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Supplemental Information

Value Proposition of Untapped Wet Wastes: Carboxylic Acid Production through Anaerobic Digestion

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Transparent Methods

Supplemental Wet Waste Feedstocks: The Untapped Potential (Related to *Introduction* section)

Wet wastes often include wastewater sludge, food waste, animal waste, and fats, oils, and greases (FOG) (BETO, 2017). Recent studies have analyzed the energy potential of these wastes and demonstrated tremendous potential when converted to fuels and chemicals as opposed to landfilling. Based on a series of billion-ton studies focusing on strategic assessment of potential biomass availability, the U.S. Department of Energy estimates approximately 50 million dry tons of combined wet organic waste streams in the United States are available every year for conversion to biofuels, bioproducts, or biopower, which represent an untapped energy potential of nearly 0.7 quadrillion British thermal units (Btu) (BETO, 2017).

The decrease in landfill capacity and stringent disposal regulations have resulted in novel waste management solutions for wet wastes around the world. These wastes are generated from different sectors, but all contain high-energy organic matter. Wastewater sludge describes the solid, semi-solid, or liquid residue generated during wastewater treatment (WWT) in a water resource recovery facility (ECFR, 2018, Seiple et al., 2017). Publicly owned treatment facilities in the United States and China process 29.6 and 19.3 billion gallons of municipal wastewater per day, respectively, and accordingly an estimated 7.2 and 3.3 million dry tons of sewage sludge per year are produced (Wichelns et al., 2015). In addition, Europe produces 10 million dry tons of sewage sludge every year (Milieu Ltd; WRc, 2008). The combined biosolids or sludge production from the United States, Europe, and Asia is estimated to be 25–60 million dry tons per year (Zhang et al., 2018).

Food waste is a biodegradable feedstock with a large organic fraction consisting of food waste created before or after meal preparation, after consumption, and discarded in the process of manufacturing, distribution, retail, and food services. Nearly one-third of the total food production for human consumption is wasted worldwide, accounting for 1.4 billion tons each year (Food and Agriculture Organization of the United Nations). The annual food waste generation from the European Union is estimated to range from 97 to 99 million tons (Fusions, 2016, Pfaltzgraff et al., 2013), whereas in the United States, it is estimated to be the second largest component (38.4 million tons) of the municipal solid waste generated (EPA, 2016).

Animal waste is another major source of wet waste. Meat production is a rapidly growing industry, especially in Asia, and the total number of pigs in the world has risen to 769.2 million (Statista, 2018, USDA, 2015). Average daily pig waste or manure production is estimated to be 4.67 kilograms (kg) per day per animal, leading to 1.4 billion tons of manure production annually worldwide (ASABE, 2005). Moreover, domestic and commercial food-producing industries generate large quantities of FOG, which are all structurally lipids and are mainly categorized by three elements: inedible animal fats, brown grease (rendered trap grease), and yellow grease (rendered used cooking oil). FOG has a high energy content making it an important feedstock for energy production (Suto et al., 2006, Long et al., 2012, Muller et al., 2010, Kabouris et al., 2009). Figure 1 shows the distribution of waste in the United States along with individual energy potential in gallons gasoline equivalent (GGE), resulting in an annual energy resource of 11.3 billion GGE (Skaggs et al., 2018).

Supplemental Issues Pertaining to Biogas Production (Related to *Biogas or Carboxylic Acids: What is the Valorization Pathway?* section)

If the biogas from AD process is not handled effectively, the emission of CH_4 in the atmosphere could be hazardous and penalized heavily for GHG emissions. Also, the overall positive impact of AD in terms of GHG emissions would be diminished if only a small percent of gas is emitted as the global warming potential of CH_4 is 23 times of CO_2 (Kleerebezem et al., 2015). Moreover, the availability of natural gas in abundance have pushed its prices to all time low which makes it an easier choice for customers to purchase cheap fossil-based fuel as compared to biogas produced from renewable sources. In addition, biogas contains a lot of impurities and requires further refining before applications, which increases production costs. Plus, obtaining air permit has been another major barrier due to air and greenhouse gas regulations.

Supplemental Carboxylic Acid Recovery Methods using TOPO (Related to *Economic Perspectives* section)

A cost-effective method is a pertractive unit that continuously extracts the acids by pulling them across a membrane with the assistance of a solvent such as tri-octyl-phosphine oxide (TOPO). This reduces the swing in pH that could happen with producing acids at higher titers. The acids-enriched solvent then is recovered via a distillation column with a targeted 100% acid recovery and 100% solvent recovery (Saboe et al., 2018). It should be noted that if the TOPO solvent does have losses this could add significant operating expenses to the process (Saboe et al., 2018). *In situ* product removal occurs continuously with AD operation. Thus, acid is produced and simultaneously removed using a liquid-liquid membrane extraction system (membrane pertraction) connected through a pump-around loop. The pertractive *in situ* product removal system relies on a TOPO assisted organic phase to selectively remove acid from the broth across a membrane. Short to medium chain acids show relatively low partitioning to the organic phase due to their significant polarity. After extraction to the organic phase, a vacuum is pulled on the mixture and it is routed to distillation for acid purification. The vacuum distillation is critical to prevent dimerization and degradation of the TOPO carrier molecule as well as reduce the boiling point improving the energy efficiency of the integrated plant. The acid is recovered in high purity from the distillate while the mineral oil and TOPO exits from the bottom and is recycled back to a storage tank for reuse in the pertractive unit.

Supplemental Uses of Carboxylic Acids (Related to *Economic Perspectives* section)

Acetic acid (AA) is used mainly for production of polymers, dyes, and chemicals, or as food additives (Maitlis et al., 1996, Qian et al., 2016, Bhatia and Yang, 2017). Butyric acid (BA) is used as an intermediate product to produce other chemicals or as a solvent (Li et al., 2002, Xu and Jiang, 2011, Zigová and Šturdík, 2000), while propionic acid (PA) is mainly used in pharmaceutical products or as a food additive (Zacharof and Lovitt, 2013, Kirillov et al., 2015, Cheryan, 2009). Lactic acid (LA) is most often sold as an 88% solution and its important end uses include lactides (the starting material for polylactic acid and other biodegradable bioplastics), lactate salts, lactate esters and lactylates (IHS Chemical, 2014, Werpy et al., 2004) for applications in food, pharmaceuticals, personal care products, industrial uses, and biodegradable polymers. Similar to PA, butyric acid (BA) has applications in food (Jha et al., 2014) and pharmaceutical industry (Entin-Meer et al., 2005) along with use as a fragrance in the perfume industry in the form of esters

(Armstrong and Yamazaki, 1986); while traditional applications of succinic acid (SA) includes food additives, detergent, cosmetics, pigments, cement additives, and pharmaceutical intermediates (Nghiem et al., 2017).

Carboxylic acids can also be used as carbon source and electron donor for biological removal of nutrients from wastewater (Zheng et al., 2010, Lim et al., 2000, Wang et al., 2015); production of biodiesel (Fontanille et al., 2012); generation of electricity by microbial fuel cells (Choi et al., 2011, Chen et al., 2013b); synthesis of biosurfactants, bioflocculants, or polyhydroxyalkanoates (PHAs) (Li et al., 2011, Chen et al., 2013a, Mengmeng et al., 2009); and synthesis of value-added chemicals such as ethanol (Ma et al., 2014, Uçkun Kiran and Liu, 2015) or yeast flavor (Mantzouridou et al., 2015). Literature have also shown carboxylates—acetate and butyrate, in particular—as a feedstock to produce H_2 via photo-fermentation (Srikanth et al., 2009).

Commercial chemicals such as methanol are used as a carbon source to biologically remove nitrogen from wastewater. However, studies have shown carboxylic acids to be an economical alternative source of carbon for denitrification and a phosphorous removal process that has a high removal rate and efficiency (Zhang et al., 2016a, Zhang et al., 2016b, Liu et al., 2016b, Liu et al., 2016a, Kim et al., 2016). Lim et al. (Lim et al., 2000) showed removal efficiency of 92% for nitrogen and phosphorous with acids obtained from food waste. Tong and Chen (Tong and Chen, 2009) have also reported 83% and 93% of nitrogen and phosphorous removal efficiencies, respectively, using acids produced from waste activated sludge. Such on-site use of carboxylic acids to replace commercial methanol can greatly reduce operating cost in WWT plants.

In addition, short-chain carboxylic acids are desired substrates in microbial electrochemical systems, which is a platform technology to generate direct electricity in microbial fuel cells (Wang and Ren, 2013), high-yield H_2 in microbial electrolysis cells (Lu and Ren, 2016), and even CO_2 reduction and biodiesel production in microbial electrosynthesis (Jiang et al., 2019). Studies have shown higher coulombic efficiency and power density from carboxylic acid-fed microbial fuel cells compared to other substrates such as sugars, proteins, or wastewaters (Chae et al., 2009, Freguia et al., 2010, Teng et al., 2010). Moreover, acids can be used to produce H_2, which is also a byproduct formed during the fermentation process. Photofermentation is one of the methods where light is penetrated through the fermented waste to convert acids—where acetate and propionate are favored in particular to H_2 (Uyar et al., 2009, Zong et al., 2009). Another method is electrohydrolysis, where electrons from direct current and protons from acid electrohydrolysis combine to produce H_2 (Lee et al., 2014, Tuna et al., 2009, Vijayaraghavan and Sagar, 2010). Recent studies have shown waste-derived acids to be an environmentally friendly source to produce microbial lipids that have similar fatty acid composition to soybean and jatropha oil, which can be used for biodiesel production (Fei et al., 2011, Chi et al., 2011, Liu et al., 2017, Huang et al., 2018, Fontanille et al., 2012). Fei et al. (Fei et al., 2011) examined the acids for lipid accumulation and found that the highest lipid content of 27.8% was achieved at 25°C and pH of 6 with high acetic acid concentrations. Similarly, Liu et al. (Liu et al., 2017) show more lipid production from carboxylic acids with high concentrations of acetic acid though it favors alkaline pH, which is best suited for lipid accumulation.

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