Microwave-assisted Extraction of Phenolic Compounds from Mixed Food Waste

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Abstract

Microwave-assisted extraction (MAE) of natural antioxidants from food waste (FW) offers an economically appealing waste management strategy. Here, we characterize five single waste streams (apple, coffee, olive, tomato, and potato peel waste) and study the MAE of phenolic acids from select feedstocks and mixtures. This library of materials enables us to unravel the relationship of the FW composition and physical properties with dielectric properties, heating, and extractive yields. For example, the protein, ash, and moisture contents affect dielectric properties the most. Our study unveils the significance of moisture in free and bound states on FW dielectric properties, heating, and target acid yields. The microwaves primarily heat the solvent (dimethylformamide) due to its superior dielectric properties compared to FW (dry and moist, single and mixtures) at ≤ 0.05 solid-to-liquid ratio. High moisture content provides higher phenolic yields at lower temperatures and shorter times due to enhanced heat and mass transfer by the microwaves. We recommend extraction before drying waste streams. Further, our data indicates significant interactions between components of mixed FW that drive 2-3x higher yields than those predicted from a simple additive model from single component results. Our work provides new insights for developing versatile MAE strategies to treat complex mixed FW feedstocks.

Keywords: food waste, microwave, mixed waste, phenolic compounds, dielectric properties

Introduction

Food waste (FW) poses an immense challenge, with one-third of the globally produced food wasted annually.[1] Harvest losses comprise ~14% of the world's food ($400 billion), and consumers and retailers discard an additional 17%.[2] FW accounts for ~10% of the global greenhouse gas emissions due to inadequate management, including landfills, combustion, anaerobic digestion, composting, fermentation, and animal feed.[2] Thus, improved valorization strategies are required.

The extraction of natural antioxidants from FW is lucrative. The global antioxidant market, including synthetic antioxidants, such as butylated hydroxyanisole, butylated hydroxytoluene, propyl gallate, and tert-butyl hydroquinone, is valued at $6.5 billion, and the natural antioxidant market is $2.3 billion.[3,4] FW is abundant in phenolics and flavonoids, which exhibit high antioxidant activity and could be a valuable substitute for synthetic antioxidants that can be toxic.[5,6] Commercially valuable hydroxycinnamic acids, such as chlorogenic, caffeic, *p*-coumaric, and ferulic acid, are desirable.[7–10]

Conventional extraction techniques, such as soxhlet, maceration, percolation, and solvent extraction, use a large amount of solvent (> 100 mL) with a solid-to-liquid ratio of ~1:30, long time (> 1 h), and substantial energy and offer modest target acid yields.[11,12] In contrast, microwave-assisted extraction (MAE) offers at least 20% higher yield than conventional extraction[13,14] in less time (30-600 s), with less energy and solvent (5-10 mL) at a solid-to-liquid ratio of ~1:20.[13,15,16] MAE enhances the mass and heat transfer of the solvent (the extractant) into the solid, resulting in enhanced extraction.[17] Microwave irradiation heats the solvent that heats the solid, causing moisture evaporation and vapor pressure to increase in the cell, leading to eventual cell wall disruption and release of extractives into the solvent. This process is influenced by several physicochemical interactions and the choice of solvent, solid-to-solvent ratio, stirring rate, temperature, power, and irradiation time that can be tuned to maximize extraction efficiency.

Extraction of phenolics from FW and non-food biomass using MAE has predominantly considered pure single feedstocks, such as tomato waste,[18–20] potato peel waste,[21,22] banana peels,[23] and grape waste.[24,25] An experimental design is widely applied to investigate the influence of microwave parameters on the extraction of the same target phenolics from different single feedstocks.[26] Microwaves likely produce analogous extraction, considering the phenolics' chemical similarity.

This work provides insights into MAE from multiple single and mixed FW. First, we characterize the composition, physical, and dielectric properties of single FW feedstocks (apple, coffee, olive, tomato, and potato peel waste) to investigate their heating and extraction behavior vs. moisture content. The heating behavior and extraction using a library of multiple feedstocks rather than a single feedstock enables us to correlate the extraction performance to the waste composition. We find that moisture, extraction temperature, time, and their interplay affect the phenolics' yields, while the specific target acid yields are determined by the amount of extractives present and their interaction with other extracted components. Interestingly, we demonstrate interactions among different FW components that enhance phenolics' yields in mixed FW.

Materials and Methods

Materials

Caffeic acid (HPLC grade (purity ≥ 98%)) and N, N-dimethylformamide (HPLC grade (purity ≥ 99.9%)) were purchased from Sigma Aldrich. *p*-Coumaric acid (purity 98%), chlorogenic acid (purity 99.45%), and ferulic acid (purity 99.4%) were purchased from Fisher Scientific. ASTM-Type 1 grade deionized (DI) water (Milli-Q ® Direct) was used in all experiments. A local Starbucks store donated spent coffee bean waste. Apples, potatoes, and tomatoes were purchased from ACME. The FW feedstocks were rinsed with water and processed to mimic industrial waste. An even quantity (by mass) of russet, yellow, and Yukon gold potatoes was peeled using a manual peeler to collect potato peel waste. Equal quantities (by mass) of Honeycrisp, Pink Lady, Cosmic Crisp, Fuji, Granny Smith, and Royal Gala apples were used to prepare the apple pomace, while red vine cluster varieties were employed for tomato waste. The tomatoes and apples' skin, seeds, stem, and core were isolated to create tomato and apple pomace. The FW was dried in an oven at 60 °C for 12 h to reduce the moisture content below 10 wt% based on the NREL LAP NREL/TP-510-42620 protocol.[27] The Sartorius moisture content analyzer was used to determine the moisture content. The dried FW was grounded using a Thomas Wiley® Mini Cutting Mills to a < 0.5 mm powder size. Five FW mixtures were prepared with different ratios of apple, potato peel, and coffee waste.

Characterization

Compositional Analysis

The ash, extractives, and carbohydrate and lignin content were determined as per NREL LAP NREL/TP-510-42622,[28] NREL/TP-510-42619,[29] and NREL/TP-510-42618 protocol,[30] respectively. In brief, 0.5 g of oven-dried FW was kept in a muffler furnace in a crucible at 575 °C for 3 h. The weight of the residual material in the crucible was measured to determine the ash content. Soxhlet extraction from 3 g of oven-dried FW and 300 mL of ethanol was conducted for 12 h to determine the extractive content. For carbohydrate and lignin content determination, 0.3 g of oven-dried FW was hydrolyzed with 3 mL of 72% sulfuric acid and stirred at room temperature for 1 h. The solution was diluted with 84 mL of water, stirred for another 1 h at 121 °C, filtered, and the residue was oven-dried at 105 °C overnight. The dried residue was weighed and kept in a muffle furnace at 575 °C for 24 h to determine the acid-insoluble ash. The filtrate was cooled and analyzed for acid-soluble lignin via UV spectroscopy. High-Performance Liquid Chromatography (HPLC) used a Waters e2695 separations module coupled to a Waters 2998 photodiode array detector to determine the carbohydrates in the filtrate after neutralizing 20 mL of the solution with $CaCO_3$. The nitrogen content was measured using a CNHS Elemental Analyzer and multiplied by 6.25 to obtain the protein content, using the standard assumption that nitrogen contributes ~16% of the mass of proteins in food. The fat was measured from the mass difference.

Physical Properties

1 g of FW was densely packed in a 10 mL graduated cylinder to determine the bulk density. The porosity of the FW was determined by nitrogen gas sorption at −196 °C using the Micromeritics ASAP 2020 Brunauer Emmett Teller (BET) Analyzer.

Dielectric Property Measurement

The dielectric constant and loss factor were measured at 25 °C and 2.45 GHz using the Microwave Dielectric Measuring Kit developed by the institute ITACA.[31] The instrument can determine the

dielectric properties of liquid, granular, and powdered materials if their dielectric constant is < 100 and the loss factor lies between 0.01 to 15. The vial was filled with the material (DMF, DMF-water mixtures, or FW powder), ensuring no voids, and rotated during measurement to minimize the effect of density, resulting in dielectric properties with < 1% relative variability. Data was collected for duplicate samples.

Moisture Content Variation

1 g of oven-dried FW was placed in a beaker and mixed with 5 mL of DI water. The mixture was allowed to stand for 5 min at room temperature and filtered. The residue was collected and oven-dried at 60 °C for 15 min to up to 2 h to obtain the desired moisture content. The Sartorius moisture content analyzer was used to determine the moisture content.

Determination of Free Water in Moist FW

A highly moist coffee waste (60 wt%) and potato peel waste (70 wt%) (as utilized for extraction; see below) were prepared as described above. The moist FW was stirred in excess of DMF for 15 min at room temperature considering that only free water would rapidly partition to the extractant upon contact. TGA was performed for high moisture FW before and after the stirring using a TA instruments Q600 SDT thermogravimetric analyzer for a temperature program of 30 to 350 °C at a heating rate of 10 °C min^{-1} under nitrogen (50 mL min^{-1}) to determine the free water content.[32]

Microwave Heating of FW-Solvent Systems

In single and mixed FW-liquid systems, the accumulation of solids at the bottom of the vial and lack of stirring result in inaccurate dielectric property measurements. Thus, we investigated the heating profiles of various FW systems in DMF, as its high polarity and superior hydrogen bonding acceptor character make it an outstanding extractant.[33] Measurements were conducted at < 10 vol% solid fractions with a particle size of < 0.5 mm at 600 rpm stirring speed to ensure uniform mixing and eliminate hot spot formation.[34]

In microwave heating, we need to consider a) the total mixture volume due to the volumetric nature of microwave heating, b) the extractant (DMF) amount, and c) the composition of the water-DMF mixtures to ensure uniformity in dielectric properties and extraction. Thus, we evaluated the mixture dielectric properties at a constant dry solid-to-extractant ratio (case 1), wet solid-to-extractant (case 2), and dry solid-to-total liquid (case 3), assuming that all moisture is transferred to the extractant (see Supplementary Table 1). The dielectric properties vary in cases 1 and 3 due to changes in total volume and mixture composition but remain relatively constant for case 2 (see Supplementary Figure 1 and Supplementary Table 2). Thus, the heating profiles of high moisture FW in DMF were evaluated at a constant wet solid-to-extractant ratio (case 2), to ensure minimal variations in total extractant volume, mixture composition, and extraction efficiency (Supplementary Tables 3 and 4).

Saturation Moisture Content

The saturation moisture content was determined using a modified method based on the Scanidivian pulp, paper, and board testing committee (SCAN-C 62:00, 2000), as applied for biomass.[35–37] 1 g of oven-dried FW was placed in a beaker and mixed with an excess of DI water (~50 mL). Typically, the mixture is centrifuged for at least 15 min, but centrifugation was not conducted as water is an extractant, which could introduce errors. Thus, the mixture was allowed to stand for 24

h, filtered, and the wet residue was weighed. The residue was then oven-dried at 60 °C overnight and weighed again. The procedure was repeated for duplicate samples. The saturation moisture content was determined using Eq. 1

$$Saturation\ moisture\ content\ (wt\%) = \frac{(mass\ of\ wet\ sample - mass\ of\ dry\ sample) \times 100\%}{mass\ of\ dry\ sample} \quad (1)$$

Extracted Target Acids Identification and Quantification

We employed HPLC to quantify the concentration of standard acids using a Waters e2695 separations module coupled to a Waters 2414 refractive index meter and a Waters 2998 photodiode array detector. A column of Agilent Zorbax SB-C18, 250 mm, was utilized at 50 °C with a mobile phase of solvent A (pure methanol) and solvent B (1% formic acid in water), flowing at 0.8 mL/min. A gradient method was established to transition from 0% B to 95% B in 35 min. The concentration was computed by measuring the absorbance peak area between 320 to 380 nm at the corresponding retention time based on pure compound calibrations.

The acids extracted from FW were identified and quantified for their concentration using Ultra performance liquid chromatography-mass spectrometry (UPLC-MS) on a Q-orbitrap mass spectrometer. A Waters Acquity UPLC BEH C18 column (1.7 µm 2.1 X 30 mm) was utilized with solvent A (water with 0.1% formic acid) and solvent B (acetonitrile with 0.1% formic acid) as the mobile phase, which flowed at 0.5 mL/min. A gradient method was established from 0% B to attain 95% B in 5 min.

Degradation Kinetics

Batch experiments were conducted. The time to attain a temperature of 90 °C to 145 °C was ~10 min. At temperatures of > 120 °C, up to ~15% target phenolics' degradation is observed in less than 60 min (see Supplementary Table 5 for decomposition data); ~1-5% degradation occurs in 2-6 h at 90 °C – 120 °C.[38,39] Consequently, experiments were conducted in the temperature range of 90 °C – 120 °C to ensure < 15% phenolics' degradation and a reaction time not strongly affected by the ramp-up time.

Standard solutions of caffeic, ferulic, *p*-coumaric, and chlorogenic acids were prepared in DMF at different concentrations (0.03 g/mL to 0.1 g/mL). The solutions were stirred for 1 h to 8 h at different temperatures. The concentrations were measured using HPLC. The initial degradation rates were calculated by taking the slope of the acid concentration over time for the first four time points before achieving 15% degradation (Supplementary Figures 2-5). The reaction order was calculated from the slope of the natural logarithm of the rate change over at least three different concentrations at a constant temperature. The procedure was repeated at a different temperature to confirm the order for caffeic, *p*-coumaric, and ferulic acid. The literature reports that the reaction order of chlorogenic acid thermal degradation is 1.[38,40] The rate constants were determined at three temperatures to construct Arrhenius plots.

Dissolution Kinetics

The solubility measurements were conducted at 25 °C per the EPA-recommended shake flask method.[41] A recent study determined that the solubility limit of target acids in DMF is > 0.1 g/mL.[33] Thus, excess solute (3 times over the screened solubility limit) was added to 5 mL of DMF in three separate vials. The vials were equilibrated at 30 °C for 24 h at 600 rpm, followed

by a 24 h equilibration without stirring at 25 °C. Equilibration at 30 °C ensures excess solids at 25 °C for accurate solubility measurement. The vials were centrifuged for 10 min at 10,000 rpm and 25 °C. The solution was filtered and quantified using HPLC. For estimation of target phenolics dissolution rates in DMF at 25 °C, excess solute was added to 5 mL of DMF and stirred at 600 rpm for 10, 30, 60, and 90 min (see data in Supplementary Figure 6). The solution was filtered and quantified using HPLC.

Determining the solubility and dissolution kinetics of target phenolics at elevated temperatures poses a challenge owing to their thermal degradation. Thus, the ADF COSMO-RS implementation in the ADF2020.101 modeling suite was employed to predict the solubility at higher temperatures. The target phenolics were optimized in vacuum using density functional theory (DFT) and put in a perfect conductor for solubility calculation. The geometry optimization was performed using the TZP small-core basis set, the Becke-Perdew (GGA: BP86) functional, the scalar ZORA, and the numerical integration quality of 4 with an energy convergence criterion of 10^{-5} Ha. COSMO-RS generates σ-profiles that capture the screening charge density distribution of molecule surfaces interacting with each other and the environment. These profiles enable the estimation of the chemical potential and solubility of components.

The dissolution kinetics was modeled using the Noyes-Whitney model (Eq. 2) with the following assumptions[42]: a) the solute particles are spherical, b) the particles dissolve uniformly, c) the thickness of the diffusion boundary layer is constant, and d) the solubility and thickness of the diffusion boundary layer are independent of the particle size.

$$\frac{dc}{dt} = k_1(c_s - c) \tag{2}$$

where c is the concentration of the solute in the solvent at time t, c_s is the solubility, and k_1 is (Eq. 3)

$$k_1 = \frac{AD}{Vd} \tag{3}$$

where A is the surface area of the solute particle, D is the diffusion coefficient, d is the thickness of the boundary layer, and V is the volume of the solution. D accounts for the temperature dependence of k_1 using an extension of Stokes' law (Eq. 4).[43]

$$D = \left(\frac{k_B T}{4\eta\pi}\right)\left(\frac{4\pi}{3\nu}\right)^{\frac{1}{3}} \tag{4}$$

where k_B is the Boltzmann constant, T is the absolute temperature, η is the solvent viscosity, and ν is molar volume of the solute (see Supplementary Table 6 for molar volumes; used a factor of 0.6023×10^{-24} to convert to cm^3 per molecule).[43] The following assumptions guide the modeling of D: a) solute and solvent are hard spheres with a friction factor of 1, b) the viscosity is that of the pure solvent, and c) the molar volume of the solute is an additive property of its constituent atoms and functional groups. The Andrade equation (Eq. 5) was applied to extrapolate the viscosity of DMF at higher temperatures (see Supplementary Figure 7 for data).

$$\eta = Ae^{\frac{B}{T}} \quad (5)$$

where T is the temperature in Kelvin and A and B are solvent-specific constants equal to 0.027 and 1017.990, respectively.

The combined degradation-dissolution model (Eq. 6) was solved numerically at different temperatures to identify an upper limit of extraction temperature.

$$\frac{dc}{dt} = k_1(c_s - c) - k_d c^n \quad (6)$$

where k_d is the degradation rate constant and n is the degradation reaction order.

Microwave Assisted Extraction

An Anton Paar microwave reactor, Monowave 450 with temperature control, was employed for batch extractions. 0.25 g of FW and 5 mL of solvent were taken in a sealed 10 mL borosilicate glass vial. The extraction was conducted at a microwave frequency of 2450 MHz, a specified temperature, power, and time, with a stirring speed of 600 rpm. A fiber-optic ruby thermometer was utilized for internal temperature control. The extracted solution was filtered using 0.45 μm syringe filters. We heated 5 mL of solvent alone and a mixture of solvent with 0.25 g FW at varying power levels to determine the power requirement for achieving the temperature set point. Various single FW and mixtures in DMF, with a constant wet solid-to-liquid ratio of 1:20, were heated to the temperature set point to determine their respective heating rates.

Total Phenolic Content

The total phenolic content in the sample was evaluated using the procedure outlined by Ismail et al.[44] The Folin-Ciocalteau (FC) reagent was diluted by a factor of 10 using DI water, and a 6 wt% sodium bicarbonate solution was prepared. Subsequently, 0.75 mL of FC reagent was transferred to a 20 mL scintillation vial, and 100 μL of the extract was added. The mixture was left undisturbed for 5 min, 0.75 mL of 6 wt% sodium bicarbonate solution was added, and the mixture was allowed to stand for 90 min after vortexing. Gallic acid standards were used to prepare the calibration curve to obtain the gallic acid equivalent (GAE). The results are reported as milligrams (mg) of GAE per g of dried FW.

Experimental Design

A two-level full factorial design of experiments with three replicates was employed to evaluate the main and interaction effects on the extraction yields from apple, coffee, and potato peel waste. The microwave power, extraction time, and temperature were varied to investigate their influence on the target acid yields. The Minitab software (version 21.4.0) was utilized for the factorial design (24 experiments for each feedstock).

HSPiP Computations

We utilized the HSPiP software (version 5.3.05) to determine the distance of DMF-water mixtures from chlorogenic acid (model compound). The HSPiP distance (Ra) between two compounds

serves as a measure of their similarity, calculated as $Ra^2 = 4(\delta D_1-\delta D_2)^2 + (\delta P_1-\delta P_2)^2 + (\delta H_1-\delta H_2)^2$, where δD, δP, and δH represent the dispersion, polar, and hydrogen bonding energies, respectively.

Results and Discussion

Composition, Physical, and Dielectric Properties of FW and Impact on Heating

The dielectric properties, dielectric constant (ε'), dielectric loss factor (ε"), and loss tangent (tanδ), are influenced by composition (carbohydrates, fats, protein, lignin, extractives, ash, and moisture), physical properties (particle size, porosity, density), temperature, and microwave frequency. The composition and physical properties of apple, coffee, olive, potato peel, and tomato waste are shown in Table 1. FW exhibits notable compositional differences: potato peel and tomato waste are protein-rich with minimal lignin. Coffee is rich in protein and lignin but has low fat and ash content. Olive pomace is characterized by high lignin but low carbohydrate and fat content, whereas apple pomace has lower lignin and ash but the highest extractive content. In contrast, the bulk density shows little variation among feedstocks, except tomato waste, due to consistent feedstock pre-treatment. Tomato waste's low bulk density implies the presence of air-filled voids. The microstructure of food transforms during drying and hydration.[45,46] These changes are influenced by intrinsic factors, such as composition and initial structure, and extrinsic factors, including air circulation, temperature, pressure, relative humidity, and gas atmosphere.

Supplementary Figure 8 shows the influence of pore size, bulk density, and saturation moisture content on dielectric properties. Figure 1a shows ε' and ε" and Supplementary Figure 9 shows tanδ of all feedstocks over a wide range of moisture. All feedstocks have a similar low $\varepsilon' \leq 2.3$, $\varepsilon'' \leq 0.1$ (~1% variability in repeated measurements for each feedstock), and $\tan\delta \leq 0.1$ at moisture content < 20 wt% (Figure 1b), despite the significant variation in composition. Due to the low tanδ values and the good absorbing properties of DMF, microwaves primarily heat the solvent. In contrast, ε', ε", and tanδ increase rapidly at higher moistures (> 20 wt%) (Figure 1a). The water in food can be either free, present within capillaries, or adsorbed on the surface of dry material. The dielectric properties are primarily governed by free water as the relaxation of bound water occurs below 2450 MHz, and the organic matter is unresponsive to microwave irradiation.[47,48] Consequently, dry FW does not interact with microwaves, while water interacting with other constituents influences high moisture systems.[49] The hydration and drying (see methods) do not significantly change the pore size of the feedstocks to alter their saturation moisture content and dielectric properties (see Supplementary Figure 8). Importantly, protein and ash negatively influence ε' and ε" (Figure 1c-e); ash positively affects tanδ (Supplementary Figure 9). Other constituents do not significantly impact the dielectric properties at any moisture, potentially due to the limited variation in the data set employed.

The binding of free water by protein is responsible for the decline in ε', ε" and tanδ with increasing protein fraction (Figure 1c, Supplementary Figure 9).[50–53] Ash in food consists of minerals and inorganic salts that bind water and restrict its reorientation under an electromagnetic field, decreasing ε' (Figure 1d and e).[54,55] The added salts break water's hydrogen bonds and introduce additional reorientation sites for water molecules, decreasing the relaxation time and increasing ε" and tanδ.[54] However, here we observe a decline in ε", potentially due to the association of salts with other FW components, such as proteins and carbohydrates.[56] Coffee waste is an outlier (with low ash but low ε' and ε") (Figure 1d), possibly due to the incomplete dissociation of salts caused by the ionic saturation in water. An increase in temperature enhances

the mobility of water molecules at all moisture contents and decreases the viscosity, penetration depth, and relaxation time.[55,57] Further, the contribution of dipole rotation to ε" diminishes at higher temperatures, while the increase in ionic conductivity increases ε".[58,59] High temperatures can cause starch gelatinization and protein denaturation that release bound water and increase the ionic conductivity of the bound salts.[60] Thus, we anticipate enhanced dielectric activity at extraction temperatures.

Table 1: Weight percent distribution of major constituents of FW feedstocks on a wet weight basis (see methods in characterization section for quantification).

Feedstock	Moisture	Protein	Lignin	Carbohydrates	Ash	Fats	Extractives	Bulk Density (g/mL)	Pore size (nm)	Saturation Moisture (wt%)
Apple pomace	12.2	3.1	14.5	12.7	2.9	16.7	38.00	0.56	39.6	94.9 ± 0.1
Coffee waste	6.4	13.2	41.0	9.3	2.2	9.7	18.20	0.50	103.2	74.1 ± 0.8
Olive pomace	8.7	4.2	33.8	6.2	6.8	10.8	29.6	0.67	71.3	66.4 ± 6.8
Potato peel waste	9.0	14.2	6.1	14.2	10.9	41.5	4.1	0.72	244.4	84.0 ± 4.4
Tomato Waste	15.6	14.0	11.1	8.9	21.1	0.7	28.6	0.20	9.2	94.4 ± 0.1

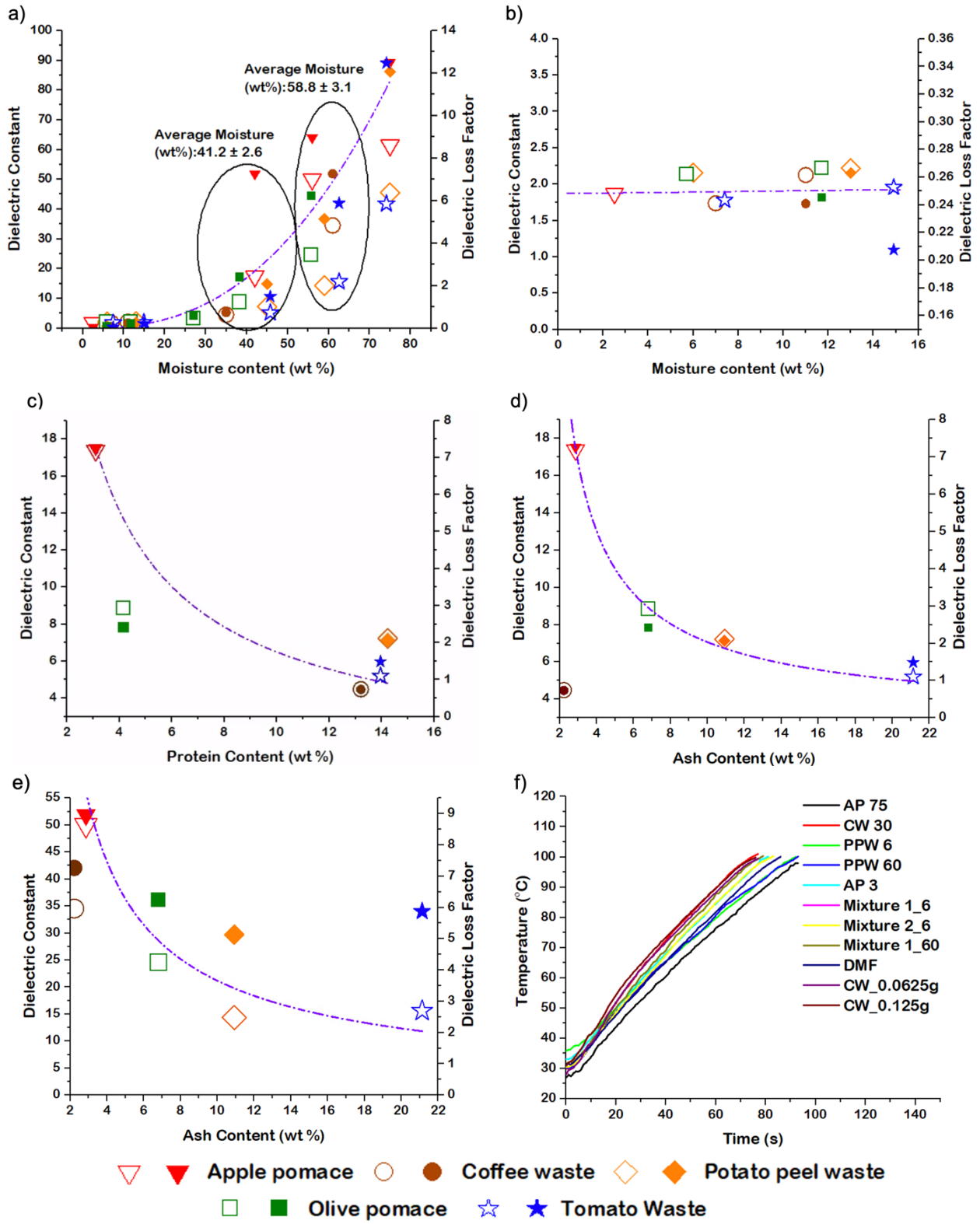


Figure 1: Dielectric constant (ε') and loss factor (ε") vs. a) moisture (full scale), b) moisture (wt% < 20; zoomed in of panel a), c) protein at 41.2 ± 4.6 wt% moisture, d) ash at 41.2 ± 4.6 wt% moisture, and e) ash at 58.8 ± 3.1 wt% moisture, for select feedstocks. The open and solid symbols represent experimental ε' and ε" data points, respectively, and the dash-dotted lines are for visual guidance. The ellipses in panel a correspond to similar wt% moisture of all feedstocks. f) Temperature vs. time for heating different feedstocks of varying moisture in DMF at 50 W and 1:20 wet solid-to-liquid ratio to reach 100 ℃. In the legend, AP 75: 0.25 g of

apple pomace with 75 wt% moisture; CW 30: 0.25 g of coffee waste with 30 wt% moisture; PPW 6: 0.25 g of potato peel waste with 6 wt% moisture; PPW 60: 0.25 g of potato peel waste with 60 wt% moisture; AP 3: 0.25 g of apple pomace with 3 wt% moisture; Mixture 1_6: 0.25 g of Mixture 1 with 6 wt% moisture; Mixture 2_6: 0.25 g of Mixture 2 with 6 wt% moisture; Mixture 1_60: 0.25 g of Mixture 1 with 60 wt% moisture; CW_0.0625g: 0.0625 g of coffee waste with 6 wt% moisture; CW_0.125g: 0.125 g of coffee waste with 6 wt% moisture. Mixture 1 contains equal proportions of apple, potato peel, and coffee waste. Mixture 2 comprises 45% potato peel, 45% coffee waste, and 10% apple pomace.

We compared microwave heating profiles of FW-solvent systems.[32] Water from high moisture FW can partition to the solvent. TGA of highly moist FW (see methods) revealed that FW contains ~30 wt% free water (see Supplementary Figure 10 for feedstock variation) that could be transferred to DMF. Thus, we estimated the solubility of chlorogenic acid (a model compound) in different DMF-water mixtures to ensure consistent extraction (see methods), assuming that all moisture from FW is transferred to DMF, using the HSPiP method. The predicted distance of chlorogenic acid from different DMF-water mixtures lies in the uncertainty range of ±1 $(MPa)^{0.5}$, indicating that water does not affect, within error, the solvent's phenolic solubility and extraction efficiency (see Supplementary Tables 3 and 4).[61] Further, given the water partitioning and its influence on microwave heating, we measured the dielectric properties of DMF-water mixtures (Supplementary Figure 1) and the heating profiles of moist FW-DMF (Figure 1f).[59] The dielectric properties of DMF (ε' and ε" are measured to be 35.98 and 4.56, respectively) and DMF-water mixtures remain relatively constant at a constant wet solid-to-liquid ratio (with < 10 vol% solid fractions) (see methods). Figure 1f shows that the mixtures reach the target temperature in ~84 ± 8 s, indicating comparable heating. Consequently, at a constant wet solid-to-liquid ratio and a high stirring rate, the FW dielectric response and the water fraction in DMF do not influence the heating rate significantly (Figure 1f).

An important finding from creating this library of FW streams, rather than a couple of them, is the ability to identify the effect of composition and physical properties on heating. Specifically, the protein and ash content are influential composition descriptors, and the moisture content is critical. For optimal extraction, one should avoid drying the food; rather, one should perform extraction first, if possible, followed by drying for preservation or direct processing of the FW.

Extraction Conditions

The solvent and operating conditions, such as the temperature, time, and power, determine the efficacy of MAE. The energy source, waveguide design, and cavity affect heating and extraction efficiency.[34,62,63] Further, the phenolic content in feedstocks and, thus, the extraction yields vary. Consequently, we exploited the parameter space to determine suitable extraction conditions. We set a minimum temperature of 50 °C, in line with conventional industrial extractions, to prevent low extraction yields and long processing times.[64–68] The solubility and yield of target phenolics increase with increasing temperature up to a point due to degradation. We estimate a maximum extraction temperature below which dissolution is faster than degradation. To achieve this, first, we estimated the degradation kinetics of pure phenolics in DMF (Supplementary Table 7). The Arrhenius parameters and reaction orders are given in Table 2. Supplementary Figure 11 shows that ferulic acid has the highest degradation rate up to 100 °C, followed by caffeic acid between 100 °C to 120 °C, and *p*-coumaric acid at temperatures > 120 °C. Temperatures of > 120°C lead to fast degradation.[69,70] Solubility kinetics of pure compounds was estimated according to Eqs. 2-5. Supplementary Table 8 summarizes the degradation and dissolution rate constants.

The combined dissolution/degradation model (Eq. 6) was solved numerically to determine the yield of ferulic acid over time, as a test case, at different temperatures. This model is approximate. For example, dissolution from real FW is expected to be slower due to diffusion through the solid. Furthermore, interactions among FW ingredients are not accounted for. Yet, it provides parameter estimates. Figure 2a shows that ferulic acid attains the highest concentration most rapidly at 100 °C without significant degradation. It exhibits slow dissolution and fast degradation at lower and higher temperatures, respectively. Caffeic and *p*-coumaric acids likely provide even lower yields at temperatures > 100 °C given their higher thermal sensitivity and comparable dissolution rates to ferulic acid (see Supplementary Information Section C and Supplementary Table 9). Thus, an upper limit of 100 °C was set. Further, a power of at least 10 W was needed to heat DMF to 100 °C and 50 W for rapid heating (~70 s) (Figure 2b).

The minimum extraction time was set to 2 min by factoring in the ramp-up and cool-down periods, with at least one-third of the total time (~6 min) allocated for extraction. We experimentally determined the time required for target acids extracted from coffee, apple, and potato peel waste to achieve their maximum yields at 100 °C and 50 W (Figure 2c – f). Chlorogenic and ferulic acid extracted from coffee waste achieved maximum yields in 20 min. Chlorogenic, caffeic, and ferulic acids extracted from potato peel attained maximum yields in 2 h (at least 200% higher yield in just 120 s than conventional extraction with a time of ~4 h),[33] while the yield of phenolics extracted from apple pomace did not significantly change over time. With lower- and upper- temperature limits, approximate powers, and processing times estimated, a factorial design was set for the three feedstocks to unravel the correlations between temperature, power, and time (Supplementary Table 10). Expectedly, a higher power leads to higher temperatures and shorter processing times, but extended degradation should be avoided.

Table 2: Arrhenius parameters of phenolics degradation from pure compound studies.

Compound	Reaction Order	Natural log of Pre-exponential Factor (ln A) ($A/min^{-reaction\ order}$)	Activation Energy (kJ/mol)	R^2
Chlorogenic acid	1	10.1	55.3	0.99
Caffeic acid	1	68.7	229.7	0.97
p-Coumaric acid	1	108.7	361.2	0.97
Ferulic acid	2.4	21.8	82.6	0.99

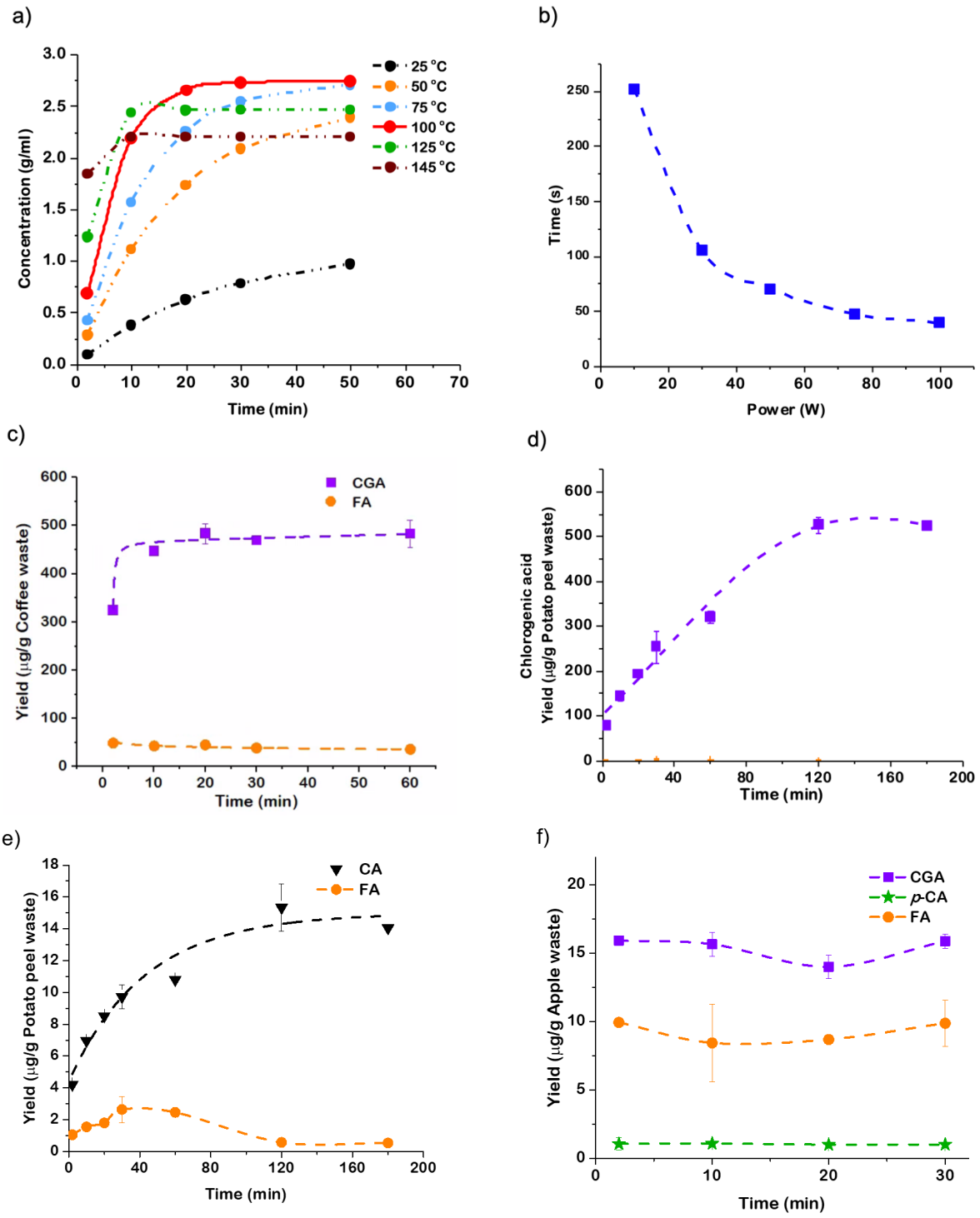


Figure 2: a) Predicted ferulic acid concentration in DMF using the dissolution-degradation model (initial concentration in solution at each temperature of c = 0 g/mL). b) Experimental time to reach 100 °C at different microwave powers. c) Chlorogenic and ferulic acid yields from coffee waste (moisture < 20 wt%) vs. time at 100 °C and 50 W. d) Chlorogenic acid yield from potato peel (moisture < 20 wt%) vs. time at 100 °C and 50 W. e) Caffeic and ferulic acid yields from potato peel (moisture < 20 wt%) vs. time at 100 °C and 50 W. f) Chlorogenic, p-coumaric and ferulic acid yields from apple pomace (moisture < 20 wt%) vs. time at 100 °C and 50 W. CGA, FA, CA, and p-CA are chlorogenic acid, ferulic acid, caffeic acid, and p-coumaric acid. In panels b-f, symbols represent experimental data points, and the dashed lines are for visual guidance.

Extraction from Dry Single Feedstocks

We first investigated the influence of temperature, time, and power on extraction from dry single feedstocks with moisture < 20 wt%, given their similar dielectric properties. Apple pomace, potato peel, and coffee waste were analyzed, as other samples contained phenolic amounts below the detection limit. The total phenolic content was determined via the conventional gallic acid equivalence (GAE) approach, employing the Folin-Ciocalteau reagent, which is not standardized in DMF due to its hydrogen bonding with the phenolics and interaction with the reagent.[33,71] Thus, the extracts were re-dissolved in water after vacuum distillation of DMF for total phenolic content estimation. However, the accuracy is compromised due to the removal of DMF at high temperatures (~90 °C), causing thermal degradation of phenolics and resulting in low measured total phenolic content (~2.14 mg GAE/g, 7.50 mg GAE/g, and 0.15 mg GAE/g of dry coffee, apple, and potato peel waste, respectively), with minimal variation (see Supplementary Figure 12). These target acid yields are comparable to the literature values. [21,72–75]

The acid yields from apple pomace were not statistically different (see Supplementary Figure 13) in the investigated parameter space, potentially due to the low levels of free phenolics present (< 10 μg/g apple pomace). Supplementary Figure 14 shows the significant factors and their influence on acid yields. As expected, increased temperature significantly enhanced the target acid yields from coffee and potato peel waste. *p*-coumaric acid yields were ~10 μg/g coffee waste and decreased by ~15% at higher temperatures. Given that *p*-coumaric acid does not degrade significantly at 100 °C (Table 2), the release of lipids and starch due to cell wall disruption at high temperatures and their supramolecular complexation with *p*-coumaric acid possibly cause the observed decline.[76–78] Further, longer times improved the chlorogenic acid yields from potato peel. In contrast, higher degradation and overestimation of the high-temperature bound (100 °C) in the factorial design of experiments (see above) possibly caused a decline in ferulic acid yields at higher temperatures and longer times. Finally, the power did not affect the target acid yields due to its narrow range and the correlation of temperature and power.[21,79]

In conclusion, one should focus on waste streams with target acids in concentration > 10 μg/g FW in free and bound states, moderately high temperatures and longer times for thermally stable acids and lower temperatures and longer times or high temperatures and shorter times for thermally labile acids.

Extraction from High Moisture Single FW Feedstocks

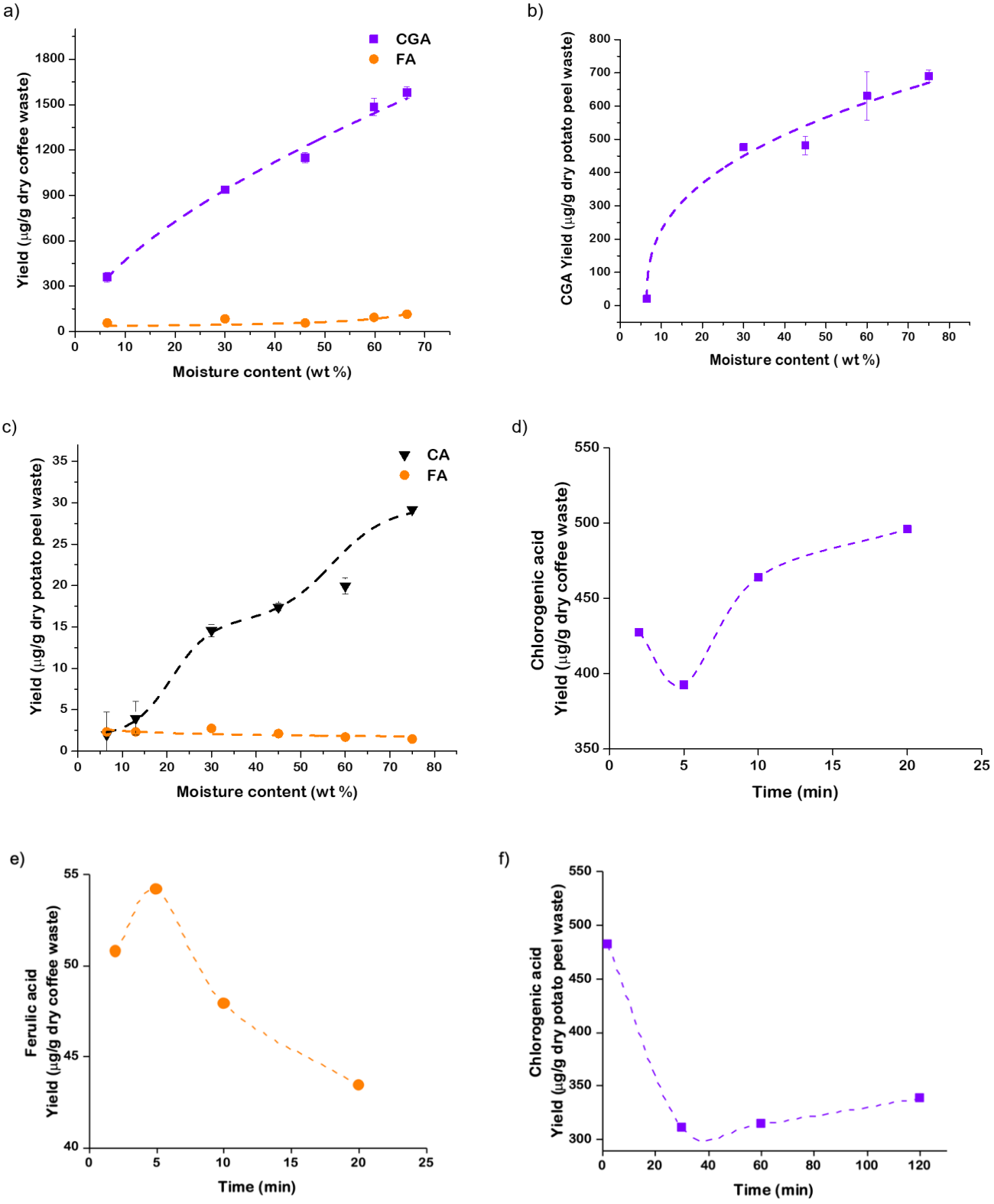
We investigated the effect of moisture content, time, and temperature on the target phenolics' extraction yields from potato peel and coffee waste, as other feedstocks do not contain substantial amounts. Notably, we observed a steep yield increase with increasing moisture except for ferulic acid from potato peel waste, which did not change significantly (Figure 3a-c). Coffee waste exhibited a 340% increase in chlorogenic acid and a 103% increase in ferulic acid at 66 wt% moisture (Figure 3a). Similarly, the chlorogenic and caffeic acid yields from potato peel waste increased by 3,310% and 492%, respectively, at 75 wt% moisture compared to dry feedstocks (Figure 3b and c). In conventional extraction from coffee waste at 100 °C and 1:20 waste-to-liquid ratio for 2 h (see Supplementary Figure 15 for method and extraction yields), the chlorogenic and ferulic acid yields increased modestly by 35% and 62%, respectively, at 70 wt% moisture compared to dry waste (see Supplementary Table 11 for a comparison of yields from MAE and

conventional extraction at different moistures). The phenolics are secondary metabolites coexisting with moisture in the cell vacuoles.[80] The moisture is heated upon exposure to microwaves, leading to vaporization and increased pressure within the vacuole. Consequently, the porous cell wall ruptures, releasing phenolics from the solid. Upon release, the extraction is limited by the diffusion from the solid to the extractant.[81] Microwaves heat the moist solids to a higher temperature than the solvent, establishing a solute, solvent, and water chemical potential gradient across the solid-liquid interface.[17,82] This promotes solvent and water transport, enhancing mass transfer. The uneven moisture distribution within the solid can form cold and hot spots, thereby impacting the reproducibility of yields on a large scale. Effective pretreatment strategies, such as maintaining a uniform particle size (< 0.5 mm) and moisture content, can minimize such heterogeneities.[83,84]

Next, we evaluated the impact of temperature and time on extraction (Figure 3d-g). For dry feedstocks, an increase in temperature increases target acid yields but long times reduce the phenolic acid yields. High moisture increases acid yields at shorter times due to cell wall rupture and accelerated heat and mass transfer, as discussed above. At longer times, phenolic acids can interact with FW-extracted components, such as starch, protein, and other phenolics, or undergo enzymatic degradation, reducing extraction yields.[33,85–88] Clearly, conducting extractions from high-moisture FW via relatively high-power MWs reduces processing time and energy consumption and increases yields. The effect of temperature (in the 50-100 ºC) is not as profound; instead, the feedstock dictates the yield (Figure 3h).

Finally, the form of (free or bound) acids affects the target acid yields from moist FW. For instance, potato peel and coffee waste yield comparable amounts of chlorogenic acid at low (< 20 wt%) moisture (Figure 2c and d) due to containing similar amounts of free phenolics. At 41.2 ± 4.6 wt% moisture, potato peel yields only 42% of the chlorogenic acid of coffee waste (Figure 3a and b). Given the similar pretreatment, it is unlikely that this difference is due to uneven moisture distribution. Instead, coffee waste exhibits higher amounts of bound phenolics than potato peel.[89–91] Moisture facilitates their release and transport, increasing yield. Apple pomace, on the other hand, contains low amounts of phenolic acids, giving no enhancement with increasing moisture (Figure 2f and Supplementary Figure 16 for chlorogenic acid yields at high moisture).

In summary, extraction efficiency is primarily influenced by the target free and bound acid amounts and the moisture content. Other components are irrelevant.


a)
CGA
FA
Yield (μg/g dry coffee waste)
Moisture content (wt %)
b)
CGA Yield (μg/g dry potato peel waste)
Moisture content (wt %)
c)
CA
FA
Yield (μg/g dry potato peel waste)
Moisture content (wt %)
d)
Chlorogenic acid
Yield (μg/g dry coffee waste)
Time (min)
e)
Ferulic acid
Yield (μg/g dry coffee waste)
Time (min)
f)
Chlorogenic acid
Yield (μg/g dry potato peel waste)
Time (min)

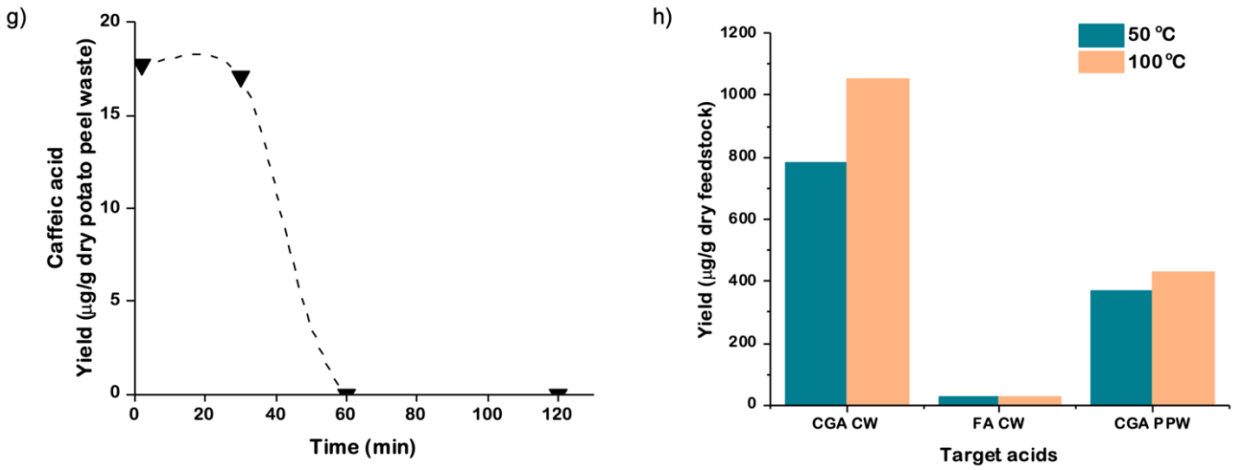


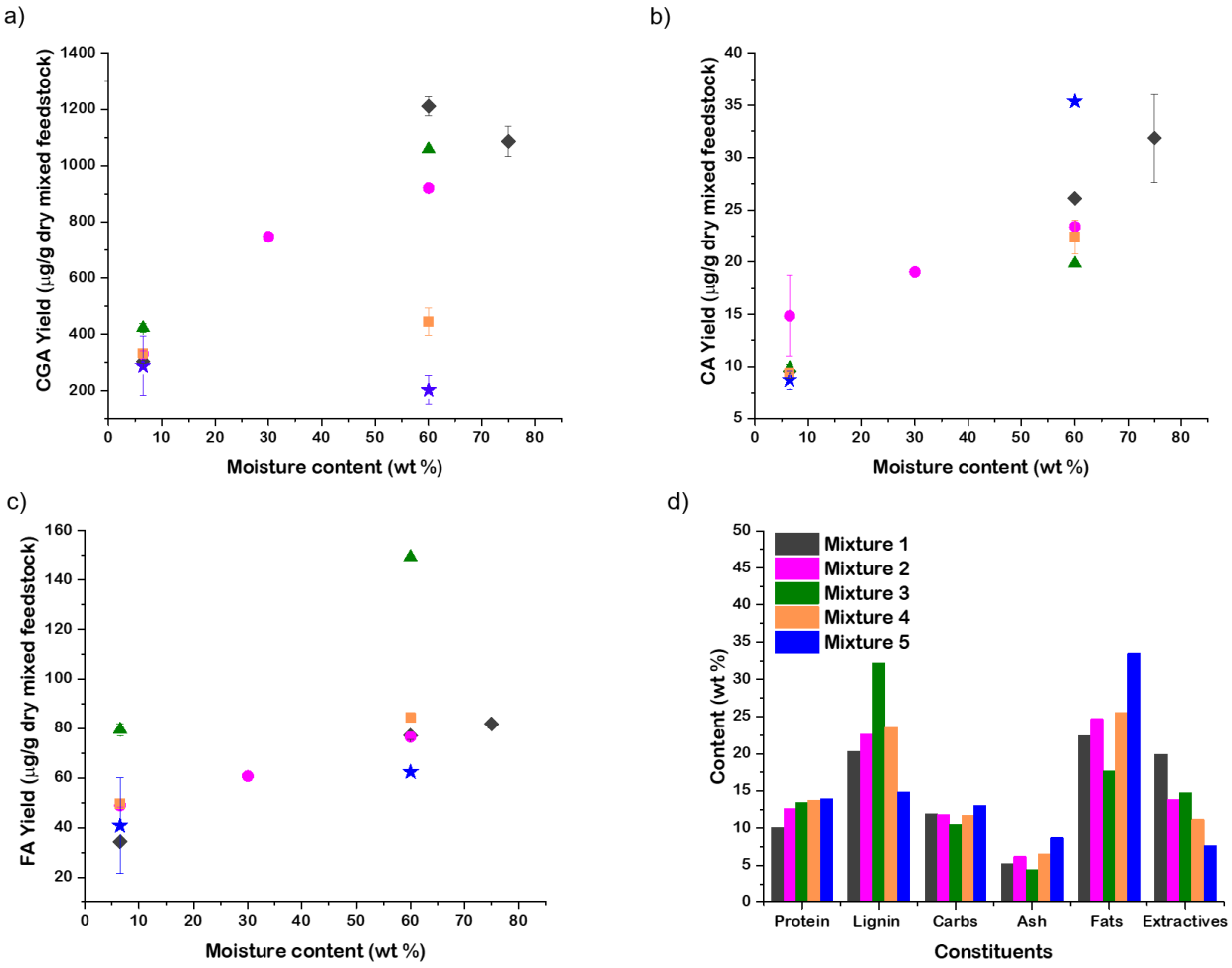
Figure 3: MAE. a) Chlorogenic and ferulic acid from coffee waste. b) Chlorogenic acid and c) caffeic and ferulic acid from potato peel waste. Conditions for a)-c): 100 °C, 2 min, and 50 W. d) Chlorogenic acid and e) ferulic acid yields vs. time from coffee waste with 30 wt% moisture at 100 °C and 50 W. f) Chlorogenic acid and g) caffeic acid yields vs. time from potato peel waste with 45 wt% moisture at 100 °C and 50 W. h) Chlorogenic and ferulic acid yields from coffee and potato peel waste with 20 wt% and 65 wt% moisture, respectively, at 50 W for 2 min at 50 °C and 100 °C. The symbols represent experimental data points, and the dashed lines are for visual guidance. CGA CW, FA CW, and CGA PPW are chlorogenic acid extracted from coffee waste, ferulic acid extracted from coffee waste, and chlorogenic acid extracted from potato peel waste, respectively.

Extraction from Mixed FW

We prepared five mixed FW feedstocks comprising equal proportions of apple, potato peel, and coffee waste (Mixture 1), 45% of each potato peel and coffee waste and 10% apple pomace (Mixture 2), 75% of coffee and 25% potato peel waste (Mixture 3), 50% of each coffee and potato peel waste (Mixture 4) and 25% of coffee and 75% of potato peel waste (Mixture 5), as shown in Figure 4d. All mixtures exhibit comparable dielectric properties when the moisture is below 20 wt% (Figure 4e), and enhanced dielectric loss factor and phenolic acid yields at > 20 wt% moisture (except chlorogenic acid yields from Mixture 5 that do not change significantly) (Figure 4a-c). The yields do not vary significantly at < 20 wt% moisture with differences due to the varying amount of free phenolics in the mixtures. As expected, the chlorogenic acid yield from Mixture 1 at 75 wt% moisture is 258% higher than the dry FW mixture. Enhancements of 180%, 150%, and 33% for Mixtures 2, 3, and 4 at 60 wt% moisture, respectively, are seen. Similar enhancements in ferulic and caffeic acid yields are seen compared to dry FW mixtures.

Interestingly, the yields from mixtures do not reflect a weighted average of yields obtained from pure feedstocks, despite the low concentrations of phenolic acids extracted (see Supplementary Figure 17 for yields at solid-to-liquid ratio < 0.05 and Figure 1f for their heating profiles). Importantly, the yield in the mixtures can be up to 2-3x higher than a simple summation of yields from individual feedstocks (Figure 4f-h). Thus, single-component data provide an underestimation of the yields from mixtures, except for chlorogenic acid yields from mixtures 2-5 at 60 wt% moisture. We believe that the interaction of phenolic acids with other extracted components in mixtures influences their yields at high moisture. The target phenolics can undergo enzymatic reaction [92] and complex with extracted proteins, carbohydrates, fats, and minerals,[93] and lignin[94] via van der Waals forces, covalent bonding, electrostatic attraction, or hydrophobic contact.[95] Other FW components can also interact with each other to promote synergistic (or antagonistic) extraction of target phenolics.[96,97] Thus, in addition to moisture and target acid

content in free and bound states, the interaction of FW components appears to affect extraction from mixtures.



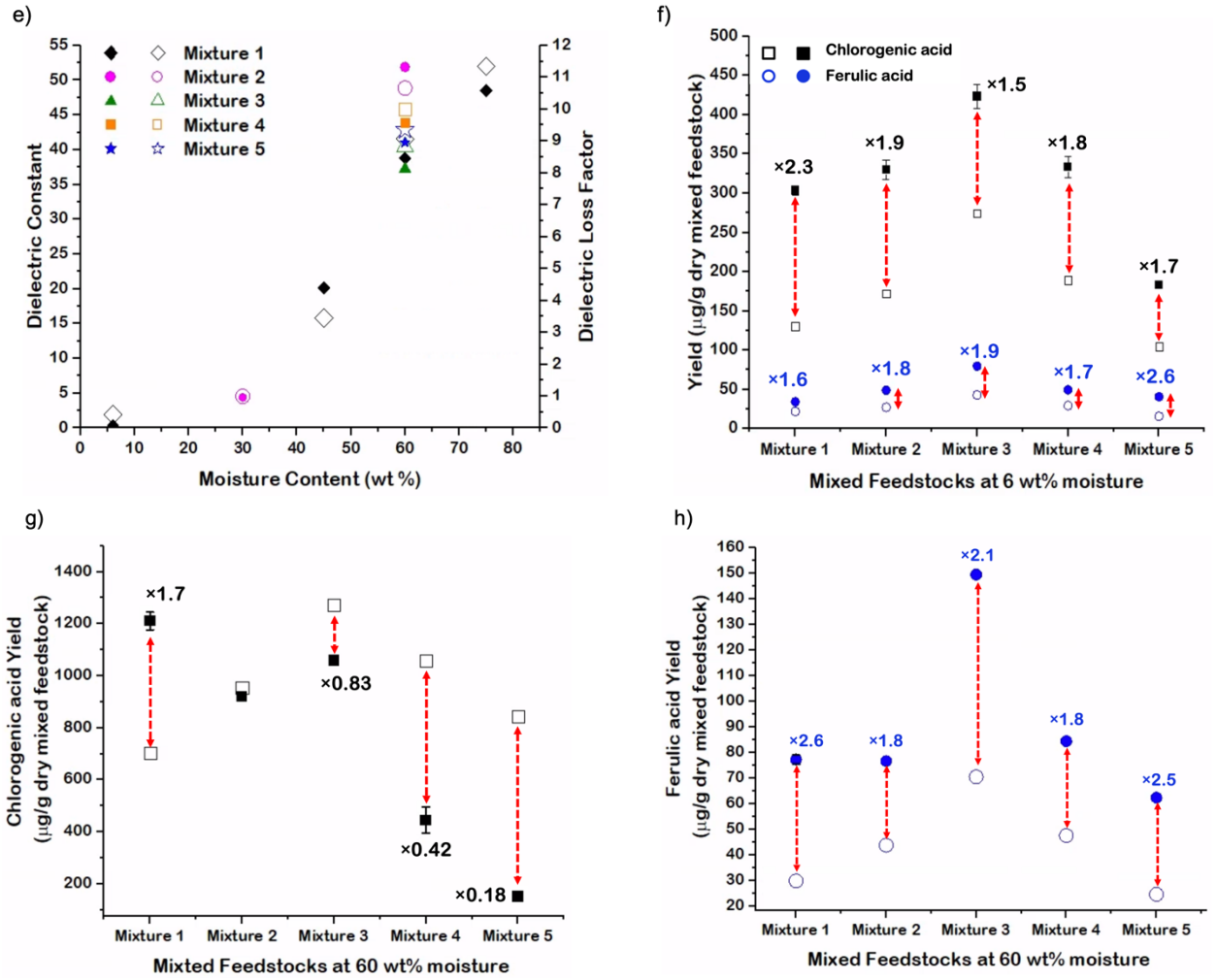


Figure 4: MAE at 100 °C, 2 min, and 50 W of a) chlorogenic acid, b) caffeic acid, and c) ferulic acid from Mixtures 1-5. d) Composition of Mixtures 1-5 calculated on a weighted-average basis from pure feedstock's composition. e) Dielectric constant (ε') and loss factor (ε") of Mixtures 1-5 vs. moisture (wt%). Weighted average estimated and experimental yields at 100 °C, 2 min, and 50 W of f) chlorogenic and ferulic acid from mixed feedstocks at 6 wt% moisture, and g) chlorogenic, and h) ferulic acid from mixed feedstocks at 60 wt% moisture. In panels a-c, CGA, FA, and CA are chlorogenic, ferulic, and caffeic acids. The symbols represent experimental data points for panels a-c and e. For panel e, the open and solid symbols represent experimental ε' and ε" data points, respectively. For panels f-h, the open and solid symbols represent estimated (composition-averaged from single feedstock) and experimental yields, respectively, the dashed double-ended arrows are for visual guidance, and the labels indicate the experimental yields' magnitude compared to the estimated yields. Mixture 1: equal proportions of apple, potato peel, and coffee waste; Mixture 2: 45% potato peel and coffee waste each and 10% apple pomace; Mixture 3: 75% of coffee and 25% potato peel waste; Mixture 4: 50% of each coffee and potato peel waste; Mixture 5: 25% of coffee and 75% of potato peel waste.

Conclusions

Microwave-assisted extraction (MAE) of natural antioxidants from food waste (FW) is appealing due to the high commercial value of the extractives. In this work, we explored five single feedstocks containing phenolic acids and synthetic mixtures to understand the physical and composition characteristics affecting the dielectric properties, heating profiles, processing times, and extraction yields. All feedstocks are microwave transparent at < 20 wt% moisture due to the inactivity of bound water and organic material to microwave irradiation. The dielectric constants and loss factors increase with increasing moisture and decrease with increasing protein and ash content. Physical properties, such as bulk density and porosity, are insignificant across all moistures. The heating of FW-extractant mixtures remains independent of the FW dielectric

response due to uniform mixing. Due to the thermal degradation of phenolic acids, lower temperatures (<100 ^{o}C) are generally favorable. Higher temperatures and longer times increase the yields of thermally stable acids, while lower temperatures and longer times or high temperatures and shorter times increase yields of thermally sensitive acids. The moisture increases heat and mass transfer, providing a significant enhancement in target acid yields, depending on the target acids' inherent concentration in bound or free states. In high moisture FW, an increase in temperature promotes higher target acid yields, while longer durations result in decreased yields due to interaction with other FW-extracted components. Thus, moisture, target acid concentration, time, and temperature are the only significant parameters for the MAE of phenolics from a single FW, with the first two being crucial. The yields from mixed FW are 2-3x higher than those estimated from a weighted average model using single-stream wastes despite the low concentration of extracted phenolics. In addition to moisture and target acid content, the interaction among various FW-extracted components appears to influence phenolic yields in FW mixtures.

Acknowledgments

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