

Article

Synthesis of Acetylsalicylic Acid Catalysed by Food Industry Waste Ash: A Preliminary Study

Dajana Gašo-Sokač ^{1,*} , Zdenko Lončarić ² , Dora Zobundžija ¹, Katja Milinković ¹, Damir Magdić ¹  and Valentina Bušić ^{1,*} 

¹ Department of Applied Chemistry and Ecology, Faculty of Food Technology Osijek, Josip Juraj Strossmayer University of Osijek, 31000 Osijek, Croatia; dora.zobundzija@ptfos.hr (D.Z.); katjamilinkovic9@gmail.com (K.M.); damir.magdic@ptfos.hr (D.M.)

² Faculty of Agrobiotechnical Sciences, Josip Juraj Strossmayer University of Osijek, Vladimira Preloga 1, 31000 Osijek, Croatia; zloncaric@fazos.hr

* Correspondence: dgaso@ptfos.hr (D.G.-S.); vbusic@ptfos.hr (V.B.); Tel.: +385-31224327 (D.G.-S. & V.B.)

Abstract

Green chemistry aims to develop more sustainable and environmentally friendly chemical processes by reducing waste, minimising the use of hazardous substances, and identifying alternative catalysts and solvents. Traditional organic synthesis often relies on catalysts that are toxic, flammable, or corrosive, such as phosphoric acid, creating a need for greener alternatives. This study investigated the potential of ash derived from food industry waste as a green catalyst. Various waste materials were utilised, including onion and garlic husks, peanut skins and shells, hop and barley residues after beer production, and cocoa shells and beans. ICP-MS analysis was used to determine the content of 25 elements (Na, Mg, P, K, Ca, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Mo, Cd, Pb, B, Al, S, Ga, Rb, Sr, Ba, La) in the food industry waste ash. The catalytic activity of the ash was evaluated in the synthesis of acetylsalicylic acid from salicylic acid and acetic anhydride. Reactions were carried out in the presence of 20 mg of ash by heating the reaction mixture in a water bath at 80–100 °C. Reaction yields ranged from 11% (peanut shell ash) to 78% (barley ash). In addition to barley ash, good reaction yields were also obtained with hop ash, cocoa shell ash, and cocoa bean ash. The results demonstrated that ash-derived materials successfully catalysed the reaction, suggesting that metals present in the ash may play a role in catalysis. These findings indicate that food industry waste may represent a promising and sustainable source of catalysts for organic synthesis.

Keywords: green chemistry; food industry waste; ash; catalysts; synthesis; acetylsalicylic acid



Academic Editor: Pasquale Crupi

Received: 6 August 2026

Revised: 11 September 2026

Accepted: 12 September 2026

Published: 14 September 2026

Copyright: © 2026 by the authors.

Licensee MDPI, Basel, Switzerland.

This article is an open access article

distributed under the terms and

conditions of the [Creative Commons](#)

[Attribution \(CC BY\)](#) license.

1. Introduction

Ashes derived from by-products and waste of the food industry represent an important group of green heterogeneous catalysts that are increasingly used in organic synthesis. These catalysts are produced by simple thermal treatment (combustion) of biomass, resulting in materials rich in inorganic components with pronounced basic active sites suitable for catalytic processes [1]. One of the most studied examples is onion peel ash, which has proven effective in various organic reactions. It serves as a catalyst in the acetylation of alcohols and amines under solvent-free conditions and without the addition of acids or bases, achieving high yields (76–96%) [2]. Additionally, it is used in multicomponent reactions for the synthesis of aminothiazole derivatives, enabling rapid production of

products with excellent yields [3]. A significant advantage of this catalyst is its ability to be reused up to four or five cycles without significant loss of activity, further confirming its sustainability and economic viability [3]. Moreover, aqueous extracts of onion peel ash are successfully applied in the synthesis of isoindoline-1,3-dione, achieving high yields and reducing the use of toxic chemicals [4]. Pomegranate peel ash is also recognised as an effective biocatalyst in condensation reactions. Burning the bark yields a material with pronounced basic properties, which can be used for aldol condensations and the synthesis of α,α' -bis(substituted benzylidene)cycloalkanones and 2-arylidene-1-tetralone [1]. These reactions occur in an aqueous medium, further enhancing the environmental acceptability of the process. Additionally, the aqueous extract of pomegranate ash has been successfully used in the synthesis of chiral sulfinyl-aldimines in high yields [5].

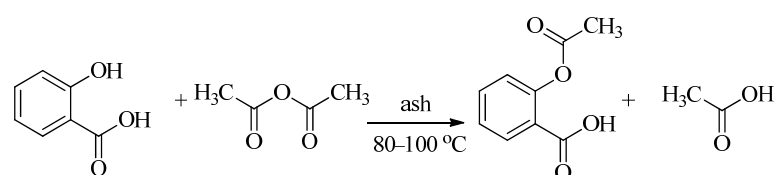
Banana peel ash, used as a catalyst in various organic transformations, also shows significant potential. It is applied in the synthesis of chalcones and flavones via aldol condensation under solvent-free conditions and at room temperature, achieving high yields [6]. Furthermore, aqueous extract of banana ash is used in Suzuki–Miyaura cross-coupling reactions, enabling the reaction to proceed without metal catalysts, ligands, or organic solvents [7]. Banana peel ash is also used as a heterogeneous catalyst in the Henry reaction for the synthesis of β -nitroalcohols, achieving high yields in a very short time [8]. Additionally, banana ash extracts are used for the biosynthesis of iron oxide nanoparticles that exhibit catalytic activity in organic reactions [9]. Ash derived from *Carica papaya* peels, rich in alkaline metal oxides such as potassium and calcium, was used as a heterogeneous base catalyst in the transesterification of waste cooking oil, achieving high biodiesel yields and providing a low-cost, sustainable alternative to conventional catalysts [10]. Ash obtained from different parts of the *Musa paradisiaca* plant—bark, trunk, and rhizome—is used as a heterogeneous base catalyst for the production of biodiesel from jatropha oil. Ash from the trunk, in particular, contains a higher proportion of potassium and shows the highest catalytic efficiency [8]. Waste sugarcane bagasse ash was used as a catalyst for synthesis of biodiesel [11,12]. The catalyst prepared by burning the dried waste *Brassica nigra* plant was used as an efficient catalyst in the transesterification of soybean oil for biodiesel production. Analysis of the catalyst indicated potassium (56.13 wt%) as the major component, followed by calcium (26.04 wt%) in the form of oxide, carbonate, and chloride [13]. Cocoa, kola nut and fluted pumpkin waste ash were used for transesterification reactions of a mixture of yellow oleander—rubber seed oils. The agrowaste mixture calcined at 500 °C for 4 h was selected due to its catalytic potential (K 48.4%, Ca 5.1%, Fe 1.1%). The catalyst, ash from unused radish (*Raphanus sativus* L.) leaves, was used to produce biodiesel using waste soybean cooking oil and oil of *Scenedesmus obliquus*. The results showed the presence of Ca, S, Si, Cl, Al, P, Mg, Mn, Na and a high proportion of potassium (57.30% by weight) in the form of carbonates and oxides [14]. A solid base catalyst was synthesised from a mixture of ripe and unripe plantain peels by calcining at 500 °C for 4 h and used for transesterification. The results showed that the synthesised catalyst predominantly contained potassium phases, with 45.16 wt.% [15]. Ashes of seed husks and inedible seed oil of *Xanthium strumarium* were used in transesterification reactions [16]. Elemental analysis showed the presence of potassium (34 wt%) in high concentrations, which can contribute effectively to the transesterification process.

In general, ash derived from biowaste acts as an effective heterogeneous catalyst due to the presence of basic sites and a porous structure that allows good contact with the reactants. Its key advantages include low cost, easy preparation, biodegradability, recyclability, and compliance with the principles of green chemistry. Such catalysts represent a viable alternative to conventional chemical catalysts, especially in the context of reducing the use of toxic reagents and valorising waste from the food industry [1].

Conventional synthesis of acetylsalicylic acid and many other industrial chemical processes rely on phosphoric acid and other strong mineral acids, such as sulphuric and hydrochloric acids, as homogeneous catalysts. Although highly effective, these catalysts are associated with several environmental concerns. Waste streams containing mineral acids exhibit very low pH values and therefore require neutralisation prior to discharge in order to prevent the acidification of surface and groundwater as well as adverse effects on aquatic and terrestrial ecosystems. Moreover, acidic effluents can increase the mobility of heavy metals in soils and sediments, facilitating their transport into water bodies and subsequent accumulation within the food chain [17–19].

Unlike sulphuric and hydrochloric acids, phosphoric acid also contributes phosphorus to wastewater. If wastewater is inadequately treated, phosphate released into the environment may stimulate eutrophication, leading to excessive algal growth, oxygen depletion, deterioration of water quality, and severe disruption of aquatic ecosystems [20,21]. The use of strong mineral acids also generates considerable amounts of secondary chemical waste because neutralisation produces large quantities of inorganic salts that require further treatment or disposal. Consequently, additional chemicals, water, and energy are consumed during wastewater treatment, increasing both environmental and economic costs. For these reasons, the development of alternative heterogeneous catalysts derived from renewable resources has attracted increasing attention. Such catalysts can minimise hazardous waste generation, simplify catalyst recovery and recycling, and contribute to the implementation of greener and more sustainable chemical processes in accordance with the principles of green chemistry [22,23].

Although the catalytic potential of individual food industry waste ashes has been previously demonstrated, most existing studies focus on a single ash type applied to a specific reaction, and a systematic comparison of multiple, diverse food waste ashes with respect to both their catalytic activity and mineral composition remains lacking. This study addresses this gap by screening a broad range of previously unexplored food industry waste ashes and examining the relationship between their mineral composition and catalytic performance. This study examines the potential of ash derived from food industry waste as green catalysts. Various waste materials were assessed, including onion and garlic husks (*Allium cepa* and *Allium sativum*), cocoa shells and beans (*Theobroma cacao*), peanut shells and skin (*Arachis hypogaea*), hops (*Humulus lupulus*), and barley (*Hordeum vulgare*) remaining as waste after beer production. The research is based on the hypothesis that metal oxides and salts present in ash can efficiently catalyse acetylation reactions, Scheme 1 [24].



Scheme 1. Synthesis of acetylsalicylic acid.

The synthesis of acetylsalicylic acid, with a global annual production estimated at 40,000 to 50,000 tonnes, was selected as a model reaction. As conventional synthesis relies on mineral acids such as phosphoric acid, the introduction of ash from food industry waste as a biocatalyst offers a viable alternative. The use of such catalysts offers the potential to valorise food industry waste that would otherwise require disposal and may enable the development of methodologies that address the shortcomings of traditional chemical processes in the pharmaceutical industry; however, a full assessment of the associated environmental impact, including the energy demand and emissions of the ash preparation step, was beyond the scope of this preliminary study.

2. Materials and Methods

All reagents and solvents were purchased and used without further purification: acetylsalicylic acid, 99% (Thermo Scientific Chemicals; Waltham, MA, USA), acetic anhydride (Thermo Scientific Chemicals; Waltham, MA, USA), hydrochloric acid (Macron Fine Chemicals, Avantor, Radnor, PA, USA), sodium carbonate (Gram-Mol d.o.o, Zagreb, Croatia), salicylic acid, ACS $\geq 99.0\%$ (Sigma-Aldrich®; St. Louis, MO, USA), and ferric chloride (Fluka, Buchs, Switzerland). Muffle furnace Nabertherm LE 14/11/R7 (Nabertherm GmbH, Lilienthal, Germany) was used for preparation of ash. Infrared (FTIR) spectra were recorded on a Cary 630 FTIR instrument (Agilent Technologies, Santa Clara, CA, USA) using an ATR (Attenuated Total Reflection) attachment.

Procedure for the preparation of ash: Waste plant material was supplied by the laboratory of the Department of Food Technologies at the Faculty of Food Technology Osijek. The samples were accurately weighed on an analytical balance and placed into previously cleaned, dried, and weighed porcelain crucibles. Carbonisation was performed on a heated electric plate inside a fume hood, with heating continued until smoke emission ceased completely. After carbonisation, the crucibles containing the samples were transferred to a muffle furnace, where combustion was carried out at $500\text{ }^{\circ}\text{C}$ for one hour. Once cooled, the resulting ash was weighed and used as a catalyst in the synthesis of acetylsalicylic acid.

Determination of the titratable basicity of ash: The titratable basicity of the ash samples was determined by potentiometric titration with standardised hydrochloric acid (HCl) [25]. Briefly, 0.100 g of ash was suspended in 10 mL of deionized water and allowed to equilibrate under continuous stirring. The initial pH was measured using a calibrated pH metre. The suspension was subsequently titrated with 0.020 mol L^{-1} standardised HCl, which was added stepwise under continuous stirring, and the pH was recorded after each addition. The equivalence point was determined from the potentiometric titration curve based on the inflexion point, corresponding to the maximum rate of pH change ($\Delta\text{pH}/\Delta V$). The volume of HCl at the equivalence point (V_{eq}) was used to calculate the titratable basicity according to the following equation. The titratable basicity was calculated from the volume of HCl required to decrease the pH of the ash suspension to 4, according to:

$$\text{basicity} = (C_{(\text{HCl})} \times V_{\text{eq}}) / (m \text{ ash})$$

where basicity is the titratable basicity ($\text{mmol H}^{+} \text{ g}^{-1}$), $c(\text{HCl})$ is the concentration of standardised HCl (mol L^{-1}) = 0.02 mol L^{-1} , $V(\text{HCl})$ is the volume of HCl consumed up to equivalence point (L), and $m(\text{ash})$ is the mass of the ash sample (g) and expressed as $\text{mmol H}^{+} \text{ g}^{-1}$ ash.

Sample preparation and Analysis: All samples were dried and milled in a heavy metal-free mill (Retsch RM200, Haan, Germany). A total of 0.4–0.5 g of milled sample was digested with 9 mL 65% (*v/v*) HNO_3 and 2 mL 30% (*v/v*) H_2O_2 in microwave vessels (CEM Mars 6, Matthews, NC, USA) for 60 min at $180\text{ }^{\circ}\text{C}$, according to [26,27]. After digestion, the cooled sample solution was transferred into a 50 mL graduated flask, which was filled with ultrapure water up to the volume of 50 mL. Concentrations of elements were determined by Inductively Coupled Plasma Mass Spectrometry ICP-MS 7800 Agilent Technologies (Santa Clara, CA, USA) using an internal pooled plasma control. Certified reference materials (hay powder, BCR-129, EUR 12473, European Commission, Joint Research Centre, Institute for Reference Materials and Measurements, Geel, Belgium; soya bean flour, INCT-SBF-4, Polish reference material, Institute of Nuclear Chemistry and Technology, Warszawa, Poland; cabbage leaf powder, NCZ ZC73012, China National Analysis Center for Iron and Steel, Beijing, China; natural soil, NCZ ZC73002, China National Analysis Center for Iron and Steel, Beijing, China) were prepared in the same way as the ash samples [26,27].

Conventional synthesis of acetylsalicylic acid: A total of 1 g of salicylic acid was weighed into a 50 mL round-bottomed flask. Using a pipette, 2 mL of acetic anhydride and 3–5 drops of 85% phosphoric acid were added. A reflux condenser was attached to the flask, and the reaction mixture was heated in a water bath with magnetic stirring for 10 min at 80–100 °C. After heating, the flask was cooled to room temperature. To decompose the excess acetic anhydride, 5 mL of cold distilled water was added carefully and dropwise, as the addition may cause slight foaming and heat evolution. The reaction mixture was then placed in a refrigerator for at least 30 min to allow the product to crystallise. The crystals were collected by vacuum filtration using a Büchner funnel and placed in a desiccator to dry [28].

Synthesis of acetylsalicylic acid catalysed by food industry waste ash: 1 g of salicylic acid was weighed into a 50 mL round-bottomed flask. Using a pipette, 2 mL of acetic anhydride was added, along with 0.02 g of food industry waste ash (derived from onion and garlic husks, peanut skins and shells, hop and barley residues, and cocoa shells and beans). A reflux condenser was attached to the flask, and the reaction mixture was heated in a water bath with magnetic stirring for 25 min at 80–100 °C.

After heating, the flask was cooled to room temperature. To decompose the excess acetic anhydride, 5 mL of cold distilled water was added carefully, and the reaction mixture was then placed in a refrigerator to allow the product to crystallise. The crystals were collected by vacuum filtration using a Büchner funnel, washed with cold distilled water, and placed in a desiccator to dry.

After drying, the crude product was purified by dissolving in 35 mL of a 5% aqueous sodium carbonate solution (Na_2CO_3) with continuous magnetic stirring until complete dissolution was achieved. The resulting clear solution was filtered through folded filter paper to remove any insoluble impurities. The filtrate was then acidified under constant stirring by the dropwise addition of dilute hydrochloric acid (prepared by dissolving 3.5 mL of concentrated HCl in 10 mL of ice-cold distilled water). The mixture was left to stand overnight, during which crystals of purified acetylsalicylic acid formed. The crystals were collected by vacuum filtration using a Hirsch funnel, thoroughly washed with cold distilled water, and transferred to a desiccator to dry. The presence of unreacted salicylic acid was assessed by the ferric chloride test, based on the formation of a violet Fe(III)-phenolate complex [29]. IR spectra were recorded and melting points were determined for the obtained products. The yields reported represent isolated yields of purified acetylsalicylic acid, calculated as the ratio of the mass of the isolated, dried product obtained after the complete purification procedure to the theoretical yield based on the amount of salicylic acid used.

3. Results

The ash yield obtained by carbonisation (500 °C, 1 h) of the tested waste plant materials showed a clear dependence on the type of raw material (Table 1). Expressed as a mass fraction relative to the mass of the sample before carbonisation, the ash yield ranged from about 2.7% for barley and peanut shells, through approximately 3–4% for peanut skins, hops, onion shells and cocoa beans, to significantly higher values of 6.7% for cocoa fruit shells and as much as 10.8% for garlic shells. Such differences were expected, given the different proportions of organic (cellulose, hemicellulose, lignin) and inorganic (mineral) fractions in individual types of plant waste; materials with a more pronounced shell-like structure (garlic, cocoa shells) naturally contain a higher proportion of mineral components that remain as ash after combustion of organic matter.

Table 1. Amount of ash obtained after combustion of the sample, pH and basicity of ash.

Waste Plant Material	Sample Mass Before Combustion (g)	Ash (g)	pH	Basicity/mmol H ⁺ g ⁻¹ Ash
Garlic husk	1.0	0.1082	10.9	1.4
Onion husk	2.0	0.0809	10.9	17.0
Peanut shell	2.0	0.0549	10.6	12.0
Peanut skin	0.97	0.0280	10.7	9.0
Hops	2.0	0.0647	10.3	5.0
Barley	2.0	0.0548	7.7	1.6
Cocoa bean	2.0	0.0710	10.5	10.6
Cocoa bean shell	2.0	0.1345	10.5	10.3

For this research, ash obtained from the carbonisation of food industry waste (onion, garlic and peanut husks and skins, hop and barley residues remaining after beer production, and cocoa shells and beans) was used as a catalyst instead of 85% phosphoric acid in the synthesis of acetylsalicylic acid from salicylic acid and acetic anhydride. Since this study was designed as a preliminary screening of the catalytic feasibility of ashes derived from food industry waste, the experiments were performed as single runs. The data in Table 2 show that none of the tested ashes fully matched the efficiency of the conventional H₃PO₄ catalyst (88%) and that there are significant differences in the reaction yields of the individual ashes. The yields of reactions catalysed by ash ranged from 78% (barley ash) to only 11% (peanut shell ash). Relative to the conventional catalyst, barley ash achieved about 89% of its efficiency, cocoa bean ash about 72%, cocoa shell ash and garlic shell ash about 69% and 67%, respectively, while hop ash, onion husk and peanut skins achieved only 64%, 50% and 45% of the relative H₃PO₄ efficiency, respectively. The poorest result, peanut shell ash, achieved only 12.5% of the conventional catalyst utilisation. It should be noted that all ashes were evaluated under a single, fixed set of reaction conditions (20 mg catalyst loading) as part of an initial screening to assess their general catalytic potential; consequently, the observed differences in yield may partly reflect differences in the suitability of these conditions for the individual ashes, given their substantially different compositions, rather than solely catalytic activity.

Table 2. Yield of the synthesis reaction.

Catalyst	Yield (%)
H ₃ PO ₄	88
Garlic husk ash	59
Onion husk ash	44
Peanut shell ash	11
Peanut skin ash	39
Hops ash	56
Barley ash	78
Cocoa bean ash	63
Cocoa bean shell ash	61

Based on the data presented in Table 1, a clear discrepancy between alkalinity parameters and catalytic performance of the ashes is observed. For example, garlic husk ash (pH 10.9; basicity 1.4 mmol H⁺/g) and onion husk ash (pH 10.9; basicity 17.0 mmol H⁺/g) exhibit nearly identical pH values but show drastically different basicities and yields (59% vs. 44%), while barley ash (pH 7.7; basicity 1.6 mmol H⁺/g) achieves the highest yield (78%) despite having the lowest pH and one of the lowest basicities. Cocoa bean ash (pH 10.5; 10.6 mmol H⁺/g) and cocoa bean shell ash (pH 10.5; 10.3 mmol H⁺/g)

show almost identical alkalinity profiles and afford similar yields (63% and 61%), whereas peanut skin ash (pH 10.7; 9.0 mmol H⁺/g) and hops ash (pH 10.3; 5.0 mmol H⁺/g) display moderate to high basicity and yet yield only 39% and 56%, respectively. These findings collectively demonstrate that neither the initial pH nor the titratable basicity can serve as reliable predictors of catalytic activity among the investigated ashes and that catalytic efficiency arises from a complex interplay of mineral composition (particularly the relative proportions of K, Ca, P, and S), chemical speciation and surface accessibility of active sites, and synergistic acid–base interactions, rather than from bulk alkalinity alone.

Furthermore, we investigated the possibility of recycling barley ash, which exhibited the best catalytic activity and gave the highest reaction yield (78%) in the synthesis of acetylsalicylic acid. After completion of the first synthesis cycle, the barley ash was separated from the reaction mixture by filtration, washed with distilled water, and reused in a subsequent synthesis of acetylsalicylic acid. The results showed that barley ash could be recycled and reused up to three times without significant loss of efficiency, as indicated by the reaction yields (Table 3).

Table 3. Recyclability study of barley ash.

Cycle	Yield (%)
Initial run	78
1st run	77
2st run	77
3rd run	75

To explain the large differences in catalytic activity between individual ashes, the yields (Table 2) were compared with the mineral composition of the ash (Table 4). In all samples, the macroelement fraction—potassium, calcium, phosphorus and magnesium—dominated, while the concentrations of microelements and heavy metals varied markedly depending on the raw material.

In all analysed samples, macroelements predominate, primarily potassium (K), calcium (Ca), phosphorus (P) and magnesium (Mg). The highest concentrations of potassium were recorded in the ash of cocoa bean (255,500 mg/kg) and peanut shells (205,200 mg/kg), followed closely by cocoa bean shell ash (217,500 mg/kg). The high potassium content observed in the peanut skin ash examined in this study (132,500 mg/kg) is consistent with previous reports identifying potassium as the main macroelement in peanut skins, further supported by mineral analyses showing potassium among the major elements present in both raw and roasted peanut skins [30]. The high potassium content measured in the peanut shell ash in this study (205,200 mg/kg) is consistent, after normalisation for the ash yield, with potassium content previously reported for peanut shells [31].

Notably, potassium was found to be overwhelmingly dominant over sodium in the cocoa bean shell ash examined here (217,500 mg/kg K versus only 936.2 mg/kg Na), which differs markedly from the sodium-dominant profile reported for cocoa bean shell ash [32,33]. This discrepancy likely reflects the considerable variability in cocoa by-product mineral composition associated with geographic origin, soil conditions, and post-harvest processing history.

On the other hand, the ash of garlic husks (270,400 mg/kg) and red onion husks (255,200 mg/kg) are characterised by an exceptionally high calcium content. The findings indicating the highest calcium content in the ash of garlic husk and red onion husk are consistent with the research of other authors [34].

Regarding trace metals, specific accumulations of individual elements were observed: peanut skin contained the highest concentrations of sodium (Na, 34,770 mg/kg), copper (Cu,

4777 mg/kg) and cadmium (Cd, 2197 mg/kg), while the highest content of manganese (Mn, 1321 mg/kg) and aluminium (Al, 10,850 mg/kg) was detected in the ash of peanut shells.

Table 4. Mineral composition of ash.

mg/kg	Barley	Cocoa Bean	Cocoa Bean Shell	Garlic Husk	Hops	Onion Husk	Peanut Skin	Peanut Shell
Na	1760	1482	936.2	7950	4066	21,890	34,770	6702
Mg	51,070	91,740	30,590	20,720	46,030	33,610	64,990	34,030
P	122,200	150,800	23,180	18,540	44,770	4376	28,750	18,690
K	55,210	255,500	217,500	65,530	86,210	90,020	132,500	205,200
Ca	47,460	26,930	29,100	270,400	186,800	255,200	170,100	117,100
Cr	82.53	5.13	18.08	9.884	16.25	11.28	8.309	24.28
Mn	734.8	666.2	609.4	158.4	1018	336.6	386.6	1321
Fe	3430	924	7692	3448	6275	4943	3681	4751
Co	1.341	10.41	11.88	1.952	2.450	2.266	13.74	3.287
Ni	33.78	149.7	56.86	13.44	14.83	8.679	166.2	16.86
Cu	225.5	531.6	231.1	48.9	1273	26.46	4777	301.4
Zn	1512	1318	459.5	168	408.8	132.9	1363	432.4
As	0.263	0.791	1.887	1.547	1.63	1.724	20.15	3.711
Se	0.480	1.320	0.871	0.264	0.303	0.29903	0.407	0.320
Mo	26.943	20.565	4.293	26.085	6.969	6.256	102.675	2.463
Cd	0.737	7.576	1.442	0.974	0.287	0.674	21.971	3.031
Pb	18.856	1.055	9.485	3.105	16.110	5.713	5.664	14.374
B	66.51	339.5	425.8	380.5	396.1	334.2	1198	469.3
Al	470.4	389	9379	5162	6083	7257	2899	10,850
S	1125	13,740	9072	7474	7617	7682	27,970	35,430
Ga	0.191	0.125	3.342	1.585	1.906	2.307	0.937	3.286
Rb	74.92	219.3	457.5	165.6	236	788.7	167	220.8
Sr	234.6	202.5	272.6	738.4	1108	4831	724.8	603.5
Ba	337.4	278.3	227.7	323.9	194.9	264.9	354.5	315.6
La	0.42550	0.3301	8.667	3.951	4.502	6.033	2.417	11.86

Notably, the two ashes with the highest phosphorus contents, barley ash (122,200 mg/kg) and cocoa bean ash (150,800 mg/kg), also achieved the highest reaction yields (78% and 63%), suggesting a possible association between phosphorus content and catalytic performance. However, this pattern was not consistent across all samples—onion husk ash had the lowest phosphorus content of all the ashes tested (4376 mg/kg), yet it achieved a moderate yield of 44%, while cocoa shell ash, despite a relatively low phosphorus content (23,180 mg/kg), achieving the third-highest yield (61%). As phosphorus speciation was not determined in this study, it cannot be established which phosphorus-containing species, if any, contribute to catalytic activity, nor can a specific catalytic mechanism be attributed to this element. Phosphorus content should therefore not be regarded as a reliable predictor of catalytic activity on its own; reaction yield more likely reflects the combined contribution of multiple mineral constituents and their distribution on the surface of the ash particles.

A particularly informative pattern was observed for sulphur. The two ashes with by far the highest sulphur content—peanut skin ash (27,970 mg/kg) and peanut shell ash (35,430 mg/kg), both many times higher than the values measured in the other samples—also gave the lowest reaction yield of the entire set (39% and only 11%, respectively). In contrast, barley ash, with the highest yield (78%), contained the lowest sulphur concentration of all the samples tested (1125 mg/kg). This inverse relationship between sulphur content and reaction yield was observed only in this limited subset of samples, and, in the absence of information on sulphur speciation or surface distribution, it does not establish a causal role for sulphur-containing phases in catalyst deactivation. Since the same samples

(peanut skin and shell) were also the poorest in phosphorus and showed extremely low yield, the poor performance of these two ashes more likely reflects the combined effect of low phosphorus and high sulphur content, together with other unmeasured surface properties, rather than a single identifiable deactivation mechanism. Further characterisation (e.g., surface analysis or sulphur speciation studies) would be required to clarify the role of sulphur in catalytic performance. In addition to phosphorus and sulphur, reaction yield is probably also influenced by the total alkalinity of the ash, determined by the content of calcium and potassium present mainly in the form of oxides and carbonates.

Ashes with very high calcium content, such as garlic husk ash (270,400 mg/kg) and onion husk ash (255,200 mg/kg), achieved medium to high yields (59% and 44%) but were not the most efficient, suggesting that catalytic activity depends on the combined effect of several mineral components rather than on calcium content alone. The combination of moderate calcium and potassium content and high phosphorus content, as recorded in barley ash, seems more favourable for achieving high conversion than the marked predominance of only one mineral component.

No clear relationship could be established between mineral composition alone and reaction yield; while barley ash combined moderate calcium and potassium content with high phosphorus content and achieved the highest yield, this remains an empirical observation. As acid catalysis by H_3PO_4 relies on proton availability, a high total phosphorus content determined by ICP-MS does not by itself indicate the presence of an acidic, proton-donating species and would depend on the specific phosphorus-containing phases present and the pH of the ash, neither of which was determined in this study. Given that ICP-MS analysis provides only bulk elemental concentrations and does not identify the specific chemical species, mineral phases, or active sites present, the exact catalytic mechanism cannot be confirmed based on the current evidence and warrants further investigation (e.g., XRD, XPS, or FTIR analysis). Nonetheless, these findings indicate that food industry waste may represent a promising and sustainable source of catalysts for organic synthesis. The first step in statistical analysis was to calculate Z-score values for proper statistical analysis. The values are calculated as:

$$Z = (x - \mu) / \sigma$$

where x represents a raw data value, μ represents the mean value, and σ represents the standard deviation. This transformation puts all variables on the same scale (mean = 0, SD = 1), making comparisons more meaningful and reducing the influence of the total mass of an element in raw samples. Standardised values facilitated the correlation analysis with reaction yield (Table 5) and between elements (Table 6).

Table 5. Significant correlations ($p < 0.05$) with reaction yield (efficiency).

Efficiency		Efficiency		Efficiency		Efficiency	
Na	−0.41507	Fe	−0.10001	Se	0.357492	S	−0.88678
Mg	0.168309	Co	−0.02641	Mo	−0.047	Ga	−0.53819
P	0.545098	Ni	0.040995	Cd	−0.26821	Rb	−0.15526
K	−0.2961	Cu	−0.22653	Pb	0.030546	Sr	−0.21473
Ca	−0.28301	Zn	0.32313	B	−0.46793	Ba	−0.1777
Cr	0.404335	As	−0.3807	Al	−0.61105	La	−0.68485
Mn	−0.40402	—	—	—	—	—	—

Legend: Minus sign “−” marks the empty cell.

Table 6. Significant correlations ($p < 0.05$) between elements.

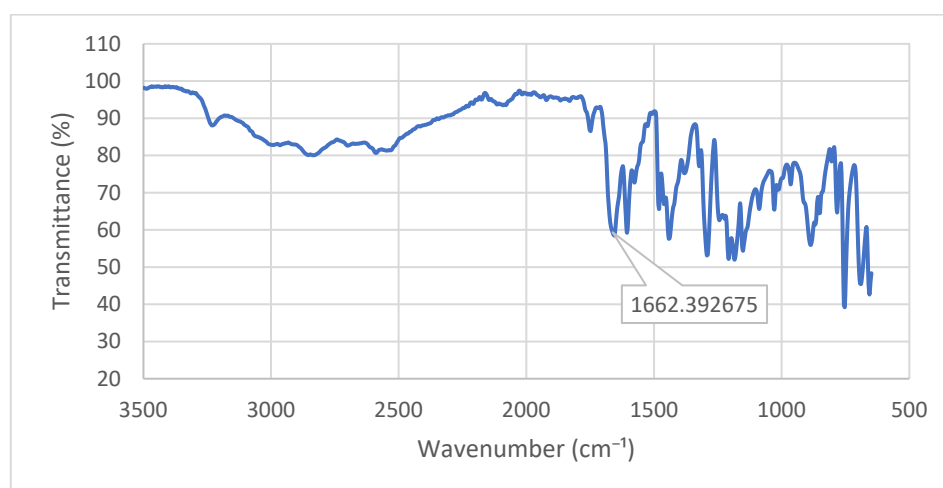
	Cu	As	Mo	Al	Ga
As	0.956085	ns	ns	ns	ns
Mo	0.907507	0.909494	ns	ns	ns
Cd	0.92138	0.933238	0.917413	ns	ns
B	0.914468	0.960717	ns	ns	ns
Ga	ns	ns	ns	0.992786	ns
La	ns	ns	ns	0.97784	0.964227

Legend: Text “ns” replaces results that are not statistically significant.

Only statistically significant correlations between elements are presented in Table 5. All others were statistically non-significant.

No single element shows a strong positive or negative correlation (except sulphur) with a reaction yield that would undoubtedly identify it as the primary active species. Only positive correlations with yield were shown for magnesium, phosphorus, chromium, nickel, zinc, and selenium. The significant negative correlation showed sulphur. The yields of the reactions appear to result from a synergistic combination of elements. Significant correlations between elements are shown in Table 6. All other determined correlations between elements were statistically non-significant.

The identity of the synthesised product was confirmed by its melting point and FTIR spectroscopy. The measured melting point of the purified product (135–136 °C) was in excellent agreement with the literature value reported for acetylsalicylic acid (135–136 °C). To confirm the identity of the synthesised product, FTIR spectra were recorded for the starting salicylic acid and the acetylsalicylic acid synthesised via the ash-catalysed acetylation reaction (Figures 1 and 2). Salicylic acid contains a carboxylic acid group (–COOH) and a phenolic hydroxyl group (–OH), whereas acetylsalicylic acid contains a carboxylic acid group and an ester group (–COO–) formed by acetylation of the phenolic –OH. Direct comparison of the FTIR spectrum of the starting salicylic acid (Figure 1) with that of the acetylsalicylic acid obtained from the ash-catalysed reaction (Figure 2) provides strong spectroscopic evidence of acetylation.

**Figure 1.** IR spectrum of commercial salicylic acid, standard (Sigma-Aldrich®; ACS $\geq 99.0\%$).

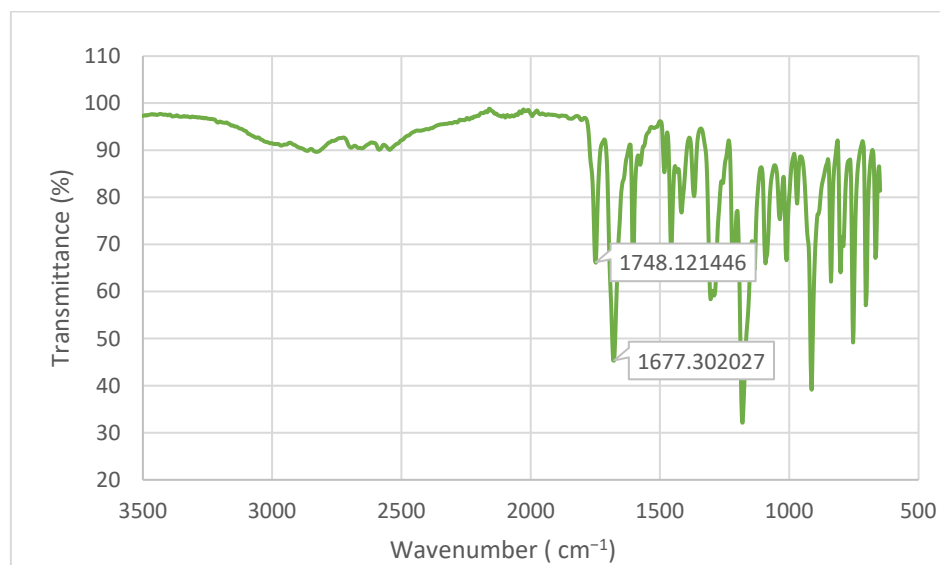


Figure 2. IR spectrum of acetylsalicylic acid obtained in a reaction catalysed by barley ash.

The most diagnostic difference between the two spectra is the appearance of a new absorption band at 1748 cm^{-1} in the spectrum of the synthesised product, corresponding to the ester carbonyl ($\text{C}=\text{O}$) stretch of acetylsalicylic acid and confirming esterification of the phenolic $-\text{OH}$ group of salicylic acid. In addition, the carboxylic acid $\text{C}=\text{O}$ stretching band shifts from 1662 cm^{-1} in salicylic acid—lowered due to intramolecular hydrogen bonding with the adjacent phenolic hydroxyl—to 1677 cm^{-1} in the product, consistent with loss of this hydrogen bond upon acetylation and in agreement with the literature values reported for acetylsalicylic acid ($1678\text{--}1690\text{ cm}^{-1}$) [34]. Together, these spectral changes, closely matching the literature values for the acetylsalicylic acid standard, provide strong FTIR evidence for the successful acetylation of salicylic acid via the ash-catalysed reaction.

4. Conclusions

This study demonstrates the possibility of using ash derived from food industry waste as a catalyst for organic synthesis and provides insight into the relationship between the mineral composition of the ash and its catalytic activity. The results of the preliminary study presented in this paper show that food industry waste ash can replace phosphoric acid as a catalyst for the synthesis of acetylsalicylic acid, although reaction yields obtained using ash were lower compared to H_3PO_4 . However, the results show that certain ashes, primarily barley ash, followed by cocoa bean ash, cocoa shell ash, and garlic husk ash, can act as a partially effective, renewable replacement for the mineral acid, achieving 67–89% of the catalytic efficiency of H_3PO_4 . Following this initial screening and the identification of the ashes with the greatest potential, future research will focus on investigating reaction conditions, temperature, reaction time, and catalyst amount in order to determine which conditions yield the highest reaction yield. In any case, it can be concluded that ash represents a promising basis for the further development of catalysts derived from the valorisation of agricultural and food industry waste, particularly considering additional advantages such as the simple separation of the solid catalyst by filtration and the absence of the corrosiveness characteristic of H_3PO_4 . Future work should also address the environmental footprint of the catalyst preparation process itself, including the energy consumption and gas/ CO_2 emissions associated with the high-temperature thermal treatment, in order to fully evaluate the sustainability of this approach in line with green chemistry principles. Beyond their catalytic application, the comprehensive mineral characterisation carried out in this study shows that food industry waste ash is rich in macroelements such as

potassium, calcium, phosphorus, and magnesium, highlighting its potential for further valorisation. However, several of the analysed ashes also contained potentially hazardous trace elements, including cadmium, lead, arsenic, chromium, and nickel, with peanut skin ash reaching a particularly high cadmium concentration. The heavy metal content of each ash should therefore be carefully evaluated against relevant regulatory limits before any application is considered.

Author Contributions: Conceptualization, D.G.-S. and V.B.; methodology, D.G.-S., Z.L., D.M. and V.B.; investigation, D.G.-S., Z.L., D.Z., K.M. and V.B.; writing—original draft preparation, D.G.-S., D.M. and V.B.; writing—review and editing, D.G.-S. and V.B.; supervision, D.G.-S.; project administration, V.B.; funding acquisition, V.B. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the European Union—NextGenerationEU, Institutional Research Project “Environmentally friendly methods for the synthesis and extraction of organic compounds with potential biological activity” (581-UNIOS-92).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available in this article.

Conflicts of Interest: The authors declare no conflicts of interest.

References

- Patil, R.C.; Patil, U.P.; Jagdale, A.A.; Shinde, S.K.; Patil, S.S. Ash of Pomegranate Peels (APP): A Bio-Waste Heterogeneous Catalyst for Sustainable Synthesis of α,α' -Bis(Substituted Benzyldiene)Cycloalkanones and 2-Arylidene-1-Tetralones. *Res. Chem. Intermed.* **2020**, *46*, 3527–3543. [\[CrossRef\]](#)
- Chia, P.W.; Chee, P.S.; Mazlan, N.W.; Yong, F.S.J.; Rozaini, M.Z.H.; Kan, S.-Y. Acetylation of Alcohols and Amines Catalyzed by Onion Peel Ash under a Base- and Solvent-Free Condition. *Songklanakarin J. Sci. Technol.* **2020**, *42*, 602607. [\[CrossRef\]](#)
- Chia, P.W.; Lim, B.S.; Yong, F.S.J.; Poh, S.-C.; Kan, S.-Y. An Efficient Synthesis of Bisenols in Water Extract of Waste Onion Peel Ash. *Environ. Chem. Lett.* **2018**, *16*, 1493–1499. [\[CrossRef\]](#)
- Wai, C.P. Water Extract of Onion Peel Ash: An Efficient Green Catalytic System for the Synthesis of Isoindoline-1,3-Dione Derivatives. *MJAS* **2019**, *23*, 23–30. [\[CrossRef\]](#)
- Naidu, B.R.; Lakshmi Devi, J.; Naik, B.S.S.; Venkateswarlu, K. Water Extract of Pomegranate Ash as Waste-Originated Biorenewable Catalyst for the Novel Synthesis of Chiral Tert-butanefulfinyl Aldimines in Water. *Mol. Catal.* **2021**, *511*, 111719. [\[CrossRef\]](#)
- Tamuli, K.J.; Sahoo, R.K.; Bordoloi, M. Biocatalytic Green Alternative to Existing Hazardous Reaction Media: Synthesis of Chalcone and Flavone Derivatives via the Claisen–Schmidt Reaction at Room Temperature. *New J. Chem.* **2020**, *44*, 20956–20965. [\[CrossRef\]](#)
- Boruah, P.R.; Ali, A.A.; Saikia, B.; Sarma, D. A Novel Green Protocol for Ligand Free Suzuki–Miyaura Cross-Coupling Reactions in WEB at Room Temperature. *Green. Chem.* **2015**, *17*, 1442–1445. [\[CrossRef\]](#)
- Rajkumari, K.; Das, D.; Pathak, G.; Rokhum, S.L. Waste-to-Useful: A Biowaste-Derived Heterogeneous Catalyst for a Green and Sustainable Henry Reaction. *New J. Chem.* **2019**, *43*, 2134–2140. [\[CrossRef\]](#)
- Pathak, G.; Rajkumari, K.; Rokhum, S.L. Wealth from Waste: *M. Acuminata* Peel Waste-Derived Magnetic Nanoparticles as a Solid Catalyst for the Henry Reaction. *Nanoscale Adv.* **2019**, *1*, 1013–1020. [\[CrossRef\]](#) [\[PubMed\]](#)
- Etim, A.O.; Elok-Eboka, A.C.; Musonge, P. Potential of Carica Papaya Peels as Effective Biocatalyst in the Optimized Parametric Transesterification of Used Vegetable Oil. *Environ. Eng. Res.* **2020**, *26*, 200299. [\[CrossRef\]](#)
- Basumatary, B.; Basumatary, S.; Das, B.; Nath, B.; Kalita, P. Waste Musa Paradisiaca Plant: An Efficient Heterogeneous Base Catalyst for Fast Production of Biodiesel. *J. Clean. Prod.* **2021**, *305*, 127089. [\[CrossRef\]](#)
- Basumatary, B.; Das, B.; Nath, B.; Basumatary, S. Synthesis and Characterization of Heterogeneous Catalyst from Sugarcane Bagasse: Production of Jatropha Seed Oil Methyl Esters. *Curr. Res. Green. Sustain. Chem.* **2021**, *4*, 100082. [\[CrossRef\]](#)
- Nath, B.; Das, B.; Kalita, P.; Basumatary, S. Waste to Value Addition: Utilization of Waste Brassica Nigra Plant Derived Novel Green Heterogeneous Base Catalyst for Effective Synthesis of Biodiesel. *J. Clean. Prod.* **2019**, *239*, 118112. [\[CrossRef\]](#)
- Eldiehy, K.S.H.; Gohain, M.; Daimary, N.; Borah, D.; Mandal, M.; Dekka, D. Radish (*Raphanus sativus* L.) Leaves: A Novel Source for a Highly Efficient Heterogeneous Base Catalyst for Biodiesel Production Using Waste Soybean Cooking Oil and Scenedesmus Obliquus Oil. *Renew. Energy* **2022**, *191*, 888–901. [\[CrossRef\]](#)

15. Falowo, O.A.; Oladipo, B.; Taiwo, A.E.; Olaiya, A.T.; Oyekola, O.O.; Betiku, E. Green Heterogeneous Base Catalyst from Ripe and Unripe Plantain Peels Mixture for the Transesterification of Waste Cooking Oil. *Chem. Eng. J. Adv.* **2022**, *10*, 100293. [\[CrossRef\]](#)
16. Chutia, G.P.; Chutia, S.; Kalita, P.; Phukan, K. Xanthium Strumarium Seed as a Potential Source of Heterogeneous Catalyst and Non-Edible Oil for Biodiesel Production. *SSRN J.* **2022**, *172*, 106773. [\[CrossRef\]](#)
17. Wood, J.M. Effects of Acidification on the Mobility of Metals and Metalloids: An Overview. *Environ. Health Perspect.* **1985**, *63*, 115–119. [\[CrossRef\]](#) [\[PubMed\]](#)
18. Shin, D.; Kim, Y.; Moon, H.S. Fate and Toxicity of Spilled Chemicals in Groundwater and Soil Environment I: Strong Acids. *Environ. Health Toxicol.* **2018**, *33*, e2018019. [\[CrossRef\]](#) [\[PubMed\]](#)
19. Rice, K.C.; Herman, J.S. Acidification of Earth: An Assessment across Mechanisms and Scales. *Appl. Geochem.* **2012**, *27*, 1–14. [\[CrossRef\]](#)
20. Withers, P.J.A.; Elser, J.J.; Hilton, J.; Ohtake, H.; Schipper, W.J.; Van Dijk, K.C. Greening the Global Phosphorus Cycle: How Green Chemistry Can Help Achieve Planetary P Sustainability. *Green. Chem.* **2015**, *17*, 2087–2099. [\[CrossRef\]](#)
21. Azam, H.M.; Alam, S.T.; Hasan, M.; Yameogo, D.D.S.; Kannan, A.D.; Rahman, A.; Kwon, M.J. Phosphorous in the Environment: Characteristics with Distribution and Effects, Removal Mechanisms, Treatment Technologies, and Factors Affecting Recovery as Minerals in Natural and Engineered Systems. *Environ. Sci. Pollut. Res.* **2019**, *26*, 20183–20207. [\[CrossRef\]](#) [\[PubMed\]](#)
22. Bennett, J.A.; Wilson, K.; Lee, A.F. Catalytic Applications of Waste Derived Materials. *J. Mater. Chem. A* **2016**, *4*, 3617–3637. [\[CrossRef\]](#)
23. Sarangi, P.K.; Singh, A.K.; Ganachari, S.V.; Pengadeth, D.; Mohanakrishna, G.; Aminabhavi, T.M. Biobased Heterogeneous Renewable Catalysts: Production Technologies, Innovations, Biodiesel Applications and Circular Bioeconomy. *Environ. Res.* **2024**, *261*, 119745. [\[CrossRef\]](#) [\[PubMed\]](#)
24. Hosseini Sarvari, M.; Sharghi, H. Zinc Oxide (ZnO) as a New, Highly Efficient, and Reusable Catalyst for Acylation of Alcohols, Phenols and Amines under Solvent Free Conditions. *Tetrahedron* **2005**, *61*, 10903–10907. [\[CrossRef\]](#)
25. American Dairy Products Institute (ADPI). Total Ash and Alkalinity of Ash. Method 008, Version 2.0, Effective 9 November 2023. Available online: <https://adpi.org/wp-content/uploads/2024/12/008-Total-Ash-and-Alkalinity-of-Ash-v2.0-Effective-09112023.pdf> (accessed on 6 September 2026).
26. Kingston, H.M.; Jassie, L.B. Microwave Energy for Acid Decomposition at Elevated Temperatures and Pressures Using Biological and Botanical Samples. *Anal. Chem.* **1986**, *58*, 2534–2541. [\[CrossRef\]](#) [\[PubMed\]](#)
27. Lončarić, Z.; Ivezić, V.; Kerovec, D.; Rebekić, A. Foliar Zinc-Selenium and Nitrogen Fertilization Affects Content of Zn, Fe, Se, P, and Cd in Wheat Grain. *Plants* **2021**, *10*, 1549. [\[CrossRef\]](#) [\[PubMed\]](#)
28. Pearson/Prentice Hall. *Vogel's Textbook of Practical Organic Chemistry*, 5th ed.; Furniss, B.S., Vogel, A.I., Eds.; Pearson/Prentice Hall: Harlow, UK, 2009; ISBN 978-0-582-46236-6.
29. John Wiley & Sons. *The Systematic Identification of Organic Compounds*; John Wiley & Sons: Hoboken, NJ, USA, 2004; ISBN 978-0-471-21503-5.
30. Muñoz-Arrieta, R.; Esquivel-Alvarado, D.; Alfaro-Viquez, E.; Alvarez-Valverde, V.; Krueger, C.G.; Reed, J.D. Nutritional and Bioactive Composition of Spanish, Valencia, and Virginia Type Peanut Skins. *J. Food Compos. Anal.* **2021**, *98*, 103816. [\[CrossRef\]](#)
31. Zhang, M.; Wang, D.; Wang, S.; Du, H.; Li, G.; Lan, R.; Li, Y. Resource Utilization of Peanut Shells: Nutritional Characteristics, Regulation of Antinutritional Factors, and Application Potential in Livestock and Poultry Production. *Food Sci. Nutr.* **2025**, *13*, e70994. [\[CrossRef\]](#) [\[PubMed\]](#)
32. Rojo-Poveda, O.; Barbosa-Pereira, L.; Zeppa, G.; Stévigny, C. Cocoa Bean Shell—A By-Product with Nutritional Properties and Biofunctional Potential. *Nutrients* **2020**, *12*, 1123. [\[CrossRef\]](#) [\[PubMed\]](#)
33. Gil-Ramírez, A.; Cañas, S.; Cobeta, I.M.; Rebollo-Hernanz, M.; Rodríguez-Rodríguez, P.; Benítez, V.; Arribas, S.M.; Martín-Cabrejas, M.A.; Aguilera, Y. Uncovering Cocoa Shell as a Safe Bioactive Food Ingredient: Nutritional and Toxicological Breakthroughs. *Future Foods* **2024**, *10*, 100461. [\[CrossRef\]](#)
34. Zhivkova, V. Determination of Nutritional and Mineral Composition Ofwasted Peels from Garlic, Onion and Potato. *CRPJFST* **2021**, *13*, 134. [\[CrossRef\]](#)

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.