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Biomass conversion to bio-oil using sub-critical water: Study of model compounds for food processing waste

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ABSTRACT

The hydrothermal conversions of three model compounds—starch, bovine serum albumin and linoleic acid—and their binary and ternary mixtures were evaluated. Batch experiments were operated at 250–350 °C, 5–20 MPa for 10–60 min. Bio-oil produced from sugars, proteins and their mixtures contained ~70% carbon and ~15% oxygen (w/w) with higher heating values than those of the substrates. When treated individually, bio-oil yields showed the following behavior: lipids > sugars > proteins. Dehydration and condensation reactions among intermediates were hypothesized to enhance the production of bio-oil via the hydrothermal conversion of sugar and lipid mixtures. The ternary mixtures (sugar + oil + protein) exhibit the best performance for bio-oil production, likely due to similar chemical reactions, catalyzed by alkalinity from protein degradation. Results of this study demonstrate that the bio-oil yields for hydrothermal liquefaction of sugars, proteins and lipids may be maximized by selective design of feedstock composition.

1. Introduction

Sustainable management of food wastes is a global challenge. Approximately one-third of food produced globally for human consumption is either lost or wasted [1]. In the U.S., industrial-scale food production produces 36 million tons of food waste per year, generated from animal processing, as well as fruits, vegetables, dairy products and grain production [2]. Natural decomposition of food wastes in landfills produces greenhouse gases such as methane, as well as sludge that contaminates soil and water [3]. On the other hand, food waste represents an excellent resource for renewable energy and nutrient products as it has high caloric and nutritional values [4]. In addition, food wastes are a suitable feedstock for the production of liquid transportation fuels [5,6].

The food industry produces a variety of waste streams that represent potential feedstocks for fuel production. The fruit and vegetable industry, for example, produces large amounts of waste such as peels, shells, seeds and bagasse [3]. These wastes are sources of valuable compounds such as sugars, fibers, fatty acids, and phenolic compounds. The grain industry produces waste generated by the production and processing of vegetable oils (mainly, soybean, sunflower and canola). Vegetable oil production generates partially defatted residues, which are rich in plant fibers, proteins and some lipids [7]. Cheese and yogurt production generates large volumes of liquid waste which is considered to be the major contributor to the environmental pollution from the dairy sector [8]. Whey, for example, is a by-product of yogurt and cheese manufacturing rich in soluble proteins as well as lactose and minerals [9]. The meat and fish processing industries represent another polluting industry due to the high organic contents of their wastes [10], which contain fats, bones, meat, blood, salts and chemicals [11]. Although some of these waste streams are reused, mainly as animal feed, the majority of food processing wastes is not valorized and should be considered as an alternative feedstock for bioenergy production [3]. In addition, all common uses of food waste, which include downstream land application (e.g., composting and animal feed), may lead to the propagation of human and livestock illnesses as a result of foodborne pathogens' survival during common waste management treatments [12].

Hydrothermal biomass processing at temperatures and pressures near and below the critical point (374.2 °C and 22.1 MPa) provides an excellent opportunity for processing food waste streams that contain high water contents [13,14]. Specifically, hydrothermal processing can produce valuable energy products, while reducing the enthalpy requirement associated with the vaporization of water [15]. Typical hydrothermal liquefaction (HTL)

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conditions range from 280 to 380 °C, 7 to 30 MPa (70 to 300 bar) for residence times of 600 to 3600 s (10 to 60 min). In contrast to biological processing, hydrothermal process conditions lead to fast conversion of biomass feedstocks into bio-crude oils that are suitable for upgrading to conventional liquid fuels. HTL also allows the direct conversion of wet biomass into liquid fuel precursors without the need for drying and therefore, it is an attractive technology for wet feedstocks including many food and agricultural waste. In addition, HTL produces an aqueous phase by-product that is completely detoxified and suitable for reuse after supercritical water oxidation post-treatment [16].

Hydrothermal processes have been applied to a variety of chemical, agricultural, and food wastes that include mixtures of organic and inorganic components [13,17–19]. For lignocellulosic feedstocks containing carbohydrates, proteins, and lipids, the hydrothermal reaction medium hydrolyzes and valorizes many components of the biomass. Polymeric macromolecules (cellulose, fatty acids and proteins) are depolymerized into smaller molecules that can be subsequently re-polymerized into oil compounds and char [19]. Since these reformation reactions vary substantially among substrates, it is important to understand the fate of specific streams produced by the food industry (e.g., sugars, protein or lipids) and their mixtures during HTL. Although a number of studies have demonstrated the feasibility for HTL of food waste to produce bio-oil, the effect of feedstock composition on bio-oil yield is only partiality understood. For example, Teri et al. [20] studied hydrothermal conversion of model compounds (cornstarch, cellulose, soy protein, albumin, sunflower oil and castor oil) into bio-crude oil in a small scale system that consisted of ~4 mL tubes. The authors found significant differences among model compounds in term of their sensitivity to temperature (300–350 °C) and reaction time (10–90 min) [20]. However, information regarding chemical interactions between model compounds in mixtures and their degradation products during HTL is missing and needed to understand their contribution to bio-crude oil yields of complex substrates, such as food waste.

The goal of this study is to elucidate the role of feedstock composition, temperature and reaction time during HTL of wet biomass, such as food waste. Model feedstocks, that represent typical polysaccharides, proteins and lipids used in this study, will increase the understanding of the hydrothermal conversion process applied to food waste. Our results may be used as an optimization tool to enhance future implementation of hydrothermal processing under sub-critical conditions.

2. Materials and methods

2.1. Substrates and chemicals

The model feedstocks used in this study, potato starch ($C_6H_{10}O_5$)n, bovine serum albumin (BSA) and linoleic acid ($C_{18}H_{32}O_2$), were purchased from Sigma-Aldrich. Starch was chosen to be the model compound for carbohydrates, as it represents the dominant polysaccharide available in food waste. It was reported that starch accounts for about 35% of food waste sourced mainly from rice and potato residues [21]. BSA was chosen as the model compound for proteins, due to its well-known structure and high water solubility [22]. Vegetable oil mainly consists of triglycerides composed of three fatty acid chains coupled with a glycerol backbone. Free fatty acids and glycerol, produced during an initial hydrolysis reaction, are subjected to further chemical reactions [4,14]. Due to their higher thermal stabilities the fate of free fatty acids in sub critical water was tested here using linoleic acid as a model compound [23]. Linoleic acid was employed as a model compound since it is one of the most common long chain fatty acid present in vegetable oils [23]. Prior to each experiment, substrates were analyzed for their C, H, O and N content (Table 1). For product separation, dichloromethane (DCM), ethyl acetate (EA) and acetone, purchased from Sigma-Aldrich, were used as selective extractants.

2.2. Experimental setup

The HTL batch reactor and sampling system used in this study consisted of a 0.5 L stainless steel, stirred and pressurized vessel (Model 4575 Parr Instruments Co., Moline, IL) (Fig. 1). A high pressure pump (Varian, PrepStar, SD1 system, Agilent Technologies, Santa Clara, CA) was used to inject the feedstock into the reactor and a custom heat exchanger was constructed and connected to the outlet of the reactor to quench the reactions by rapidly cooling the reactor products, and to facilitate sampling at specific reaction times. Prior to each reaction run, 100 mL of deionized water was added to the reactor, and the air was removed by purging with pure nitrogen (N_2) for 5 min. Then, the reactor was pressurized with N_2 up to a pressure of 2 MPa (20 bar) and heated to a specified target temperature. For each run 2 g of biomass dissolved in 100 mL of deionized water were loaded using the high pressure pump. The heating of the biomass feed was rapid by direct contact mixing with the preheated water in the reactor, In fact, the reactor temperature dropped less than 5 °C after the injection. Then, this temperature drop was recovered in less than 3 min due to the temperature controller action. The contents of the reactor were stirred for a specific reaction time using a magnetic agitator. The process variables were controlled through temperature and pressure controllers. After the treatment at the desired temperature, the reaction was quenched by running the effluent through the heat exchanger. In order to clean residual effluents from the reactor and associated tubing, 100 mL of acetone was pumped into the reactor followed by a wash with 100 mL deionized water. This experimental setup improves the precision of batch mode operation compared to traditional batch reactors, as it avoids the extensive heating and cooling periods that are commonly used, which lead to uncontrolled and under designed reactions, and thus, to incorrect conclusions.

2.3. Experimental conditions

The reactor was operated at 250, 300 and 350 °C and 5, 10 and 20 MPa (50, 100, and 200 bar), respectively. For each of these conditions, the experiments were conducted in triplicates for two reaction times: 1200 and 3600 s (20 and 60 min). Severity factor, often used to describe conditions during HTL, combines the effects of processing temperature and reaction time into a single parameter. The severity factor (R_0) provides a measurement of how much reaction has occurred in time t_i at temperature T_i relative to a reference temperature T_b has taken place. Similar values of R_0 *would* lead to similar effects on the reactions than the studied conditions. R_0 scales directly with anticipated conversion of the hydrolysis reactions assuming a lumped first order kinetics model where the log of the conversion is linearly proportional to residence time, and thermal enhancement follows an exponential temperature dependence of the first-order rate constant consistent with Arrhenius behavior [24]. A formula for the severity factor (R_0) that combines a constant reaction temperature with reaction residence time is given in Eq. (1)

$$\log R_0 = \log\left[\sum_{i=1}^{n} t_i \times exp\left(\frac{T_i - T_b}{\bar{\omega}}\right)\right] \quad (1)$$

where t is the reaction time (min) and T_i is reaction temperature (°C), T_b is the base or reference temperature (°C) which in most studies is assigned to 100 °C, ω is a fitted parameter (Eq. (2)), which