Coupling hydrothermal liquefaction and anaerobic digestion for energy valorization from model biomass feedstocks

Roy Posmanik [a,b,*], Rodrigo A. Labatut [c], Andrew H. Kim [d], Joseph G. Usack [d], Jefferson W. Tester [a,b,f], Largus T. Angenent [b,d,e,f]

[a] School of Chemical and Biomolecular Engineering, Cornell University, Ithaca, NY, United States
[b] Cornell Energy Institute, Cornell University, Ithaca, NY, United States
[c] Department of Hydraulic and Environmental Engineering, Pontificia Universidad Catolica de Chile, Santiago, Chile
[d] Department of Biological and Environmental Engineering, Cornell University, Ithaca, NY, United States
[e] Centrum for Applied GeoSciences, University of Tübingen, Tübingen, Germany
[f] Atkinson Center for a Sustainable Future, Cornell University, Ithaca, NY, United States

HIGHLIGHTS

- Anaerobic digestion was tested as a complementary step to hydrothermal conversion.
- Hydrothermal liquefaction (200–350 °C) of model feed mixtures was evaluated.
- Changes in hydrothermal conditions substantively altered aqueous phase composition.
- Higher temperature resulted in higher oil yields and lower aqueous phase yields.
- Biodegradability of hydrothermal aqueous phase was lower for higher temperatures.

GRAPHICAL ABSTRACT
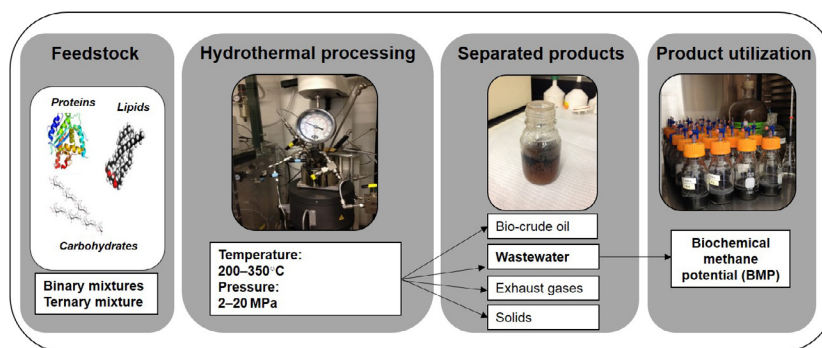
ARTICLE INFO

ABSTRACT

Hydrothermal liquefaction converts food waste into oil and a carbon-rich hydrothermal aqueous phase. The hydrothermal aqueous phase may be converted to biomethane *via* anaerobic digestion. Here, the feasibility of coupling hydrothermal liquefaction and anaerobic digestion for the conversion of food waste into energy products was examined. A mixture of polysaccharides, proteins, and lipids, representing food waste, underwent hydrothermal processing at temperatures ranging from 200 to 350 °C. The anaerobic biodegradability of the hydrothermal aqueous phase was examined through conducting biochemical methane potential assays. The results demonstrate that the anaerobic biodegradability of the hydrothermal aqueous phase was lower when the temperature of hydrothermal processing increased. The chemical composition of the hydrothermal aqueous phase affected the anaerobic biodegradability. However, no inhibition of biodegradation was observed for most samples. Combining hydrothermal and anaerobic digestion may, therefore, yield a higher energetic return by converting the feedstock into oil and biomethane.

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1. Introduction

Because worldwide population continues to increase, so does global demand for food. Developed industrialized countries are required to steadily increase food production, which consequently increases the production of food waste. The amount of food waste in the U.S. has increased by 50% since 1974 (Hall et al., 2009), while based on the National Resource Defense Council (NRDC) the U.S. food-processing industries contributed more than 35 million tons of food waste per year (NRDC, 2012). Recovering nutrients and energy from food waste not only constitutes an opportunity, but also an essential necessity for sustainable operations, especially when considering the negative impacts that landfilled organic materials have on the environment. Anaerobic digestion (AD) has been widely applied for the conversion of food waste and other readily-biodegradable organic waste streams into biomethane, which is then used for heat and electricity generation (Labatut et al., 2011; Zhang et al., 2007). However, in most countries, the lower costs of traditional, fossil-based energy sources have historically challenged the economic feasibility of AD projects as viable renewable energy systems. Furthermore, AD of particulate materials is characterized by slow kinetics, which considerably limits overall biomass conversion and energy yield.

Among other biomass conversion processes, thermochemical processes present an opportunity to reform organic waste into biofuels and bio-based chemicals. Traditional thermochemical processes, such as pyrolysis, can convert biomass to bio-oils or syngas (Pham et al., 2014). However, these processes require a relatively dry feedstock, and thus are not suitable for biomass with high water content such as food waste. In contrast, hydrothermal biomass conversion is a promising technology for resource recovery from wet organic waste streams, because the water in the feedstock is utilized as a reaction medium (Déniel et al., 2016; Peterson et al., 2008; Toor et al., 2011). Hydrothermal processes can produce valuable energy products, while reducing the enthalpy requirement associated with the vaporization of water (Peterson et al., 2008). Specifically, hydrothermal liquefaction (HTL) occurs at temperatures and pressures near and below the critical point of water (374.2 °C and 22.1 MPa), providing ideal conditions for wet biomass conversion into bio-crude oil (Theegala and Midgett, 2012; Toor et al., 2011). Therefore, HTL has been applied to a range of chemical, agricultural, and food wastes (Chen et al., 2014a; Jena et al., 2011; Vardon et al., 2011; Yin et al., 2011). Typical HTL conditions range from 250 to 350 °C and 5–20 MPa for residence times of 10–60 min. These operational parameters enable the rapid hydrolysis of biomass feedstock, which is immediately followed by re-polymerization, decarboxylation, and dehydration processes to produce bio-crude oil (Chen et al., 2014b). HTL bio-crude oil (referred to here as "oil") has similar characteristics to the streams produced during conventional oil refining. Therefore, future production of biofuels, using the available infrastructure for oil refining without large capital investments, is a reasonable and promising application (Elliott et al., 2015).

In addition to having typical oil yields ranging between 40 and 60% (w/w) (Chen et al., 2014a; Elliott et al., 2013; Tommaso et al., 2015), HTL also produces a considerable amount of dissolved organic carbon in the form of an aqueous phase (referred to here as "aqueous phase"). The aqueous phase may be composed of monosaccharides, oligosaccharides, fatty acids, amino acids, and the corresponding degradation products of all macromolecules (Toor et al., 2011). Although there is a lack of information regarding the composition of the aqueous phase, it will largely depend on the characteristics of the feedstock and the operating conditions of the HTL process. For a carbohydrate-rich feedstock as an example, the aqueous phase may contain a considerable amount of 5-hydroxymethylfurfural (HMF) that is a thermo-chemical degradation product of fructose and glucose, and that plays an important role as a chemical building block for bio-oil (Rosatella et al., 2011). In addition, due to their low solubility in water, some oil compounds may be found at low concentrations in the aqueous phase (Elliott et al., 2013). Reducing the amount of dissolved organic carbon in the aqueous phase and/or recapturing this carbon *via* a complementary process should be considered an essential step in HTL development and future deployment.

AD constitutes a potential complementary process that may allow further processing and concomitant resource recovery from the aqueous phase. An initial screening for the biochemical methane potential (BMP) is often performed to quickly gauge whether AD of a certain substrate makes technical and economic sense (Labatut et al., 2011; Owen et al., 1979). In contrast to the initial feedstock, the aqueous phase contains dissolved organic carbon that may be suitable for AD systems and later recovered as biogas (a mixture of CH_4 and CO_2), while a further-treated water can be reused. Tommaso et al. (2015) studied a similar process integration, using algae as the feedstock for HTL. They suggested that the operating conditions (reaction time and temperature) may substantially affect the biodegradability of the aqueous phase. Moreover, they showed a negative correlation between the concentration of cyclic hydrocarbons (derived from the HTL processing of algae) and lag phases observed in the anaerobic digestion of the aqueous phase. In contrast to algae, food wastes are composed of a complex mixture of carbohydrate, protein, and lipid polymers. During HTL, interactions between those compounds may alter further reformation reactions, which may also depend on the different thermal conditions (Savage et al., 2010).

Thus, successful integration of HTL and AD processes will require understanding how the interaction of feedstock heterogeneity and HTL operating conditions affects the composition of the aqueous phase. Specifically, the objectives of this study were to evaluate the energy recovery potential from model feedstocks subjected to combined HTL-AD processing at different thermal conditions and to determine the biodegradability of the resulting aqueous phase. The experimental approach included HTL of four different feedstocks that are relevant as representable proxies for food waste. After reaction in the HTL vessel and phase separation, the aqueous phase was subjected to BMP. The discussion documents the overall energy outlook that can be expected from combining HTL with AD for treating food waste.

2. Materials and methods

2.1. Substrates and chemicals

Here, the four feedstocks consisted of three binary mixtures (1:1) and one ternary mixture (1:1:1, w/w) of carbohydrates (Ch), proteins (Pr), and lipids (Li), resulting in: (1) Ch-Pr; (2) Ch-Li; (3) Pr-Li; and (4) Ch-Pr-Li as feedstocks (Table 1). All model compounds were purchased from Sigma-Aldrich. Potato starch $(C_6H_{10}O_5)_n$ was chosen as the model compound for Ch, because it represents the dominant polysaccharide available in food waste when sourced mainly from potato, corn, and rice residues (Li et al., 2016). Bovine serum albumin (BSA) was chosen as the model compound for Pr because: (i) its chemical structure has been fully-characterized; and (ii) it is highly soluble in water (Rogalinski et al., 2005). Finally, linoleic acid $(C_{18}H_{32}O_2)$ was chosen as the model compound for Li, because it is one of the most common long-chain fatty acids in vegetable oils (Lalman and Bagley, 2000). Each feedstock was analyzed for their C, H, O, and N content. A 1% solution (w/w, 1 g of solid biomass in 100 mL deionized water) of each mixture was subjected to HTL. The total organic carbon (TOC) for each raw feedstock (g/L) was calculated, and the chemical oxygen