKA C200)

ASTM, American Society for Testing and Materials

Tab S2. Antioxidant capabilities and functionalities of biogenic extracts derived from agricultural residues employed in the initial research on controlling the autogenous generation of CO_2 in wood pellets

Variable	Peanut shells	Spent coffee grains	Sugarcane leaves
DPPH• radical scavenging activity, %	78.3	89.5	56.3
Reducing power, µg g^{-1}	3.85	2.75	10.25
Total polyphenols, mg GAE g^{-1}	53.9	78.4	61.75
Ascorbic acid, µg mL^{-1}	285.7	352.5	298.4
Carotenoids, µg mL^{-1}	8.2	9.45	3.85
SOD activity, U g^{-1}	158.4	127.4	121.5
CAT activity, U g^{-1}	54.1	84.5	62.4
POD activity, U g^{-1}	32.1	46.85	29.3

Tab S3. Technical specifications of the pelleting system

Key	Unit
Load capacity of the hoper	250 kg
Feeding rate	75 kg h^{-1}
Engine potency	20 hp
Production capacity	250 kg h^{-1}
Nominal diameter of compressing channel	200 mm
Nominal diameter of tungsten pressing rollers	2 × 100 mm
Maximum nominal pressure in hydraulic system	300 MPa
Maximum nominal temperature of flat die	150 °C
Nominal diameter of the pellet	6-8 mm
Bulk density of the pellet	1000-1400 kg m^{-3}
Mass	850 kg
Dimension of the pelletizer machine	4200 mm × 2450 mm × 1750 mm

Tab S4. Parametrization and appropriateness of Gompertz model for emissions of permanent gases (CO_2, CO, and CH_4) and VOCs from wood pellets with and without the addition of SCG's biogenic extract as an antioxidant to control off-gassing

Source	alpha	beta	k	AIC	BIC	r^2
	CO (ppm)					
Treatment	3800.5	28.4	8.05e-2	342.1	367.1	0.9
Control	5100	14.9	7.5e-2	340.15	369.4	0.9
	CO_2 (ppm)					
Treatment	13025	27.45	8.25e-2	361.4	387.4	0.9
Control	14500	12.3	8.5e-2	358.1	386.1	0.925
	CH_4 (ppm)					
Treatment	381.9	34.5	4.15e-2	370.8	394.7	0.775
Control	461.5	15.45	3.65e-2	373.1	395.1	0.75
	VOCs					
Treatment	38.7	23.4	9.35e-2	405.6	419.3	0.6
Control	42.5	8.6	9.15e-2	406.9	416.4	0.65
	Total (ppm)					
Treatment	18300.5	27.5	9.75e-2	398.5	428.1	0.7
Control	21050.4	14.3	10.5e-2	391.4	430.9	0.65
	O_2 (%)					
Treatment	100	1.45	-8.75e-3	403.7	415.1	0.55
Control	100	1.5	-9.5e-3	405.6	420.6	0.5

CHAPTER V – Final Considerations

1. Significance for Off-Gassing Control, Sustainable Energy Development, and Waste Management in Agriculture

Our research provides innovative and practical solutions for controlling off-gassing, thereby improving air quality, safeguarding human welfare, and reducing the environmental impact associated with biomass energy production. By focusing on the efficacy of biogenic extracts, specifically the extract derived from spent coffee grains, we offer valuable insights into mitigating off-gassing and minimizing emissions of CO_2, CO, CH_4, and VOCs during storage. Implementing our research findings can contribute to the transformation of biomass energy systems, promoting socially responsible, environmentally friendly, and sustainable alternatives.

Additionally, our research has implications for sustainable energy development. By enhancing the properties and performance of renewable energy sources, such as pinewood pellets, through the addition of biogenic extracts, we contribute to improved combustion efficiency and reduced emissions. This advancement aligns with the transition towards a more sustainable energy sector, reducing reliance on fossil fuels and mitigating climate change.

Furthermore, agricultural waste management presents a global challenge, and our research addresses this by showcasing the potential for sustainable practices in the agriculture sector. By utilizing abundant waste products like peanut shells, spent coffee grains, and sugarcane leaves, we extract antioxidants and transform agricultural waste into valuable bioresources. This approach aligns with the principles of the circular economy, reducing waste generation, promoting waste valorization, and mitigating the environmental impact associated with waste disposal. Our research contributes to the adoption of more sustainable agricultural practices.

To recapitulate, our research highlights the significance and implications of biogenic antioxidants for controlling off-gassing, sustainable energy development, and waste management in agriculture. By providing practical solutions, enhancing the properties of renewable energy sources, and transforming agricultural waste into valuable resources, our findings advance societally responsible, environmentally friendly, and economically sustainable practices. These insights are crucial for addressing off-gassing challenges, promoting sustainable energy development, and fostering sustainable agricultural practices, ultimately contributing to a more sustainable and resilient future.

2. Potential Economic Opportunities: Waste Valorization Industry, Value-Added Products, and Market Expansion

The utilization of peanut shells, spent coffee grains, and sugarcane leaves for the production of biogenic antioxidant extracts not only offers practical solutions for controlling biomass off-gassing but also presents substantial economic opportunities. It opens up avenues for the development of a thriving waste valorization industry, where bioactive compounds are extracted and processed from various agricultural byproducts beyond coffee waste. This industry encompasses the establishment of cutting-edge extraction facilities, state-of-the-art processing plants, and advanced manufacturing units, thereby creating a multitude of employment opportunities and driving robust economic growth.

Additionally, the application of biogenic extracts extends far beyond biomass energy systems. With their remarkable antioxidant properties, these extracts find wide-ranging applications in diverse industries such as food, pharmaceuticals, cosmetics, and nutraceuticals. This diversification of product offerings not only contributes to revenue generation but also ensures long-term economic sustainability. By incorporating biogenic extracts derived from agricultural by-products like peanut shells, spent coffee grains, and sugarcane leaves into fuel-grade pellets or other high-value applications, forward-thinking producers can effectively tap into the surging market demand for sustainable and eco-friendly products. This strategic move enhances their competitiveness, enables distinct market differentiation, and translates into improved profitability.

Furthermore, the utilization of agricultural waste for the production of value-added products holds tremendous potential for expanding existing markets and creating novel market opportunities. As the global appetite for sustainable products continues to escalate, the integration of biogenic extracts derived from agricultural by-products becomes an imperative. By strategically catering to this burgeoning market segment, businesses not only augment their market reach but also make meaningful contributions to the overall sustainability of agricultural practices and waste management.

To recapitulate, the utilization of peanut shells, spent coffee grains, and sugarcane leaves for the production of biogenic antioxidant extracts presents a realm of compelling economic prospects. It paves the way for the emergence of a dynamic waste valorization industry, stimulates the creation of value-added products, and positions proactive businesses at the forefront of the growing market for sustainable and eco-friendly offerings. By seizing the tremendous potential inherent in agricultural by-products, companies assertively drive economic growth, spearhead market expansion, and actively contribute to a more sustainable and circular economy.

3. Social and Environmental Benefits: Impact Reduction, Resource Management, Circular Economy, and Human Welfare

Our original research on controlling off-gassing in biomass energy systems holds significant implications for reducing greenhouse gas emissions and improving air quality. By effectively addressing off-gassing, which releases substantial amounts of CO_2, CO, CH_4, and VOCs into the atmosphere, our study plays a direct role in combating climate change, safeguarding occupational safety, and protecting human health. Furthermore, our research showcases the utilization of agricultural waste, particularly spent coffee grains, as a means of promoting sustainable resource management. Rather than discarding these waste materials, we repurpose and transform them into valuable resources. This not only reduces the strain on landfills but also minimizes the extraction of virgin resources, aligning with ongoing efforts to conserve natural resources and foster a more sustainable approach to resource management.

Additionally, our study strongly aligns with the principles of the circular economy by advocating for waste valorization and resource efficiency. Through the utilization of peanut shells, spent coffee grains, and sugarcane leaves as sources for biogenic extract, we exemplify the potential for circularity within the agricultural sector. By closing the loop and transforming waste into valuable products, our research encourages stakeholders to embrace circular economy practices and actively contribute to the transition towards a more sustainable and resource-efficient economy. The economic opportunities that arise from waste valorization and the development of value-added products have positive social impacts as well. The establishment of new businesses and job creation not only stimulate local economies but also reduce unemployment rates, ultimately enhancing the overall well-being of communities. Additionally, by promoting sustainable practices and eco-friendly products, our research generates consumer awareness and engagement, fostering a sense of social responsibility and driving the adoption of sustainable lifestyles.

Furthermore, our original research indirectly promotes sustainable agricultural practices by emphasizing waste management and valorization within the agricultural sector. By recognizing the value of agricultural byproducts and transforming them into valuable resources, our study supports a more sustainable and circular approach to agricultural production. This shift towards utilizing agricultural waste leads to improved resource efficiency, reduced environmental impacts, and the adoption of sustainable practices by farmers and producers.

To recapitulate, our original research not only contributes to the reduction of greenhouse gas emissions, improved air quality, and enhanced occupational safety but also aligns with the principles of the circular economy. By promoting waste valorization, resource efficiency, and sustainable agricultural practices, our study drives positive social and environmental change. It offers innovative solutions for mitigating climate change, conserving natural resources, creating economic opportunities, and fostering sustainable and circular economies.