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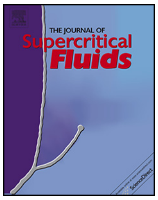

Supercritical water gasification of fructose as a model compound for waste fruits and vegetables

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ABSTRACT

Generous amount of waste food as refused fruits and vegetables are obtained on a global scale that is usually disposed in landfill or oceans. The waste fruits are enriched with fructose, glucose and sucrose along with minor amounts of cellulose and hemicellulose that could potentially be converted to biofuels and biochemicals. With this objective, fructose was used as a model compound of waste fruits and vegetables for gasification in supercritical water using a continuous flow tubular reactor. Different parameters influencing supercritical water gasification were investigated in this study such as temperature (550–700 °C), residence time (30–75 s), feed concentration (4–10 wt%) and catalyst concentration (0.2–0.8 wt%) at a constant pressure of 25 MPa. Total gas yields, carbon gasification efficiency and hydrogen yields improved at an optimal temperature (700 °C), feed concentration (4 wt%) and residence time (60 s). Fructose gasification with 0.8 wt% KOH enhanced the selectivity for hydrogen (10.67 mol/mol) compared to those by 0.8 wt% NaOH (9.86 mol/mol) and non-catalytic gasification (3.37 mol/mol).

1. Introduction

The pragmatic impacts of climate change via increased greenhouse gas (GHG) emissions and overwhelming usage of fossil fuels are global. Substantial quantities of waste food in the form of rotten fruits and vegetables are obtained worldwide that are tossed out in landfill or oceans. These refused food materials by microbial composting or anaerobic digestion release CH_4 that is about 25 times more potent GHG than CO_2 [1]. Waste food is accountable for nearly 20 million tons of CO_2 equivalent GHG emissions per year [2]. There are several reasons for the generation of waste food, a few of which include: (1) overproduction; (2) physical damage to fruits and vegetables during harvesting or threshing; (3) damage by microorganisms, insects and pests on-farm or in-storage facilities; (4) bulk transportation and long lead times; (5) post-harvest sorting of only fresh quality fruits/vegetables by supermarkets and food companies; (6) leftovers from food processing; and (7) consumer behavior for overwhelming purchase and delayed consumption leading to food spoilage [2–4].

The current estimate by Food and Agricultural Organization indicates that about $750 billion worth waste food is generated worldwide every year [5]. In Canada, nearly 40% of the domestic food production goes to the garbage attributing to $27 billion annually [6]. The Canadian estimates indicate that waste food originate as: 51% from household, 18% from packaging/processing, 11% by retail stores in quality control or sorting, 9% on-farm, 8% at restaurants, and 3% during bulk transportation [4,7]. In USA, nearly 40% of food remains unconsumed and tossed out which is worth $43 billion only as household waste [8] and $165 billion as total food waste [9]. An average family of four members in North America usually throw food (including fruits, vegetables, grains and meat) worth $590 annually [8]. In the European Union, about 50% of all fruits and vegetables go to waste throughout the entire food chain

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Abbreviations: CGE, carbon gasification efficiency; CFTR, continuous flow tubular reactor; COSY, correlation spectroscopy; DEPT, distortionless enhancement by polarization transfer; GC, gas chromatography; GHG, greenhouse gas; HMBC, heteronuclear multiple-bond correlation; HMF, 5-hydroxymethylfurfural; HSQC, heteronuclear single quantum coherence; LHV, lower heating value; NMR, nuclear magnetic resonance; SCW, supercritical water; SCWG, supercritical water gasification; TCD, thermal conductivity detector.

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from “farm to fork” [3]. In the European Union, the loss of food produced is attributed as: 5.5% by improper post-harvest handling, 20% by supermarkets and food industries, 7.5% due to expiring best-before-date, and 13% as consumer household garbage for not being consumed.

Fruits and vegetables are quickly perishable due to their higher moisture, acidity and carbohydrate levels. The waste fruits are rich in fermentable sugars such as fructose, glucose and sucrose along with minor amounts of structural cellulose and hemicellulose. In a study on different fruit residues, Choi et al. [10] determined the variation of fruit sugar contents as: 21–39% glucose, 0.7–25% fructose and 17–36% mixed sugars (i.e., arabinose, galactose, mannose, rhamnose and xylose). While, glucose occurs as the structural sugar in fruits, fructose and sucrose are present as soluble free sugars. Sucrose is a disaccharide covalently linking monosaccharides glucose and fructose together. Fructose is a ketonic monosaccharide (6-carbon polyhydroxy ketone) predominantly found in fruits, berries and vegetables.

Due to their high polysaccharide content, waste fruits and vegetable have promising potential for being converted into value-added products such as fuels and chemicals through thermochemical (e.g., pyrolysis, liquefaction, gasification, etc.) and biological (e.g., enzymatic hydrolysis and fermentation) pathways [11]. Recently, a few studies have been reported on the biological conversion of waste fruits and vegetables to ethanol. Choi et al. [10] performed enzymatic hydrolysis and fermentation of various waste fruit residues such as orange, lemon, lime, grapefruit, mandarin, apple, banana and pear. The fermentation using *Saccharomyces cerevisiae* in an immobilized cell reactor resulted in ethanol concentrations of 14.4–29.5 g/L with conversions approaching 90.2–93.1%. Patle and Lal [12] performed acid/enzymatic hydrolysis and fermentation using *Zymomonas mobilis* and *Candida tropicalis* for the reducing sugar and ethanol yields from apple, pineapple, carrot, mango and sapota residues. They reported that acid hydrolysis resulted in 49-84 g reducing sugar and 29–32 g/L ethanol, while enzymatic hydrolysis led to 36–123 g reducing sugars and 11–54 g/L ethanol. With regards to waste food conversion, thermochemical technologies could be more efficient than biological conversion. This is because microbial cell growth is often inhibited by certain components in the waste food such as oils, fatty acids and organic acids e.g., acetic, butyric, lactic and propionic acids [13].

Supercritical water (temperature > 374 °C and pressure > 22.1 MPa) can potentially be used for lignocellulosic biomass gasification to generate a hydrogen-rich gas product [14]. Due to high carbohydrate content in waste fruits and vegetables, their gasification in supercritical water (SCW) could potentially yield H_2-rich syngas and eliminate the cost involved in feedstock drying and acid/enzymatic pretreatment [11]. SCW acts as a reactant, medium and catalyst in the gasification of biomass [15]. However, several parameters such as temperature, pressure, feed concentration, residence time and catalyst influence the gasification of biomass in SCW.

Although promising, there is no available literature on the gasification of waste food to syngas. It is crucial to understand the thermochemical degradation (i.e., pyrolysis, hydrolysis, partial oxidation and reforming) behavior of a biomass model compound before gasifying the real biomass. With this objective, supercritical water gasification (SCWG) of fructose as a model sugar compound for waste fruits and vegetables was performed in this study. The parameters that influence gasification efficiency and gas product composition such as temperature, feed concentration and residence time were thoroughly investigated. Additionally, alkali-based homogeneous catalysts, i.e., KOH and NaOH were employed in the catalytic gasification of fructose for comparative evaluation of gas yield and composition.

2. Materials and methods

2.1. Feedstock and catalyst

D-(−)-Fructose (purity: ≥ 99%, powdered form) was used as a model sugar compound of fruits/vegetables for gasification in SCW. Homogeneous alkali catalysts such as KOH (purity: 99.99%, pellets) and NaOH (purity: 99.99%, pellets) were used to examine their impacts on total gas yields and composition. All the chemicals were purchased from Sigma–Aldrich Canada Co., Oakville, ON, Canada.

2.2. Supercritical water gasification reactor assembly

The gasification experiments were performed in a custom-built stainless steel continuous flow tubular reactor (CFTR). The schematics of the reactor are shown in Fig. 1. The gasification apparatus sequentially consisted of a feed tank, high-pressure pump, pressure gauge, relief valve, check valve, preheater, tubular flow reactor, thermocouple, water-cooled tube cooler, 2 μ filter, back pressure regulator, gas–liquid separator, mass flow meter and other necessary valves and tube connectors. All the tubing, fittings, filters, hoses, valves and tube accessories used in the assembly were made up of stainless steel (SS 316) with pressure resistance more than 35 MPa, and purchased from Swagelok® (Swagelok Central Ontario, Mississauga, ON, Canada).

The feed (fructose) solution was introduced into the reactor using a high-pressure LabAlliance Prep pump (Scientific Systems Inc., State College, PA, USA). The preheater (outer diameter: 0.25 inch, inner diameter: 0.12 inch, length: 12 inch) was placed prior to the SCWG reactor to preheat the feed solution to a desired temperature range of 80–100 °C. The tubular flow reactor (outer diameter: 0.5 inch, inner diameter: 0.37 inch, length: 18 inch) was placed inside an electronically-controlled ATS Series 3210 furnace (Applied Test Systems, Butler, PA, USA). The temperatures of the preheater and furnace were monitored by an ATS Type K, T/C temperature control system (Applied Test Systems, Butler, PA, USA) and recorded using Omega USB 4718 portable data acquisition module (Spectris Canada Inc., Laval, QC, Canada) connected to a computer. The gasification products exiting the tubular reactor were cooled below room temperature by passing through the tube cooler. The pressure of the apparatus during the gasification was controlled by a TESCOM™ 26-1700 series back pressure regulator (Tescom Corporation, Elk River, MN, USA).

The condensed gasification products (liquid and gases) were collected and separated using a gas–liquid separator. The gases passed through a moisture trap (Praxair Canada Inc. Mississauga, ON, Canada) before entering the Delta Smart II mass flow meter (Brooks Instrument, Hatfield, PA, USA). The moisture trap retained any moisture in the gas while the mass flow meter measured the gas flow rates for a particular experiment. The gases were then collected in 500 mL gas sampling Tedlar® bags (Environmental Sampling Supply, San Leandro, CA, USA) for compositional analysis in gas chromatography.

The experiments were conducted at the constant feed flow rates. The products were collected at steady flow rates of feed solution, gas product and liquid effluent after the system attained the steady state condition. The system took nearly 30 min to attain steady state conditions after the set temperature reached the actual/desired stable temperature (550–700 °C). While the high-pressure LabAlliance Prep pump maintained steady flow rate of the feed solution, the flow rate of the gas products was monitored by the Delta Smart II mass flow meter. After each experiment, 2 M H_2O_2 solution was passed through the entire reactor assembly for removing any residual organic species present in the reactor [16]. The H_2O_2 purging was done at room temperature for 40–60 min at the flow rate of 3 mL/min. Prior to each experiment, the reactor was cleaned by