Electricity Generation from Defective Tomatoes

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Abstract

The United States faces a significant burden in treating 0.61 billion kg of defective tomatoes (culls) every year. We present a proof-of-concept for generating electricity from culled tomatoes in microbial-electrochemical systems (MESs). This study delineates impedance behavior of the culled tomatoes in MESs and compares its impedance spectra with that of soluble substrates (dextrose, acetate, and wastewater). A series of AC and DC diagnostic tests have revealed the superior performance of the culled tomatoes compared to the pure substrates. Cyclic voltammetry results have indicated the active role of indigenous, diffusible redox-active pigments in the culled tomatoes on overall electricity production. Electrochemical impedance spectroscopy results have elucidated the role of peel and seed on the oxidation behavior of the culled tomatoes.

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1. Introduction

Tomato packinghouses in the United States (U.S.) generate 6.12×10^8 kg of culled (defective) tomatoes every year. The culled tomatoes fail customer requirements for firmness and color due to freezing traces and growth cracks; they have a stem over 3 inches of length, anthracnose, mold, decay, gray wall, or virus mottling; and they have cloudy spots, ghost spots, internal browning and sunscalds [1]. With U.S. tomato production reaching as high as 1.53×10^9 kg/year (~ 81% production in CA, AL, FL, GA, NC, SC, TN, and VA) [2], the packaging houses incur significant disposal costs. Similarly, processing plants generate culls during washing, inspection, pulping, juice finishing, evaporation, sterilization, packing, and storage (Fig. S1). A kilogram of processed tomatoes generates 20 grams of culls and 20 grams of peel and skin residues (Fig. S1). The packaging houses often hire third-party vendors [3] to dispose of the culls, incurring significant transportation costs [4].

Available biotechnologies are not designed to optimize energy production from culled tomatoes [5]. Activated sludge processes are suited to diluted wastewater (WW); they also require significant energy inputs (~112 KW per million gallons of WW) [6]. The land application of culls is not an attractive option [4] due to ever-increasing stringent regulations [7]. On-site composting requires expensive equipment during site preparation [4, 8, 9], demands lengthy treatment periods, and poses odor and dust issues [10]. Anaerobic digestion (AD) is an established technology for generating methane-rich biogas

[11-14] but requires a purification step to recover methane. Dark fermentation generates hydrogen-rich biogas [15], but requires a purification step for separating hydrogen [16].

Microbial electrochemical systems (MESs) support an array of engineering applications [17, 18] including biosensors [19, 20], electrolysis [21], desalination [22], reverse electrodialysis [23], and struvite production [24]. The use of solid organic wastes (SOWs) (e.g. food waste [25], sludge [26], soybean residue and rice husk [27], leaves [28], marine sediment [29], wheat straw [28]) as electron donors for MESs is well established [30]. Specifically, in our previous study [31], we showed that tomato pomace is a viable electron donor in microbial fuel cells. There are a fair number of impedance studies on the use of pure substrates (e.g. lactate) [32], wastewater [33], and marine wastes [34] in MESs. However, there is a notable paucity of literature investigating the impedance behavior of SOW-based MESs [35, 36].

The overarching objective of this study was to demonstrate a proof-of-concept for generating electricity from culled tomatoes. To our knowledge, there are no prior studies that provide time-variant impedances to Faradaic processes related to oxidation of culled tomatoes in MESs. We delineate the long-term oxidative behavior and impedance contributions of the particulate fraction (i.e., peel & seed) of the cull. We use a series of DC techniques (voltammetry), AC techniques (electrochemical impedance analysis (EIS)), and spectrophotometry tests (chemical oxygen demand (COD)) to compare oxidation behavior of *as is* culls with its peel and seed (P&S) and readily soluble substrates including pure dextrose (represent monosaccharides in the cull), pure acetate (fermentation product of dextrose), and municipal wastewater. We hypothesize that the indigenous redox

shuttles (e.g. carotenoids, flavins, flavonoids) and nutrition-rich flesh in the cull promotes its oxidation, while its peel & seed impedes its degradation kinetics [37].

There are several reasons why the oxidation behavior of *as is* culls is different from soluble substrates. First, the following indigenous nutritional compounds in culls serve an excellent energy source for growth of anode-respiring bacteria (ARB) in MESs: sucrose ($\Delta G_f^0 = -1551.8$ kJ/mole), amino acids ($\Delta G_f^0 = -763$ kJ/mole), oleic acid ($\Delta G_f^0 = -50.88$ kJ/mole), palmitic acid ($\Delta G_f^0 = -305$ kJ/mole), stearic acid ($\Delta G_f^0 = -50.88$ kJ/mole) and linoleic acid ($\Delta G_f^0 = -50.88$ kJ/mole) [38-41] (Table 1b). The skin and seed in the culls are rich in micronutrients (Cu, Mn, Ni, and Zn) and macronutrients (Fe, Na, K, Ca) (Table 1a). Tomatoes contain a variety of redox-active species [42, 43] such as carotenoids, kampferol, malvin, myricetin, naringenin, naringin, petunidin, quercetin, and riboflavin (Table 1b), which qualify as redox-active mediators in MESs for following reasons [44-52]; they are characterized by: i) fast redox equilibration; ii) fully reversible reactions (oxidized and reduced form of mediators do not yield irreversible reactions); iii) experimentally established standard redox potentials; and iv) defined stoichiometry with respect to the number of electron and protons during Faradaic processes. These mediators catalyze extracellular electron transfer from ARBs to solid electrode in MESs. For example, flavins ($E'_{\text{FMN/FMNH}_2} = -190$ mV vs. SHE) are known to promote extracellular electron transport capabilities of *Shewanella Oneidensis* MR1 [31]. Quercetin in tomatoes exhibits electrochemical activity in aqueous electrolytes under a range of pH conditions (pH=4.3-11.2) [53]. Table 1b provides a list of indigenous species in tomatoes, their standard redox potential, and the number of electrons transferred during the redox processes.

Second, the peel and skin components of *as is* cull represent complex, particulate COD (pCOD) matter that is known for its sluggish disintegration and hydrolysis kinetics in biological systems. The MESs using the pCOD will suffer from the diffusion-limited performance. Third, unlike municipal wastewater, the culls are more beneficial in MESs due to their carbohydrate content (39 mg per gram of cull), low pH, and high electrical conductivity [54]. Furthermore, as explained earlier, unlike wastewater, culled tomatoes contain redox-active carotenoids and flavonoid molecules (Table 1b). From a large-scale treatment perspective, it is important to distinguish electrical performance of culls from municipal wastewater.

Finally, the dextrose in culled tomatoes will promote the growth of methanogens. Based on the above background, it becomes important to distinguish the polarization response and impedance behavior of MESs with culls from the peel & seed, the fermentable (dextrose) and non-fermentable (acetate) substrates, and the municipal wastewater. At the typical low current densities ($<10 \text{ A/m}^2$) [55] encountered in MESs, we anticipate *as is* culls to outperform seed & skin and municipal wastewater. While counterintuitive, we have also observed that the culled tomatoes outperform pure chemicals (dextrose and acetate). Since the peel and seed are integral components of the cull, we performed a 125 days long, EIS study to distinguish the temporal impedance contributions (charge transfer resistance, ohmic, and diffusion limitations) of the peel and skin to the oxidation of culls.

2. Materials & Methods

2.1. Reactor configuration and Electrolyte Composition

We used a two-chambered microbial fuel cell [1] as a laboratory model for microbial electrochemical systems (MESs). A hydrated Ultrex membrane provided a hydraulic separation between the anode and cathode chambers. The 100 mM ferricyanide (in 50 mM phosphate buffer) was used as the electron acceptor in the cathode. The reactor design is similar to that in our earlier study [31] (Details in Fig. S2). The tests were carried out in five identical MESs varying in the type of carbon substrate 1) as is cull, 2) peel & seed, 3) dextrose, 4) acetate, and 5) municipal wastewater (Table S1). The five test MESs are herein referred as CULL, P&S, DEX, ACE, and WW. A MES that lacked a carbon source was run simultaneously to provide a control. The anode was inoculated with an enriched mixture of electrochemically active microbial population described in our earlier study [31]. We evaluated the performance of five test MESs in 14 consecutive cycles extended during 125 days of fed-batch operation. We eliminated planktonic microbes at the end of each cycle by draining anolyte and gently washing the anode with 50 mM phosphate. We used the following minimal media to prepare the anolyte: NH_4Cl , 1.24 g/L; KCl , 0.52 g/L; $\text{NaH}_2\text{PO}_4\cdot\text{H}_2\text{O}$, 2.45 g L^{-1} ; $\text{Na}_2\text{HPO}_4\cdot 7\text{H}_2\text{O}$, 4.576 g/L; vitamin mix, 10 ml/L; and trace minerals, 10 ml/L. The anolyte in test MESs was obtained by modifying the minimal media with carbon substrates (Table S1).

2.1.1. CULL: Fresh tomato culls obtained from Immokalee farm, Naples, FL, were quartered and boiled in distilled water for 5 minutes; cooled at 11 °C for 10 minutes; placed on an aluminum foil; heat-dried at 60 °C for 18 hours. 9.7 mg of powdered cull was mixed with one litre of minimal media.

2.1.2. P&S: The cull was quartered and boiled in distilled water for 5 minutes and cooled at 11 °C for 10 minutes. The skin and seeds were manually separated from the dried cull and heated at 60 °C for 18 hours. The skin and seed were combined in a ratio of 3:4 (w/w) and mixed in minimal media to achieve 9.7 mg/L.

2.1.3. DEX, ACE, and WW: The DEX used 1 g/L of dextrose (180.16 g/mol; melting point 146 °C; CAS Number: 50-99-7, G8270, Sigma Aldrich) [56] and ACE used 1 g/L of acetate (59.04 g/mol; MP 16.6 °C; CAS Number: 127-09-3, S2889, Sigma Aldrich [57]). The WW used primary clarifier effluent from Rapid City wastewater treatment facility, SD (COD concentration approx. 828mg/L, pH 7±0.7). The initial pH values for anolyte in both DEX and ACE ranged from 6.9-7.1.

2.2. Analytical Methods, Data acquisition & AC impedance

5 mL of anolyte was periodically collected using a gastight syringe to measure its pH (Cole-Palmer probe) and soluble Chemical Oxygen Demand (sCOD) (Method 5220 Hach COD system). Voltage data was acquired with a DAQ/54 module configured with an external resistor. The polarization data was obtained for test MESs on day 1, 45, 59, 74, 86, and 105 by recording the steady state voltage values at a specified value of external resistor. The EIS for CULL, P&S, and DEX was performed with a CHI electrochemical workstation. The ACE and WW were evaluated with a Gamry600 workstation. The EIS tests were performed at open circuit potential using an AC signal with an amplitude of ±10 mV (vs. Ag/AgCl) and the EIS spectra were obtained in the frequency range of 10000 to 0.01 Hz. The EIS tests used the anode as the working electrode and the cathode as counter and reference electrodes. The temporal EIS responses for CULL and P&S were recorded on days 1, 16, 21, 45, 72, 88, 103, and 107. The solution resistance was interpreted from the

Nyquist plot as the real axis value at the high frequency intercept. The real axis value at the low frequency intercept of Nyquist plot corresponds to the sum of the polarization resistance and the solution resistance.

2.3. Cyclic Voltammetry (CV)

A CV technique was used to analyze CULL, ACE, and WW using the anode as the working electrode, cathode as the counter electrode respectively, and Ag/AgCl system as reference electrode. We scanned the working electrode in a potential region of -0.8 and 0.8 V at a sweep rate of 10 mV/s (vs. Ag/AgCl). The Randles Sevcik equation [58] was used to analyze the cyclic voltammograms for CULL, ACE, and WW.

$$i_p = (2.687 * 10^5) * n^{\frac{3}{2}} * v^{\frac{1}{2}} * D^{\frac{1}{2}} * A * C \quad (1)$$

Where i_p is peak current, n is number of electrons transferred, A is electrode area, F is Faraday Constant, D is diffusion coefficient of the species, v is scan rate, C is bulk concentration of the species and T is temperature.

3.0 Results and Discussion

The performance data for CULL, P&S, DEX, ACE, and WW are summarized in Table S2.

3.1. Unique oxidation behavior in CULL and P&S compared to soluble substrates

Fig. 1-9 compares the oxidation behavior for the cull and the soluble substrates. Unlike the DEX, ACE, and WW (Fig. 1b), the CULL develops a reddish-orange color due to the carotenoids (e.g. lycopene [55] and redox-active β -carotene [31]). The CULL promotes the formation of two distinct phases (Fig. 1a): i) the particulate phase (the peel & seed) characterized with pCOD and ii) a clear aqueous phase dominated by sCOD from the

flesh (tissue, columella, pericarp, vascular bundle, and locular activity). Given the slow-kinetics of pCOD oxidation and the sluggish disintegration and hydrolysis reactions [59-61] that characterize the P&S substrate, we can better understand the inferior performance of P&S compared to CULL (Fig. 1-9). As expected, the DEX, ACE, and WW did not yield any color nor did the solid sludge (Fig. 1b).

In our earlier study [31] on the EIS analysis of the microbial fuel cell with the peel and seed (P&S) of culled tomatoes as the sole carbon source, we have observed the three distinct time constants in the three different frequency regions of the Bode phase angle plots: i) a low frequency region (LFR) peak representing the charge transfer resistance (CTR) to the slow kinetics related to the oxidation of peel and seed; ii) a high frequency region (HFR) peak due to the fast redox processes associated with metallic salts in the anolyte; and iii) a mid-to-low frequency region (MFR) peak attributed to the CTR [32] of the Faradaic processes related to indigenous mediators in the tomato (Table 1b). Further, these MFR peaks showed a facile response to the changes in the bias potential (-50 mV to 450 mV (vs. Ag/AgCl)), confirming the influence of the indigenous mediators on the Faradaic processes in tomato systems [31]. In contrast to the multiple time constants observed in the EIS spectra for the peel and seed systems [31], contemporary EIS studies on the MESs with wastewater [62] and pure substrates [63] have reported a single time constant in Bode phase angle plots.

Though we observed the three time constants (including the MFR peak) in the Bode phase angle plots for CULLs, they were less dominant (compared to that in our earlier study with peel and seed [31]) (Fig. 1C). Further, the EIS results for the CULL, for different cycles of the fed-batch operation shown in Fig. 2, did not yield a consistent

impedance spectra pattern in each of the three frequency regions (e.g., corresponding frequencies for the phase angle minima ($f_{\min}$) and the maxima ($f_{\max}$)). Further studies are required to evaluate if the monosaccharide components in the flesh of the culled tomatoes (See Table 1b) delay or diminish the time constants in the LFR and MFR (compared to the impedance spectra for peel & seed) [31], especially for different values of the DC bias potential, and in response to the biofilm history and the media replacement during the fed-batch operation. Nevertheless, the CV results described in section 3.3 indicate a strong role of the indigenous redox-active species (esp., flavonoids and carotenoids in Table 1b) on the CULL performance.

Finally, as expected, the temporal profiles for sCOD consumption in the ACE and WW followed a linear pattern and demonstrated a 92% sCOD removal (Fig. 3b). However, the sCOD profiles for CULL and P&S followed a non-linear pattern (Fig. 3a). This is due to the complex dynamics of pCOD--->sCOD conversion influenced by the synergistic effects of the factors related to disintegration and hydrolysis kinetics, biofilm history, mass transfer limitations, and electrical parameters. Further, the sCOD_{initial} for DEX, ACE, and WW was manually adjusted to 1000 mg/L (Fig. 3b); the different mass inputs of the cull and peel&seed resulted in different sCOD_{initial} values for CULL (2000 mg/L) and P&S (3000 mg/L) (Fig. 3a). The sCOD removal efficiency in the DEX was less than 50% and this is due to the fact that the dextrose can be fermented to sCOD-bearing organic acids and ethanol [64, 65].

3.2. Defective tomatoes are superior to pure chemicals

The electrical performance of the P&S was inferior to CULL (Fig. 2b, 2c, 4, S3; Fig. 7, 8) throughout the hundred days of MES operation (Fig. S4). While counter-intuitive [30, 66], the CULL has outperformed DEX and ACE that used pure substrates (open circuit, Fig. 2a; closed-circuit, Fig. 2b,2c,S3). The average OCV_{max} (vs. Ag/AgCl) for CULL (0.71 V) is higher than P&S (0.67 V), DEX (0.7 V), ACE (0.63 V), and WW (0.41 V). Considering that P&S is characterized with the pCOD, it is interesting to note that its OCV is equivalent to CULL and DEX. One-way ANOVA analysis confirmed the absence of statistically significant differences between the mean OCV for CULL, P&S, and DEX ($n=22$; $P\text{-value}=0.274>0.05$, $F=1.31$; Bartlett's statistic $=0.9266$, $p\text{-value}=0.629>0.05$) (Table S3). As anticipated, the OCV in the ACE is lower than DEX and higher than WW.

Fig. 2b, 2C and S3 indicates identical start-up behavior of five test MESs (2400 data points) under closed circuit conditions (load $\sim$ 1000 Ω). The CULL, P&S, and DEX exhibits a lag of 70 h to register minimal electrical output, and additional 700 h to register $current_{max}$: CULL, 1.03 A/m²; P&S, 0.97 A/m²; and DEX, 0.98 A/m² (Fig. 2, S3). However, as shown in Fig. 4, 5, S4, the performance differences between test MESs are pronounced at higher current densities. Given the identical reactor configuration, the variation in polarization responses (Fig. 4, 5, S5, S6) is attributable to the differences in the oxidation behavior of the carbon substrates. The polarization losses were ranked as: CULL<DEX<P&S<ACE<WW; the corresponding power densities were in the order: CULL>DEX>P&S>ACE>WW (Fig. S5, S6, S7).

The bar plot in Fig. S4 compares the magnitude of power densities and current densities for CULL, P&S, and DEX. The CULL outperformed DEX during the fourteen different cycles (Fig. S8): the peak current density (1504 mA/m²) and peak power density

(256.1 mW/m²) in the CULL was 56% and 55% higher than that in DEX (peak current density: 964.3 mA/m², peak power density: 163.4 mW/m²), respectively. Similarly, the peak current density (1504 mA/m²) and peak power density (256.1 mW/m²) in CULL were 38% and 20.5% higher than that in ACE (1092.9 mA/m²; 212.6 mW/m²), respectively (Fig. 4, 5). The superior performance of CULL is attributed to its monosaccharides (3 grams of sugar per gram of cull), and redox-active species (e.g. carotenoid, flavins, and quercetin) characterized with high electron-transfer rates (Table 1b). The inferior performance of the DEX is attributed to methanogens that thrive in glucose substrates and divert electron flux towards reduced products (e.g. fatty acids) [65]. This observation is consistent with our prior findings where glucose substrates yielded lower performance compared to the solid algae [34].

3.3. Redox shuttles in CULL appears at a potential of 0.3 V higher potential than contemporary species

We have carried out CV studies to study the electrochemical behavior of plausible mediators involved in the oxidation of culled tomatoes. As shown in Fig. 6, the biofilm-coated anodes in the CULL exhibited non-sigmoidal voltammograms indicating a single electron-transfer process [58]. This behavior is attributed to the indigenous, redox-active carotenoids and flavonoids in tomatoes. As shown in Table 1b and discussed in earlier sections, these redox-active species [67-70] can serve as mediators to catalyze extracellular electron transfer in ARBs. As shown in Fig. 6, the CULL exhibits oxidation and reduction peaks at 0.255 V (vs. SHE) and 0.425 V (vs. SHE) respectively. The midpoint peak potential (0.335 V vs. SHE) for CULL occurs at higher values (more positive) compared to

ACE (-0.34 V vs. SHE). In fact, the peak potential for the CV in the CULL is 0.3 V higher than that for contemporary MESs using *Geobacter*, *R.palustris* DX-1, and *T.ferriacetica*. [31] The higher-potential-redox-active-species (HPRAS) in the CULL dominated the CVs at all the tested scan rates (Fig. 6b). At a low-scan rate, the ratio of cathodic and anodic peak currents (i_{pc}/i_{pa}) in CULL was 1.56 indicating the quasi-reversible nature of the HPRAS that undergoes structural reorganization without disrupting its molecular structure. The peak potential of 0.33 V (vs. SHE) for HPRAS corresponds to quercetin compounds in tomatoes (0.33 V vs. SHE) [71-74]. Quercetin is a bioactive flavonoid compound which can yield one, two, three or even four anodic peaks in aqueous electrolytes [53].

The peak potential for HPRAS also overlaps with carotenoids (0.204- 0.449 V vs. SHE) [75, 76]. Among the diverse range of carotenoids, lycopene and β -carotene are primarily responsible for orange color in matured tomatoes [77, 78]. As shown in Fig. 1a, we have observed a distinct reddish-orange color in anolyte media which can be attributed to carotenoids [79] that are known to influence electron transfer processes [76]. For example, an electrochemical study by Liu et al. [76], has delineated a series of electrochemical parameters (oxidation potential, reaction rate constant, and kinetic equilibrium constants) for 12 naturally occurring carotenoids, and confirmed that oxidation peaks for carotenoids occur at lower potential compared with the reduction peaks. As shown in Fig. 6b, we have observed anodic peaks at lower potential compared to cathodic peaks (Fig. 6b), corroborating the presence of redox-active carotenoids in CULL-MESs.

Prior high-performance liquid chromatography (HPLC) studies have established the presence of quercetin and carotenoid pigments (lycopene and β -carotene) in tomatoes [43, 80-82] (See Table 1b for details). Further studies are required to decipher the specific

chemical characteristics of these HPRAS molecules. Nevertheless, the findings from DC tests (Fig. 6a, 6b, and 6c) agree with those of AC tests (Fig. 1c, S9, S10; Fig. 7, 8) and corroborate the role of indigenous redox mediators on Faradaic processes related to oxidation of culled tomatoes. The redox mediators can be lost during the media replacements in the fed-batch operation. However, it is critical to note that mediators are indigenous to culled tomatoes—each new cycle in fed-batch operation will replenish the mediators. Further, the start-up curves in Fig. 2 indicate the formation of resilient, electrochemically active biofilm on the anode surface, indicating that these mediators can also be accumulated in biofilms. Further studies are required to discern the relative contribution of IRMs on electricity production.

Unlike CULL, the ACE exhibited redox peak at a lower voltage (-0.34 V vs. SHE) corresponding to known electron acceptors such as ferredoxin (-0.398 vs. SHE) and cytochrome OmcB (-0.19 V vs. SHE) [83-86]. For a 1 mV/s scan rate, the i_{pc}/i_{pa} ratio for ACE was close to unity suggesting the reversible nature of participating redox-active species. This is an anticipated result, given the purity of the ACE compound compared with the complex particulate nature of the defective tomatoes in the CULL. The WW exhibited a mid-point peak at low potential (-0.19 V vs. SHE) whose peak current (i_p) (both anodic and cathodic sweeps) was an order of magnitude lower than the CULL (Fig. 6a-c).

The i_{pc}/i_{pa} ratio for both CULL and ACE decreased with increasing scan rates (Fig. 6b). The slow scan rate provides adequate time for redox-active species to participate in electrochemical reactions and contribute to higher faradic current (Fig. 6a). As scan rates grow faster and the voltage range scanned is wider, the diffusion rates decreased and the separation between the anodic and cathodic peak potentials (ΔE_p) increased (Fig. 6b). The

increase in ΔE_p with increasing scan rate is attributed to the charge transfer limitations induced by the electrostatic factors, chemical interaction between electrolyte ions and anode and interactions of redox couples [87]. The Randles-Sevcik equation (Eq. 1) was used to confirm that the values of peak current (I_p) are directly proportional to the $v^{1/2}$ (square root of scan rate) indicating the diffusion-controlled, current regime in the CULL (n=8; $r^2=0.85$; F=12.4; p=0.77) and ACE (n=20; $r^2=0.81$; F=35; p=0.0005). However, the slope (0.00135) of the $I-v^{1/2}$ curve in ACE is 27 fold higher than the CULL (slope = 0.00005), indicating a higher transfer coefficient of the participating redox-shuttles in the ACE. The differences in the magnitudes for the slopes can be attributed to differences in the diffusion coefficient (D) of their respective redox couples. The easy electrocatalytic behavior of the redox shuttles and the higher peak current (i_p) in ACE can be explained by the fact that the bio-kinetic rates for the acetate oxidation is significantly higher than that for the pCOD oxidation.

3.4 The higher impedance in P&S induces its skewed polarization behavior at higher currents

The P&S exhibited a skewed polarization behavior (i.e. concave-shaped power density curves) on Day 45, 59, and 74 (Fig. 4, S5), while the CULL yielded a smoother polarization response (Fig. 4, S5). The recalcitrant behavior of the pCOD in the peel and seed limits the ability of P&S to meet the larger over potential required at higher current densities, while the readily available sCOD from the flesh sustains the performance of CULL at all the current densities. The long-term EIS studies have corroborated the

dominant impedance behavior of the peel & seed at a range of frequencies (10 kHz-10 mHz) and time-scales (1-107 days) (Fig. 8).

The operational changes (e.g. media replacements) have resulted in the diverse impedance behavior of both the P&S and CULL (see the diverse shapes for the bell-shaped curves in the Nyquist plots; Fig. 8) throughout the 103 days of fed-batch operation. For instance, the Nyquist plots for Day 21 and Day 103 yielded three distinct loops; Day 16 and Day 72 yielded two incomplete semicircles; and the Day 45 and Day 107 yielded a single time constant but characterized with the diffusion resistance (extended arc in low-frequency region). It is therefore not feasible to identify a common model (e.g. Randle's circuit) that fits the entire range of the impedance data shown for 106 days (Fig. 8). Instead of using the electrical equivalent circuit fitting method, we have obtained the polarization resistance (R_{polz}) as the real axis value at low frequency intercept.

We found that the R_{polz} for the P&S was 17-39% greater than the CULL during all the time scales (Fig. 9). For example, the R_{polz} in the P&S was 1.7 fold higher than the CULL on day 45. The one-tailed t-test (95% confidence interval) confirms statistically significant differences between the R_{polz} for P&S and the CULL (paired test: p-value 0.0245; $t=2.213$; $n=11$; mean of difference = 6.674, $R^2=0.3081$). The EIS analysis indicates that the peel & seed will impede the oxidation of the culls at higher current densities. We did not observe significant differences in the R_{ohm} in five test MESs (Fig. 7) (One-way ANOVA analysis; $n=12$; P-value=0.1375>0.05, $F=2.109$; Corrected Bartlett's statistic =1.647; p-value=0.439>0.05).

4.0. CONCLUSIONS

We demonstrate the feasibility of generating electricity from defective tomatoes. The performance of culled tomatoes was equivalent, or better than that of pure chemicals. For example, the polarization resistance in optimized CULL was 10-40% lower than the DEX. The peak power densities in the CULL were 1.5 fold higher than the DEX and 1.3 times higher than the ACE. Our studies suggest that performance of CULL will be impeded at higher current densities due to sluggish oxidation kinetics of its particulate matter (peel and seed) in culled tomatoes. Nonetheless, the exceptional nutritional components (carbohydrates, amino acids) and redox-active species (flavonoids and carotenoids) in culled tomatoes render it an attractive feedstock for electricity production. Unlike typical solid wastes such as food scraps, the culled tomatoes are available throughout the year in diverse geographical locations, often with a well-defined composition, enabling monoculture-based, large-scale electricity production.

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Supporting Information Mass balance for culls in Fig. S1. Reactor Design details in Fig. S2. Start-up data for DEX, WW, and ACE in Fig. S3. Bar plots for peak power in Fig. S4. Temporal performance of CULL and P&S in Fig. S5. Temporal performance of DEX, ACE, and WW in Fig. S6. Comparative performance of CULL and ACE in Fig. S7. Temporal performance of CULL and DEX in Fig. S8. Bode phase angle plots for WW, DEX and ACE in Fig. S9 and Fig. S10. Table S1 and S2 presents experimental design and

results respectively. Table S3 describes one-way ANOVA analysis of temporal OCV values in CULL, DEX, and ACE.

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Fig. 1. (A) Photograph of the reddish-orange anolyte in MES with culled tomatoes. (B) Photograph of anolyte with readily soluble substrates (acetate in this case). (C) Bode phase angle plots for MESs with cull (green squares, ■) and peel&seed (blue triangles, ▲) (Biofilm age ~100 days) (NOTE: See Fig. S1. for Bode phase angle plots for wastewater, dextrose, and acetate)

Fig. 2 (A) Steady state OCV response during 3000 hours of continuous fed-batch operation (Green line —■— Cull, Blue line —▲— peel & seed, red line —●— dextrose, black line —■— Acetate and grey line —◆— Wastewater) (B) steady state electrical performance with cull under closed circuit (C) steady state electrical performance of peel & seed (NOTE: L^* - Lag time, S^* - Start output, M^* - Maximum output. See Fig. S3. for start-up of MESs with soluble substrates (dextrose, acetate, and municipal wastewater).

Fig. 3. (A) Remaining chemical Oxygen Demand (sCOD) in MESs with solid substrates (cull (green squares —■—) and peel & seed (blue triangles —▲—). (B) sCOD remaining in MESs with wastewater (brown diamonds —◆—), dextrose (red circles —●—), and acetate (black squares —■—) (SD<5%; n=3)

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Fig. 5. Temporal data for power densities and polarization in MESs with three soluble substrates (dextrose (red circles —●—), acetate (blue diamonds —◆—), and wastewater (black dotted line — — —) NOTE: Media replacements were performed on Days 12, 27, 43,47, 53, 60, 67, 74, 84, 89, 95, and 103. See Fig. S6 for details.

Fig. 6. A) Cyclic voltammograms for as is culls (blue solid line ———), acetate (purple dotted line - - -), and soluble chemical oxygen demand in municipal wastewater (dotted brown line - - -) B) Cyclic voltammograms with varying scan rates for three test MESs (blue line ——— 1mv/s, red line ——— 5mv/s, green line ——— 10 mv/s, purple line ——— 50 mv/s) C) Peak current against the square root of the scan rate for three test MESs (solid circles, ●- cull, ●- acetate and ●-wastewater) represent measured value and the black solid line represents fitted data). The CVs were generated after 365 days of fed-batch operation. Prior

to obtaining CVs, the anolyte was totally drained, and washed with phosphate buffer two times.

Fig. 7. Nyquist plots for MESs with wastewater (brown diamonds—◆—), dextrose (red circles—●—), acetate (purple cross—×—), peel & seed (blue squares—■—), and as is solid culls (green triangles—▲—). Inset graph shows a clear view of the high frequency region.

Fig. 8. Comparative Nyquist responses for MES with peel and seed (blue triangles—▲—), and cull (green squares—■—), for 100 days of fed-batch operation. AC signal: Frequency = 10 kHz -100 mHz; Amplitude = ± 10 mV. Impedance measurements were performed on a full cell configuration.

Fig. 9. Temporal changes in the ohmic losses (green bar, ■) and polarization losses (blue bar, ■ for: i) cull, ii) peel and seed, and iii) dextrose

List of Tables

Table 1a: Nutritional constituents in defective tomatoes and their role in microbial electrochemical systems

Table. 1b Redox-active species found in defective tomatoes, their standard reduction potential and number of electrons transferred to and from redox species

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Fig. 1. (A) Photograph of the reddish-orange anolyte in MES with culled tomatoes. (B) Photograph of anolyte with readily soluble substrates (acetate in this case). (C) Bode phase angle plots for MESs with cull (green squares, ■) and peel&seed (blue triangles, ▲) (Biofilm age ~100 days)

(NOTE: See Fig. S1. for Bode phase angle plots for wastewater, dextrose, and acetate)

Fig. 2 (A) Steady state OCV response during 3000 hours of continuous fed-batch operation (Green line $\blacksquare$ - Cull, Blue line $\blacktriangle$ - peel & seed, red line $\bullet$ - dextrose, black line $\blacksquare$ - Acetate and grey line $\blacklozenge$ - Wastewater) (B) steady state electrical performance with cull under closed circuit (C) steady state electrical performance of peel & seed (NOTE: L^* - Lag time, S^* - Start output, M^* - Maximum output. See Fig. S3. for start-up of MESs with soluble substrates (dextrose, acetate, and municipal wastewater).

Fig. 3. (A) Remaining chemical Oxygen Demand (sCOD) in MESs with solid substrates (cull (green squares —■—) and peel & seed (blue triangles —▲—)). (B) sCOD remaining in MESs with wastewater (brown diamonds —◆—), dextrose (red circles —●—), and acetate (black squares —□—) (SD<5%; n=3)

Fig. 4. Temporal data for power densities and polarization in MESs with two solid substrates (culls (green squares $\text{---}\blacksquare\text{---}$) and peel & seed (blue triangles $\text{---}\blacktriangle\text{---}$))

NOTE: Media replacements were performed on Days 12, 27, 43, 47, 53, 60, 67, 74, 84, 89, 95, and 103. See Fig. S5 for details.

Fig. 5. Temporal data for power densities and polarization in MESs with three soluble substrates (dextrose (red circles —●—), acetate (blue diamonds —◆—), and wastewater (black dotted line — — —))

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Fig. 6. A) Cyclic voltammograms for as is culls (blue solid line —), acetate (purple dotted line - - -), and soluble chemical oxygen demand in municipal wastewater (dotted brown line - - -) B) Cyclic voltammograms with varying scan rates for three test MESs (blue line — 1mv/s, redline — 5mv/s, greenline — 10 mv/s, purple line — 50 mv/s) C) Peak current against the square root of the scan rate for three test MESs (solid circles, ●-cull, ●- acetate and ●-wastewater) represent measured value and the black solid line represents fitted data). The CVs were generated after 365 days of fed-batch operation. Prior to obtaining CVs, the anolyte was totally drained, and washed with phosphate buffer two times.

Fig. 7. Nyquist plots for MESS with wastewater (brown diamonds $\blacklozenge$), dextrose (red circles $\bullet$), acetate (purple cross $\times$), peel & seed (blue squares $\blacksquare$), and as is solid culls (green triangles $\blacktriangle$). Inset graph shows a clear view of the high frequency region.

Fig. 8. Comparative Nyquist responses for MES with peel and seed (blue triangles— $\blacktriangle$), and cull (green squares— $\blacksquare$), for 100 days of fed-batch operation. AC signal: Frequency = 10 kHz -100 mHz; Amplitude = ± 10 mV. Impedance measurements were performed on a full cell configuration.

Fig. 9. Temporal changes in the ohmic losses (green bar ■) and polarization losses (blue bar ■) for: i) cull, ii) peel and seed, and iii) dextrose

Power Density

Impedance Losses

Graphical Abstract

Table. 1a Nutritional constituents in defective tomatoes and their role in microbial electrochemical systems

Defective Tomatoes	Nutrition Elements	Role in microbial electrochemical systems
Cull	Sucrose	Electron donor ($\Delta G^0_f = -1,551.85$ KJ/mole) ^{36,67}
Peel	Amino Acids	Electron donor ($\Delta G^0_f = -763$ KJ/mole) ^{38,67}
Seed	Oleic Acid	Electron donor ($\Delta G^0_f = -50.88$ KJ/mole) ^{38,37}
Seed	Palmitic Acid	Electron donor ($\Delta G^0_f = -305.0$ KJ/mole) ^{37,39}
Seed	Stearic Acid	Electron donor ($\Delta G^0_f = -50.88$ KJ/mole) ^{37,39}
Seed	Linoleic Acid	Electron donor ($\Delta G^0_f = -50.88$ KJ/mole) ^{37,39}
Peel/Seed	Cu, Mn, Ni, Zn	Microelements for bacterial metabolism ³⁸
Cull/Seed/ Peel	Fe, Na, K, Ca	Macroelements for bacterial metabolism ^{38,67}
Cull	Vitamin A, C	Growth factors for bacterial metabolism ^{38,67}

Table. 1b Redox-active species found in defective tomatoes, their standard reduction potential and number of electrons transferred to and from redox species

Constituents	E° (V vs SHE)	# of electron transferred	Oxidized Species	Reduced species	Notes
Carotenoids	0.204 to 0.449 ⁷⁴	1 or 2	$\text{Car} \rightleftharpoons \text{Car}^{\cdot+}$ $\text{Car}^{\cdot+} \rightleftharpoons \text{Car}^{2+}$ $\text{Car}^+ \rightleftharpoons \text{Car}^-$		Redox potentials of cation radicals and di-cations were used to elucidate reaction mechanisms for carotenoids. ⁷⁴
Iron	0.772 ⁶⁷	1	$\text{Fe}^{2+} \rightleftharpoons \text{Fe}^{3+}$		Iron redox mediator was described in the context of two-step water splitting reaction. ⁶⁸
Kampferol	0.443 ⁴²	2			High-performance liquid chromatography (with UV detection) was used to establish the presence of kampferol in tomatoes. ⁷⁸ Redox activity of kampferol is different in aprotic medium (Dimethyl sulfoxide) compared to water. Nitrogenous nucleophile (e.g. imidazole) was observed to facilitate the electron transfer from kampferol. ⁴³
Malvin	0.49 ⁷²				Liquid chromatography–mass spectrometry confirmed the presence of malvin in tomatoes. ⁴⁰ Electronic absorption spectra revealed the structural changes of malvin, caused by pH changes in the medium, which appeared in its voltammetric behavior. ⁴⁴

Myricetin 0.31⁴² 2

High-performance liquid chromatography with UV detection confirmed the presence of myricetin in tomatoes.⁷⁸ Redox activity of myricetin is pH dependent because of deprotonation. The final oxidation product of myricetin adsorbs on the electrode surface and blocks electron transfer.⁴⁵

Naringenin 0.45⁷² 2

Liquid chromatography–mass spectrometry with UV detection showed the presence of naringenin in tomatoes.⁴¹ The oxidation was irreversible and involved diffusion characteristics.⁴⁶

Naringin - 2

Liquid chromatography–mass spectrometry with UV detection showed the presence of naringin in tomatoes.⁴¹ The peak corresponding to the reduction of the carbonyl group in naringin became smaller with increasing pH, finally vanishing completely in strongly alkaline solutions. Due to this, determination of naringin can be challenging.⁵⁰

Petunidin

-

2

Liquid chromatography–mass spectrometry showed the presence of petunidin in tomatoes.⁴⁰ Hydroxyl groups of petunidin can be electrochemically oxidized. This oxidation is pH dependent process, with the occurrence of adsorption and of oxidation products blocking the electrode surface.⁴⁷

Quercetin

0.33⁴²

2

High-performance liquid chromatography with UV detection showed the presence of quercetin in tomatoes.⁷⁸ Cyclic voltammetry established the electrochemical activity of quercetin in pH range of 4.3 to 11.2.⁵¹

Riboflavin

-0.42²⁹

2

Riboflavins are ubiquitously found in tomatoes.²⁹ Riboflavin molecules impart extracellular respiratory capabilities in *Shewanella oneidensis*.⁶⁶

Liquid chromatography–mass spectrometry with UV detection showed the presence of rutin in tomatoes.⁴¹ The electrochemical oxidation involves a complex process—first, it is oxidized by a two-electron – two-proton reversible oxidation reaction, followed by an irreversible oxidation reaction due to the 5,7-dihydroxyl group. Both mechanisms are pH dependent.⁴⁸

Vitamin C is a ubiquitous component in tomatoes. It facilitates electron transfer to the cytochrome C within the *Chloroflexus aurantiacus*.⁴⁰

Power Density

Impedance Losses

Graphical Abstract