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Research paper

Valorization of tomato pomace by sequential lycopene extraction and anaerobic digestion

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ABSTRACT

Tomato pomace, a major byproduct of tomato paste production, is an abundant solid waste stream from food processing in California. Tomato pomace is a rich source of lycopene, a red carotenoid and antioxidant, and lignocellulose, the recalcitrant but energy-rich polysaccharide matrix that comprises plant cell walls. Harvesting both of these co-products could add substantial value to the pomace and potentially reduce waste. In this study, lycopene was extracted from tomato pomace using a mixed organic solvent approach. Yields of lycopene from the tomato pomace tended to be higher than most literature values reported for raw tomatoes, and consistent with many reported values for lycopene in tomato pomace and other products. However, review of the current literature indicates that reported lycopene content of tomatoes products varies by roughly two orders of magnitude, which suggests a need for investigation of the factors responsible for this unusually wide range. After lycopene extraction, direct bioconversion to methane via anaerobic digestion and pretreatment with the ionic liquid 1-ethyl-3-methylimidazolium acetate ahead of anaerobic digestion were explored. Under certain conditions, especially 100 °C for 1 h, pretreatment was beneficial to enzymatic digestion of cellulose. Extraction resulted in a statistically significant reduction in methane yield compared to raw pomace after 90 days of anaerobic digestion. However, supplementation of extracted pomace with the non-lycopene-containing aqueous fraction from the extraction is expected to restore the methane yield to that of raw pomace based on measured values for chemical and biochemical oxygen demand. Ionic liquid pretreatment decreased methane production of extracted pomace.

1. Introduction

Tomato pomace is the principal solid waste stream from tomato paste processing, comprised of skins, pulp, and seeds that are separated from the juice prior to evaporation. California grows and processes most of the United States' tomatoes, and accounts for just over a third of global production [1], which results in at least 60 kt of tomato pomace per season [2], much of which is routed to landfill or animal feed [3]. Since this value was published in 2007, annual production of tomato paste in California has increased by an average about 15% [4], indicating that greater annual quantities of tomato pomace are being produced currently. Value-added coproduct isolation and production from tomato pomace, therefore, represents an opportunity to manage these residues more sustainably, and creates an incentive for industries to facilitate the transition towards renewable bioproducts.

Tomatoes are a rich source of the lipophilic carotenoid lycopene [3], which accounts for up to 98% of carotenoids in tomato [5]. Since it was discovered to be a carotenoid with strong singlet oxygen quenching capability [6,7], lycopene has been characterized as an important dietary antioxidant that may play a protective role against cardiovascular disease and some cancers, and these biological activities have been reviewed previously [8–12]. Additionally, its bright red color allows it to be used as a natural food colorant to replace artificial food dyes that are decreasing in consumer popularity [13].

Many studies over decades have evaluated extraction of lycopene from tomato fruit [3,14], tomato skins [15] and/or tomato products [16,17]. It has been shown previously that lycopene tends to concentrate more in the skins and pulp of tomatoes compared to the water-soluble portions of the fruit [18], and that the quantity therein is often dependent on the cultivar of tomatoes used and the growing conditions [19]. Indeed, several studies have already been

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conducted for extracting lycopene from tomato pomace using both traditional solvents [3,20,21] and supercritical carbon dioxide [3,20,21], and values for lycopene yield tend to be higher than those for whole tomatoes. Currently, lycopene extract for use in food, as outlined by the Food and Agriculture Organization and World Health Organization, is made using crushed whole tomatoes of a variety that tends to be highest in lycopene [22]. The FDA has approved lycopene from tomato as a food additive [23], but not lycopene derived from other sources or made synthetically. Established protocols for lycopene extraction from tomato from the FDA, outlined in the United States Code of Federal Regulations (CFR) [23] and the FAO [22] utilizes traditional solvent extraction with ethyl acetate. Traditional solvent extraction is also used for many other color and nutrient additives obtained from fruit and vegetable extracts listed in the CFR. Solvents are also used in other extraction processes, including soybean oil, where solvent extraction is the most widely used method of oil extraction [24]. Updating the process to utilize tomato pomace, an existing low-value waste stream, as a source of lycopene instead of whole tomatoes expressly grown for lycopene extraction could help to reduce food waste.

In addition to lycopene, tomato pomace is also a source of both simple sugars (roughly 26%) [25] and the more complex carbohydrates that comprise the plant cell wall, also known as lignocellulose (approximately 65% on a dry mass basis) [25,26]. Together, these carbohydrates can serve as a feedstock for biofuel production technologies such as anaerobic digestion. Anaerobic digestion utilizes a diverse community of microorganisms to degrade and convert larger biological molecules into methane through a sequential process consisting of four stages— hydrolysis, acidogenesis, acetogenesis, and methanogenesis [27]. Biomass that is rich in lignocellulose, particularly graminaceous biomass such as wheatgrass or corn stover, is often difficult to ferment because of the recalcitrance of the lignocellulose network. Pretreatment is often used to increase the accessibility or digestibility of this matrix to enzymes and/or microorganisms prior to fermentation. Many types of pretreatment exist for these types of feedstocks, and among the most effective is the use of ionic liquids – salts that are molten at room temperature [28–36]. These solvents have particular appeal because most of them are non-toxic and have the ability to be recycled and reused [37]. Most pretreatment research has focused on these graminaceous residues, and investigations of the pretreatment of fruit and vegetable wastes have been scarce. In a recent study, it was demonstrated that ionic liquid pretreatment can significantly increase the efficacy of enzymatic digestion of tomato pomace with cellulases. However, this effect did not translate to anaerobic digestion process, where ionic liquid pretreatment was shown to have a detrimental effect on methane yield compared to untreated pomace [26]. There is some evidence that a small amount of residual ionic liquid can remain in the pretreated biomass even after thorough rinsing [38], and this could have played a role in reactor performance, as ILs have been demonstrated to be toxic to both yeasts [39] and bacteria [40,41], and it has been demonstrated that adding ILs directly to anaerobic reactors inhibits performance [42]. However, several studies of lignocellulosic biomass have found a beneficial effect of ionic liquid pretreatment on methane production during anaerobic digestion [29,30,42], so it was concluded unlikely that residual IL was the main culprit of the reduction in methane potential. It was hypothesized that antimicrobial compounds may be generated under the high temperature of pretreatment due to reactions between compounds in the pomace that are not typically abundant in conventional lignocellulosic feedstocks, such as water soluble sugars, protein, and oil. Lycopene extraction prior to pretreatment for anaerobic digestion may help to remove other reactive components that contribute to inhibitor formation through pathways such as Maillard browning. Coupling these two processes can also incentivize industry rerouting of waste, and offset the use of fossil fuels for energy.

Previously, extraction of lycopene with traditional solvents has been conducted using moderate temperatures, such as room temperature [3,14,16,17,21,43] to 40 °C [15] and up to 60 °C [20]. Higher temperatures have been investigated for supercritical carbon dioxide extraction, where it has been shown that higher temperatures generally lead to higher lycopene yields up to 70 °C [44], 80 °C [45], 90 °C [46], 86 °C [47], 100 °C [48], and even 110 °C [49]. In addition, enzymatic digestion prior to supercritical CO_2 extraction has been demonstrated to enhance lycopene yield [50]. However, higher temperatures have not been well investigated for traditional solvent extraction, as is evidenced by the literature review summarized in Table 3. It is, however, well established that higher temperatures play an important role in pretreatment of the lignocellulosic material. Often, very high temperatures above 150 °C are used with steam, liquid hot water, or organic solvents and/or caustics, but some studies have investigated lower temperatures to enhance biomass digestibility. Supercritical carbon dioxide extraction at high pressures has been shown to increase the enzymatic digestibility of corn stover and switchgrass at 120 °C [51], and even as low as 60 °C in sugar cane bagasse and crystalline cellulose preparation [52]. Lycopene extraction at higher temperatures and pressures has the potential to affect the digestibility of the tomato pomace and act as a pretreatment to improve lignocellulose bioconversion. However, the benefits of using an extraction procedure as a de facto pretreatment for lignocellulose must be weighed against the possibility of stripping nutrients that could benefit downstream anaerobic digestion.

In this study, lycopene was extracted from tomato pomace using a mixed-solvent approach, using a central composite design to optimize the temperature and extraction duration for maximal lycopene yield. This mixed-solvent approach yielded two phases of extract: a nonpolar phase containing lycopene and other nonpolar compounds, and a polar phase containing soluble sugars, proteins, and other polar compounds. Lycopene in the nonpolar extracts was quantified using a spectrophotometric assay and standard solutions. Reducing sugar content, soluble protein content, chemical oxygen demand (COD), and biochemical oxygen demand (BOD) were determined for the polar extracts. To determine any effect of the extraction process on the enzymatic digestibility of cellulose, extracted pomace was tested for reducing sugar yield during cellulase digestion. Moreover, methane yield of extracted pomace during anaerobic digestion was determined and compared to raw (non-extracted) pomace.

It was previously hypothesized that inhibitor generation during ionic liquid pretreatment stifled methane production during anaerobic digestion [26]. As a follow-up investigation to this phenomenon, some extracted pomace was pretreated with ionic liquid, using pretreatment parameters chosen based on earlier digestibility studies. Reactants for creation of inhibitory compounds were likely to be compounds not found in other graminaceous biomass such as soluble sugars, oils, and unique proteins; therefore, extraction was hypothesized to mitigate the negative effect of pretreatment on the anaerobic digestion process. To test this hypothesis, the extracted and pretreated pomace was also tested for both enzymatic digestibility and methane yield during anaerobic digestion alongside the extracted and raw pomace.

2. Materials and methods

2.1. Tomato pomace

Tomato pomace, consisting of residual skins and seeds from