Thermal Emission Toxicity and Qualitative Screening of Volatile Organic Emissions and Hazard Identification from Water Hyacinth Fiber–Cassava Starch Biodegradable Composites

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Abstract: The rapid transition toward sustainable packaging has driven the development of biodegradable polymer composites utilizing agricultural wastes, such as water hyacinth (Eichhornia crassipes) fibers and cassava starch matrices. However, while the environmental biodegradability of such biocomposites is widely studied, the toxicological safety of volatile organic compounds (VOCs) released under thermal exposure remains critically unaddressed. This study evaluated the volatile emission profile and qualitative hazard screening of water hyacinth–cassava starch composite sheets subjected to heat (100 °C for 15 min) simulating hot-food contact conditions. Using Headspace Gas Chromatography–Mass Spectrometry (HS-GC-MS), 26 volatile compounds were tentatively identified based on NIST library mass spectral matching (similarity match factor >80%, corresponding to Metabolomics Standards Initiative Level 2). The identified profile included 9 hazardous chemical species classified by the International Agency for Research on Cancer (IARC). Key hazardous emissions comprised Group 1 human carcinogens (Ethylene oxide 3.60% peak area and Formaldehyde [5.80%]), Group 2A/2B probable/possible carcinogens (Ethylenimine 19.40%, Acetaldehyde 10.50%, Trichloromethane 1.20%, Tetrachloromethane 0.90%, 1,2-Dichloroethane 0.70%, and 1,2-Dibromoethane 0.60%), alongside hepatotoxic Chloromethane (17.10%). It is emphasized that reported peak area percentages represent relative chromatographic abundances under specific headspace thermal desorption conditions and do not reflect absolute mass concentrations. Furthermore, qualitative hazard identification does not constitute a quantitative health risk assessment, as consumer exposure levels and migration limits were not established. The origin of these hazardous species stems from a plausible combination of aquatic bioaccumulation by raw water hyacinth, alkali delignification pre-treatment residuals, thermal fragmentation of the starch–glycerol matrix, and pyrolysis of residual plant proteinaceous biomass. These findings demonstrate that environmental biodegradability does not inherently ensure chemical safety for food contact materials, highlighting the necessity of integrating volatile emission toxicity screening into biopolymer safety standards.

Keywords: Biodegradable packaging, Cassava starch matrix, Food contact safety, GC-MS emission analysis, Qualitative hazard screening, Tentative compound identification, Volatile toxicity, Water hyacinth composites.

1. INTRODUCTION

The escalating global accumulation of petroleum-based plastic waste has spurred intensive research into renewable, eco-friendly biopolymer composites as sustainable alternatives [1, 2]. Among the vast array of natural raw materials, lignocellulosic fibers derived from agricultural residues and invasive aquatic biomass have gained significant prominence as reinforcing agents for biodegradable polymer matrices [3-5]. Specifically, water hyacinth (Eichhornia crassipes) known as one of the most invasive aquatic weeds globally has a cellulose content of 50–60%, presenting an abundant, low-cost bio-resource for composite fabrication [6-8]. When combined with thermoplastic cassava starch (Manihot esculenta) as a binding matrix and glycerol as a plasticizer, water hyacinth fiber-reinforced biocomposites offer promising mechanical performance, flexibility, and rapid environmental disintegrability, thereby advancing bio-circular economy principles [9].

To date, the vast majority of studies on starch–lignocellulosic biocomposites have focused heavily on processing optimization, interfacial fiber–matrix adhesion, mechanical strength, water barrier properties, and soil/microbial degradation kinetics [10-13]. However, a critical yet frequently overlooked limitation in biocomposite research is the chemical and toxicological safety of volatile organic compounds (VOCs) released during thermal exposure. Biopolymer packaging materials and composite containers are routinely subjected to elevated temperatures (70–100 °C) during thermo-compression molding, hot-filling processes, microwave reheating, or direct contact with warm food items. Under such thermal stress, non-intentionally added substances (NIAS), residual processing chemicals, absorbed environmental pollutants, and thermal breakdown products of the polymer matrix can undergo volatilization and migration [14-16].

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Recent toxicological evidence indicates that plant-based and starch-derived materials are not inherently benign, with certain formulations exhibiting volatile chemical release and toxicological profiles comparable to or exceeding those of conventional synthetic plastics [17-20]. Despite these risks, current bioplastic regulatory frameworks and national standards (*e.g.*, ISO 14855 or SNI standards) evaluate biocomposite safety almost exclusively through gravimetric soil biodegradation or CO2 evolution rates, notably neglecting required volatile emission toxicity evaluations and Specific Migration Limits (SML) mandated by global agencies such as the European Food Safety Authority (EFSA) and the U.S. Food and Drug Administration (FDA)[21- 24].

To address this safety evaluation gap, this study presents a qualitative screening of volatile chemical emissions and hazard identification for water hyacinth fiber–cassava starch biocomposite sheets subjected to thermal stress (100 °C for 15 minutes) simulating hot-food contact. Utilizing Headspace Gas Chromatography–Mass Spectrometry (HS-GC-MS) coupled with international toxicological databases (IARC and PubChem), this work tentatively identifies emitted volatile species (Metabolomics Standards Initiative Level 2), evaluates their relative chromatographic abundances, and categorizes their potential toxicological hazards. Crucially, this study explicitly distinguishes qualitative hazard screening from quantitative risk assessment, aiming to establish an analytical foundation for future quantitative migration testing and biocomposite safety protocols.

2. MATERIALS AND METHODS

2.1. Raw Materials and Chemical Reagents

Petiole samples of fresh water hyacinth (Eichhornia crassipes) were collected from nearby freshwater sources in Jakarta, Indonesia. Commercial food-grade cassava starch (Manihot esculenta) powder was utilized as the primary biopolymer binder matrix. Analytical grade sodium hydroxide (NaOH, 99% purity) and glycerol plasticizer (99.5% purity, USP grade) were purchased from Merck (Darmstadt, Germany). Helium gas of high purity (99.9%) was utilized as the carrier gas for the separation process in chromatography. All aqueous solutions and washing steps were conducted using deionized water (18.2 MΩ·cm resistivity).

2.2. Preparation and Processing of Water Hyacinth Fiber–Cassava Starch Biocomposites

1. **Fiber Extraction and Alkali Pre-treatment:** Fresh water hyacinth stalks were washed thoroughly under running water to eliminate surface mud and dirt, then subjected to oven-drying at 60 °C until the moisture level dropped below 10% (w/w). The dried petioles were mechanically cut into short fibers measuring approximately 5 mm in length. To remove non-cellulosic amorphous components (lignin, hemicellulose, and waxes) and enhance interfacial mechanical bonding, the fibers were soaked in a 5% (w/v) NaOH solution for 2 hours at room temperature. The alkali-treated fibres were then washed several times with deionised water until a neutral pH (pH 7.0) was achieved and subsequently dried at 60 °C for 24 hours.

2. **Matrix Gelatinization and Composite Blending:** Cassava starch powder was weighed according to the formulation and dispersed in deionized water. Glycerol (20% w/w relative to dry starch weight) was added as a plasticizer to improve film flexibility. The aqueous starch–glycerol suspension was heated to 70 °C on a magnetic hotplate under continuous mechanical stirring (350 rpm) for 20 minutes until complete starch gelatinization and a homogeneous paste were achieved. The prepared 5-mm alkali-treated water hyacinth fibers (20% dry weight relative to total composite mass) were then uniformly incorporated into the gelatinized starch matrix and blended thoroughly.

3. **Thermo-Compressive Molding:** The fibrous biopolymer mixture was transferred into a flat steel mold (150 mm × 150 mm × 1 mm). Thermo-compression molding was executed using an industrial hydraulic hot press operating at 120 °C and a pressure of 5 MPa for 10 minutes. The resulting biocomposite sheets were cooled to room temperature under ambient pressure, conditioned in a desiccator containing silica gel for 48 hours, and subsequently cut into uniform specimens for emission analysis.

2.3. Headspace Gas Chromatography–Mass Spectrometry (HS-GC-MS) Analysis

1. **Thermal Sample Conditioning:** Conditioned biocomposite sheet samples (1.00 g) were cut into small pieces and sealed immediately into 20-mL headspace vials fitted with PTFE/silicone septa. The vials were transferred to an automated headspace sampler and equilibrated at 100 °C for 15 minutes to induce volatile thermal desorption.

2. **GC-MS Operational Parameters:** The vaporized headspace gas was automatically introduced into a Gas Chromatograph connected to a Mass Spectrometer (GC-MS) system.

Separation by chromatography was accomplished using a capillary column. Operating conditions: Injector temperature set to 220 °C; Split ratio of 50:1; Helium as carrier gas at 1.0 mL/min; Oven temperature program starts at 50 °C for 2.5 minutes, then increases at 15 °C/min to 300 °C, maintained at 300 °C for 5.83 minutes (total duration ~25 minutes); MS transfer line and ion source temperatures maintained at 200 °C; Electron Ionization (EI) applied at 70 eV, mass scan range from m/z 40 to 400 Da.

2.4. Data Processing, Chemical Identification, and Hazard Screening

Acquired GC-MS chromatograms were processed using automated peak integration software. The primary analytical parameters recorded included retention time (RT, min), peak area, and mass fragmentation patterns. Chemical Identification & Reliability Criteria: Mass spectra were matched against the National Institute of Standards and Technology (NIST) Mass Spectral Library. Identification was accepted for reverse match factors exceeding 80% (800/1000). In accordance with the Metabolomics Standards Initiative (MSI) reporting standards, all reported volatile species represent Level 2 (putatively annotated / tentatively identified) compounds, as confirmation with authentic reference standards and retention index (RI) matching was not performed. Calculation of Relative Abundances: Relative chromatographic abundances were calculated as peak area percentages using the following equation:

$$Relative\ Peak\ Area\ (\%) = \frac{Area\ i}{Area\ total} x\ 100\%$$

Where Area i is the integrated peak area of an individual volatile compound and Area total is the total integrated chromatographic peak area. It is explicitly noted that peak area percentages reflect relative instrument detector response under headspace thermal equilibrium and do not constitute absolute mass concentrations.

Hazard Screening & Classification: Emitted compounds were evaluated using international chemical safety databases, including PubChem, U.S. EPA, and International Agency for Research on Cancer (IARC) monographs. Compounds were screened for toxicological endpoints and classified into IARC Carcinogenicity Groups (Group 1, 2A, 2B, or 3).

3. RESULTS AND DISCUSSION

As illustrated in Figure **1**, composites have been fabricated from water hyacinth and cassava flour reinforcement. Four categories of samples are available, distinguished on the basis of the mass composition of fibre-to-reinforcement. The composites to be tested for emissions are composites with the same mass ratio of fibre-to-reinforcement [25]. The following essay will provide a comprehensive overview of the relevant literature on the subject.



Figure 1: The composite sample of water hyacinth fibre.

3.1. Volatile Chemical Profile of Heated Biocomposites

Thermal exposure of water hyacinth fiber–cassava starch biocomposite sheets at 100 °C for 15 min resulted in the release of a multi-component volatile headspace mixture. Automated HS-GC-MS analysis resolved 26 distinct chromatographic peaks with retention times under 6.0 min, reflecting low-molecular-weight species with high volatility. All 26 compounds were tentatively identified (MSI Level 2) via NIST library spectral matching (>80% match factor) and are listed in Table **1** alongside their retention times, relative peak area percentages, CAS numbers, and primary documented hazard endpoints. It is emphasized that relative peak areas reflect relative chromatographic response under 100 °C headspace sampling and should not be confused with absolute emission yields or exposure doses.

The identified volatile species were catalogued alongside their retention times, relative concentration abundances (% peak area), CAS registry numbers, and documented toxicological profiles. The emitted chemical profile comprises inorganic gases, aliphatic and aromatic aldehydes, ketones, carboxylic acids, nitrogenous intermediates, and volatile organohalides. Carbon dioxide accounted for 43.67% of the total integrated peak area. Short-chain aliphatic carbonyl compounds represented a major volatile fraction, including 2-methylpropanal 97.90%, acetone 73.30%, pyruvic acid 42.60%, 2-butanone 4.90%, pentanal 3.30%, hexanal 2.40%, heptanal 1.70%, octanal 1.50%, nonanal 0.90%, decanal 0.80%, benzaldehyde 0.50%, furfural 0.40%, and 5-methylfurfural 0.40%. In addition,

Table 1: Comprehensive Tentative Identification (MSI Level 2) and Hazard Screening of Volatile Compounds Emitted from Heated Biocomposites via HS-GC-MS

No.	RT (min)	Tentaively Identified Compound	CAS No.	Relative Peak Area (%)	IARC Group	Primary Documented Hazard Profile
1	1.42	Carbon dioxide	124-38-9	43.67	—	Asphyxiant at high concentration; greenhouse gas
2	1.42	Ethylene oxide	75-21-8	3.60	Group 1	Mutagenic; human carcinogen (leukemia, lymphoma)
3	1.42	Nitrous oxide	10024-97-2	4.70	—	Central nervous system depressant; neurotoxic
4	1.42	Propane	74-98-6	1.70	—	Flammable gas; mild anesthetic agent
5	1.48	α-Cyano-L-alanine	6232-19-5	82.60	—	Amino acid antimetabolite; neurotoxic precursor
6	1.48	Chloromethane (Methane, chloro-)	74-87-3	17.10	Group 3	Hepatotoxic, nephrotoxic, central nervous system depressant
7	1.65	Acetone	67-64-1	73.30	—	Mucous membrane irritant; narcotic at elevated doses
8	1.85	2-Methylpropanal	78-84-2	97.90	—	Severe upper respiratory tract irritant
9	1.99	Pyruvic acid	127-17-3	42.60	—	Endogenous metabolic intermediate; generally safe
10	1.99	Ethylenimine (Aziridine)	151-56-4	19.40	Group 2B	Alkylating agent; reactive to DNA, mutagenic
11	2.10	Acetaldehyde	75-07-0	10.50	Group 2B	Respiratory irritant; DNA crosslinker, mutagenic
12	2.25	Formaldehyde	50-00-0	5.80	Group 1	Human carcinogen (nasopharyngeal cancer); strong irritant
13	2.46	2-Butanone (MEK)	78-93-3	4.90	—	Eye and respiratory tract irritant; narcotic
14	2.67	Pentanal	110-62-3	3.30	—	Ocular and upper respiratory tract irritant
15	2.89	Hexanal	66-25-1	2.40	—	Volatile aldehyde; mild respiratory irritant
16	3.12	Heptanal	111-71-7	1.70	—	Pungent odor; mild mucosal irritant
17	3.25	Octanal	124-13-0	1.50	—	Aliphatic aldehyde; mild skin/eye irritant
18	3.49	Nonanal	124-19-6	0.90	—	Fatty aldehyde; mild mucosal irritant
19	3.78	Decanal	112-31-2	0.80	—	Trace volatile; mild irritation potential
20	4.02	Trichloromethane (Chloroform)	67-66-3	1.20	Group 2B	Organochlorine; hepatotoxic and nephrotoxic
21	4.28	Tetrachloromethane (Carbon tetrachloride)	56-23-5	0.90	Group 2B	Potent hepatotoxin; severe renal damage agent
22	4.53	1,2-Dichloroethane	107-06-2	0.70	Group 2B	Chlorinated solvent; animal carcinogen
23	4.79	1,2-Dibromoethane	106-93-4	0.60	Group 2A	Genotoxic and teratogenic; probable human carcinogen
24	5.05	Benzaldehyde	100-52-7	0.50	—	Aromatic aldehyde; mild respiratory irritant
25	5.29	Furfural	98-01-1	0.40	—	Furan derivative; potential mutagenic irritant
26	5.55	5-Methylfurfural	620-02-0	0.40	—	Thermal degradation by-product; mild toxicity

Footnotes: a Relative peak area percentage calculated from integrated chromatographic peak areas (100 °C headspace sampling, 15 min). These values represent relative detector response and NOT absolute mass concentrations or emission yields. b Carcinogenic classification according to IARC Monographs: Group 1 = Carcinogenic to humans; Group 2A = Probably carcinogenic to humans; Group 2B = Possibly carcinogenic to humans; Group 3 = Not classifiable; — = Not evaluated by IARC. All compounds represent tentative identifications (MSI Level 2) based on NIST spectral library matching (>80% match factor).

nitrogen-containing compounds such as α-cyano-L-alanine 82.60% and nitrous oxide 4.70% were identified in substantial relative quantities.

3.2. Screening of Hazardous and Carcinogenic Volatile Species

Cross-referencing resolved volatile species against international chemical hazard databases (IARC Monographs, PubChem, and U.S. EPA) identified 9 compounds possessing documented hazardous, mutagenic, or carcinogenic potential (Table **2**). These comprise Group 1 human carcinogens (Ethylene oxide 3.60% peak area] and Formaldehyde 5.80%), Group 2A probable human carcinogen (1,2-Dibromoethane 0.60%), Group 2B possible human carcinogens (Ethylenimine 19.40%, Acetaldehyde 10.50%, Trichloromethane 1.20%, Tetrachloromethane 0.90%, and 1,2-Dichloroethane 0.70%), and Chloromethane (17.10%, Group 3). The detection of potential Group 1

Table 2: Qualitative Hazard Screening and IARC Classification of Hazardous Volatiles Tentatively Identified in Biocomposite Headspace

No.	Tentatively Identified Compound	CAS Number	IARC Group	Relative Peak Area (%)	Primary Documented Hazard Endpoint
1	Ethylene oxide	75-21-8	Group 1	3.60	Alkylate DNA base pairs; significantly increases risks of human leukemia, lymphoma, and breast cancer.
2	Formaldehyde	50-00-0	Group 1	5.80	Forms DNA-protein crosslinks; strongly implicated in nasopharyngeal carcinoma and sinonasal cancer.
3	1,2-Dibromoethane	106-93-4	Group 2A	0.60	Highly reactive alkylating agent; exhibits strong genotoxicity, mutagenicity, and reproductive toxicity.
4	Ethylenimine (Aziridine)	151-56-4	Group 2B	19.40	Electrophilic aziridine ring; induces chromosomal aberrations and direct DNA strand breakage.
5	Acetaldehyde	75-07-0	Group 2B	10.50	Forms covalent DNA adducts; induces upper respiratory tract tumors and cellular mutations.
6	Trichloromethane (Chloroform)	67-66-3	Group 2B	1.20	Metabolized to phosgene in liver; causes severe hepatic necrosis, renal tubule dysfunction, and tumors.
7	Tetrachloromethane (Carbon tet.)	56-23-5	Group 2B	0.90	Triggers lipid peroxidation via trichloromethyl radicals (CCl3•); severe hepatotoxin.
8	1,2-Dichloroethane	107-06-2	Group 2B	0.70	Bioactivated via glutathione conjugation; induces multi-organ hemangiosarcomas in animal models.
9	Chloromethane	74-87-3	Group 3	17.10	Readily crosses the blood-brain barrier; induces central nervous system toxicity and hepatic stress.

Footnotes: a Relative peak area percentage from 100 °C headspace GC-MS profiles. Values represent relative chromatographic detector response and NOT absolute concentration or consumer exposure dose. Identifications are tentative (MSI Level 2).

and Group 2 carcinogens under 100 °C headspace sampling indicates that biomass-derived composites can release hazardous chemical species upon heating. However, as noted in Section 2.4, this qualitative hazard screening does not confirm actual consumer risk or regulatory non-compliance, which requires quantitative migration testing against Specific Migration Limits (SML).

3.3. Origin Pathways and Chemical Mechanisms of Toxic Volatilization

To provide a rigorous scientific basis for the presence of hazardous volatile species in biocomposites derived from natural biomass, four mechanistic origin pathways are formulated below based on plant biochemistry, chemical pre-treatment reactions, and biopolymer thermal degradation.

Path A: Aquatic Phytoextraction and Bioaccumulation by Water Hyacinth. Water hyacinth (Eichhornia crassipes) is an invasive aquatic plant commonly used in phytoremediation because of its ability to absorb dissolved heavy metals, organochlorine pesticide residues, and industrial halides from contaminated waterways [26,27]. During growth in wild aquatic habitats, the highly porous aerenchyma petiole tissue bioaccumulates ambient organohalides and halogen precursors. When the composite is heated to 100 °C, these physically trapped volatile halogenated compounds undergo thermal desorption from the lignocellulosic microfibril matrix. This phytoextraction pathway provides a plausible scientific mechanism for the tentative identification of chloromethane 17.10%, trichloromethane 1.20%, tetrachloromethane 0.90%, 1,2-dichloroethane 0.70%, and 1,2-dibromoethane 0.60%.

Path B: Alkali Delignification Residuals and Thermal Side-Reactions. The chemical pre-treatment of water hyacinth petioles involves immersion in 5% NaOH solution to remove amorphous lignin, hemicellulose, and waxes. Although subsequent rinsing is conducted to reach neutrality, trace sodium ions, unreacted alkaline groups, and wash-water halide ions remain bound to the cellulosic microfibrils [28]. Under thermo-compressive molding (120 °C, 5 MPa) and subsequent 100 °C headspace heating, these residual alkaline sites catalyze localized thermal cleavage and nucleophilic cyclization side-reactions of 2-haloethanol intermediates, yielding ethylene oxide 3.60%.

Path C: Thermal Degradation and Fragmentation of Starch, Glycerol, and Cellulose. The binding matrix consists of gelatinized cassava starch plasticized with 20% (w/w) glycerol. Under 100 °C thermal stress, the hygroscopic glycerol network and glucan chains undergo thermal scission and oxidation. Thermal dehydration of glycerol produces acrolein-like reactive species that fragment into simple aliphatic aldehydes. Concurrently, thermal degradation of glycosidic bonds releases formaldehyde

5.80%, acetaldehyde 10.50%, pentanal 3.30%, hexanal 2.40%, and pyruvic acid 42.60%, consistent with reported starch bioplastic degradation kinetics.

Path D: Thermal Pyrolysis of Residual Plant Proteins and Bound Nitrogenous Biomolecules. Raw water hyacinth petioles naturally contain 10–20% crude protein and nitrogenous cellular fractions [29-31]. If chemical delignification does not fully eliminate these non-cellulosic nitrogenous components, residual amino acids remain incorporated within the composite. Heating at 100 °C induces decarboxylation and C–N bond cleavage of amino acid residues (cysteine, glycine, lysine), releasing nitrogenous volatiles such as ethylenimine aziridine, 19.40%, α-cyano-L-alanine 82.60%, and nitrous oxide 4.70%.

3.4. Food Safety Risk Assessment and Regulatory Implications

From a food packaging safety perspective, the thermal volatilization of Group 1 human carcinogens (ethylene oxide, formaldehyde) and Group 2A/2B carcinogens (ethylenimine, acetaldehyde, chloroform) presents a direct migration hazard. When biodegradable composite packaging is used to contain hot foodstuffs, emitted VOCs can condense directly onto the food matrix or pollute headspace air, leading to consumer exposure via ingestion or inhalation. International safety frameworks enforced by EFSA and US FDA require strict compliance with Specific Migration Limits (SML) for volatile packaging chemicals [32-34]. International packaging safety frameworks (EFSA, 2022; US FDA) enforce strict compliance with Specific Migration Limits (SML) for food contact materials. In contrast, bioplastic regulatory standards in several developing nations evaluate materials almost exclusively via gravimetric soil disintegration or CO2 evolution rates (ISO 14855 / SNI standards). While our detection of potential Group 1 and 2 carcinogens highlights the necessity of expanding regulatory evaluations beyond biodegradability, we emphasize that qualitative headspace screening alone cannot determine food safety compliance. Quantitative migration studies into food simulants (aqueous, acidic, alcoholic, fatty media) are mandatory before concluding actual consumer health risks [35].

3.5. Material Engineering Mitigation and Safe-by-Design Strategies

To eliminate hazardous volatile emissions while preserving biocomposite mechanical integrity and biodegradability, future composite formulations should adopt a Safe-by-Design engineering framework: (1) Exhaustive Fiber Extraction using multi-stage Soxhlet washing with deionized water and chelating agents (*e.g.*, citric acid) to leach out absorbed aquatic halogens and residual pesticides; (2) Delignification Neutralization optimizing post-alkali washing to completely remove residual sodium hydroxide; and (3) Natural Antioxidant Incorporation introducing natural polyphenol antioxidants (*e.g.*, tannic acid, green tea catechins) into the starch–glycerol matrix to scavenge free radicals and retard thermal oxidation.

3.6. Limitations of Current Findings

To ensure objective interpretation, the analytical limitations of this study must be explicitly acknowledged:

1. Tentative Compound Identification: Volatile identification relies on NIST mass spectral library matching (>80% match factor, MSI Level 2). Confirmation with authentic chemical reference standards and retention index (RI) calibration was not performed.

2. Relative Peak Area Metrics: Reported peak area percentages represent relative chromatographic detector response under 100 °C static headspace equilibrium. They do not reflect absolute emission concentrations (*e.g.*, μg/g or ppm) or mass emission yields.

3. Absence of Quantitative Risk Assessment: No migration testing into food simulants or dietary exposure modeling was conducted. Consequently, no definitive conclusions regarding actual consumer health risks or non-compliance with Specific Migration Limits (SML) can be made.

4. Static Single-Temperature Testing: Testing was restricted to 100 °C for 15 minutes. Emission kinetics across dynamic temperature-time profiles remain to be investigated.

4. CONCLUSION

This study demonstrates that environmental biodegradability does not inherently ensure chemical and toxicological safety in biomass-based packaging biocomposites. Headspace Gas Chromatography–Mass Spectrometry (HS-GC-MS) examination of water hyacinth (Eichhornia crassipes) fiber–cassava starch biocomposite films exposed to thermal stress (100 °C for 15 minutes) identified 26 distinct volatile organic compounds (VOCs). Crucially, 9 of these volatile species are classified as hazardous or carcinogenic agents by the International Agency for Research on Cancer (IARC): Group 1 Human Carcinogens: Ethylene oxide (3.60% peak area) and Formaldehyde (5.80% peak area). Group 2A Probable Human

Carcinogen: 1,2-Dibromoethane (0.60% peak area). Group 2B Possible Human Carcinogens: Ethylenimine (aziridine, 19.40% peak area), Acetaldehyde (10.50% peak area), Trichloromethane (chloroform, 1.20% peak area), Tetrachloromethane (carbon tetrachloride, 0.90% peak area), and 1,2-Dichloroethane (0.70% peak area). Group 3 / Hepatotoxin: Chloromethane (17.10% peak area).

Four plausible chemical origin pathways were formulated, combining aquatic phytoextraction by water hyacinth, alkali delignification pre-treatment residuals, thermal fragmentation of the starch–glycerol matrix, and pyrolysis of residual plant proteinaceous biomass. Critically, reported peak area percentages represent relative chromatographic detector response and must not be interpreted as absolute mass concentrations or consumer exposure doses. Future research must focus on quantitative emission testing (ppm), migration studies into liquid food simulants per EFSA/FDA protocols, *in vitro* / *in vivo* toxicity bioassays, and Safe-by-Design fiber purification strategies.

DECLARATION OF CONFLICTING INTEREST

The authors declare that there are no relevant financial or non-financial competing interests to report.

AUTHORS' CONTRIBUTION

Acep Musliman conceptualized the study, performed toxicological emission analysis, and drafted the manuscript. Fitri Damayanti conducted data curation, literature synthesis, and critical manuscript revision. Tri Rushandayani contributed to composite fabrication and technical testing procedures. All authors read and approved the final manuscript.

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