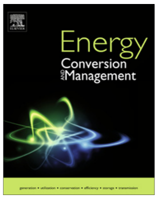
Energy Conversion and Management 110 (2016) 296–306

Contents lists available at ScienceDirect

Energy Conversion and Management

journal homepage: www.elsevier.com/locate/enconman



Gasification of fruit wastes and agro-food residues in supercritical water

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ARTICLE INFO

Article history:
Received 16 October 2015
Accepted 28 November 2015
Available online 30 December 2015

Keywords:
Fruit wastes
Agro-food residues
Supercritical water gasification
Temperature
Reaction time
Feed concentration

ABSTRACT

Considerable amounts of fruit wastes and agro-food residues are generated worldwide as a result of food processing. Converting the bioactive components (e.g., carbohydrates, lipids, fats, cellulose, hemicellulose and lignin) in food wastes to biofuels is a potential remediation approach. This study highlights the characterization and hydrothermal conversion of several fruit wastes and agro-food residues such as aloe vera rind, banana peel, coconut shell, lemon peel, orange peel, pineapple peel and sugarcane bagasse to hydrogen-rich syngas through supercritical water gasification. The agro-food wastes were gasified in supercritical water to study the impacts of temperature (400–600 °C), biomass-to-water ratio (1:5 and 1:10) and reaction time (15–45 min) at a pressure range of 23–25 MPa. The catalytic effects of NaOH and K_2CO_3 were also investigated to maximize the hydrogen yields and selectivity. The elevated temperature (600 °C), longer reaction time (45 min) and lower feed concentration (1:10 biomass-to-water ratio) were optimal for higher hydrogen yield (0.91 mmol/g) and total gas yield (5.5 mmol/g) from orange peel. However, coconut shell with 2 wt% K_2CO_3 at 600 °C and 1:10 biomass-to-water ratio for 45 min revealed superior hydrogen yield (4.8 mmol/g), hydrogen selectivity (45.8%) and total gas yield (15 mmol/g) with enhanced lower heating value of the gas product (1595 kJ/Nm^3). The overall findings suggest that supercritical water gasification of fruit wastes and agro-food residues could serve as an effective organic waste management technology with regards to bioenergy production.

1. Introduction

Climate change, global warming and greenhouse gases (GHG) have become some of the customary terminologies in everyday dialogue. In spite of their rising prices and apparent depleting resources, the increasing consumption of fossil fuels has led to the rise in GHG emissions and resulting global warming. Recently, both edible (e.g., corn and grains) and non-edible (e.g., straw, grasses, sawdust, husk, etc.) plant-derived biomasses have been deployed to produce carbon-neutral biofuels and supplement the energy demand [1]. Furthermore, low cost and refused materials including waste cooking oil as well as plant-based and animal-derived fats have been identified as feasible feedstocks for the production of renewable fuels such as biodiesel [2]. Several thermochemical (e.g., pyrolysis, gasification, liquefaction and torrefaction) and biochemical (e.g., enzymatic hydrolysis and fermentation) pathways are available to convert these biomass to process-specific products such as bio-oils, synthesis gas (or syngas), ethanol and butanol [3,4].

Every year, nearly 20 million tonnes (Mt) of CO_2 equivalent GHG emissions result from waste food [5]. According to a recent report by Food and Agricultural Organization (FAO), about $750 billion worth of waste food is generated globally every year [6]. Annually, 40% of the domestic food production is trashed in USA and Canada, attributing to $165 billion [7] and $27 billion [8], respectively. Food wastes are usually disposed in landfills or incinerated raising several environmental concerns and health risks. Inappropriate management of landfill wastes results in odors, pests and GHG emissions, whereas incineration releases pollutants such as dioxins, furans and particulates [9]. The decomposition of food wastes in landfills is responsible for ~8% of anthropogenic CH_4 emissions [10]. Biogas is a product of anaerobic digestion of organic wastes (e.g., municipal solid waste, plant biomass, livestock manure and food wastes) by methanogenic bacteria.

Abbreviations: BTW, biomass-to-water ratio; CHNS, carbon–hydrogen–nitrogen–sulfur; CGE, carbon gasification efficiency; P_c, critical pressure; T_c, critical temperature; DTA, differential thermogravimetric analysis; FTIR, Fourier transform infrared; GHG, greenhouse gas; HHV, higher heating value; LHV, lower heating value; Mt, million tonne; SEM, scanning electron microscopy; SCW, supercritical water; SCWG, supercritical water gasification; TGA, thermogravimetric analysis; WGS, water–gas shift.

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http://dx.doi.org/10.1016/j.enconman.2015.11.060
0196-8904/

The central component of biogas is CH_4 – a GHG that is 72 times, 25 times and 7.6 times more potent than CO_2 over a period of 20 years, 100 years and 500 years, respectively [11].

The possible reasons for the generation of waste food include: (i) overproduction; (ii) damage to fruits and vegetables during threshing; (iii) damage by microorganisms, insects or pests; (iv) sorting of only fresh quality fruits/vegetables by supermarkets, and (v) overwhelming purchase and delayed consumption [12]. The food waste comprises of spoiled materials from fruits and vegetables, meat and dairy products, and fruit processing wastes (e.g., carp, husk, peel, seeds, shell, skin, etc.) from threshing of fruits. The fruits and vegetables are quickly perishable due to their large carbohydrate and moisture levels. The fruits are rich in fermentable sugars including fructose, glucose and sucrose along with minor amounts of polysaccharides such as cellulose and hemicellulose.

The residues from citrus fruits constitute around 15 Mt of food waste annually [13]. The citrus fruits include grapefruit (*Citrus paradisi*), lemon (*Citrus limon*), orange (*Citrus sinensis*), mandarin (*Citrus reticulata*), pomelo (*Citrus maxima*) and tangerine (*Citrus tangerina*). The global citrus production in 2013 was 135 Mt [14]. The current top five leading orange producers are Brazil (17.5 Mt), USA (7.6 Mt), China (7.3 Mt), India (6.4 Mt) and Mexico (4.4 Mt) [14]. The citrus waste contains both soluble and non-soluble carbohydrate polymers that are potential feedstocks for biofuels and biochemicals.

With extensive farming in tropical and sub-tropical regions, pineapple (*Ananas comosus* L.) production was 24.8 Mt per annum in 2013 [14]. The top five producers of pineapple in 2013 were Thailand (2.2 Mt), Brazil (2.1 Mt), Philippines (1.8 Mt), Costa Rica (1.3 Mt) and India (1.2 Mt) [14]. After harvesting the pineapple, the plant is either used for composting or incinerated to add soil carbon also contributing to air pollution. The stems and leaves of pineapple plants contain ~16% hemicellulose that is hydrolysable to fermentable sugars (pentose and hexose) [15]. Pineapple peel contains high levels of water-insoluble fibers i.e. ~42% of peel by weight [16].

Aloe vera is a succulent plant species cultivated worldwide for its jelly-like parenchyma. It is mainly grown in dry regions including USA, Mexico, South America, India, Africa, Australia, Caribbean and Iran [17]. The mucilaginous gel from parenchymatous cells found under the aloe vera rind is used in medical, cosmetic and nutraceutical industries. With much industrial interest on the gel, the aloe vera rind has deprived attention. Recently, Cheng et al. [18] have demonstrated the production of cellulose nanofibers-reinforced films from aloe vera rind. Aloe vera rind contains glucose, fructose and polysaccharides including glucomannans and polymannose that can supplement biofuel production and promote the local economy.

In 2013, the worldwide production of banana (*Musa acuminata*) was 106.7 Mt with India ranking as the leading producer (27.6 Mt) followed by China (12.1 Mt), Philippines (8.6 Mt), Brazil (6.9 Mt) and Ecuador (6 Mt) [14]. Banana peel is the main banana residue accounting for 30–40% of the total fruit weight [19]. Banana peel contains 60–65% cellulose, 6–8% hemicellulose and 5–10% lignin [20]. Banana peel is gaining industrial interest as a source of livestock feed, antioxidants, proteins, ethanol, methane, pectins, natural flavors, extracts, enzymes and bioabsorbent materials [21]. After harvesting the banana, the pseudostem is considered as a waste that is usually composted as organic fertilizer or used as fodder [22].

Coconut (*Cocos nucifera*) is an essential crop across humid tropical countries with the worldwide production of 62.5 Mt per year [14]. Indonesia (18.3 Mt), Philippines (15.3 Mt) and India (11.9 Mt) are the top three leading coconut producing countries [14]. The coconut flesh has diverse commercial (e.g., cosmetics, shower gels, shampoo, etc.), industrial (e.g., flavors, medicinal and nutraceutical) and household (e.g., food, cooking oil, pest control, etc.) uses. Several wastes generated as a result of the plucking of coconut flesh are the shell, husk and coir. India is the global producer of coir from coconut with quantities as high as 0.6 Mt [14]. Coconut husk and coir are of local interest especially in India (e.g., handicrafts, home décor, mattress, etc.) [23] and gaining worldwide attention as prospective biomaterials for activated carbon, biofibres, biosorbent for heavy metals, particle boards, etc. [20,24,25]. Coconut shell comprises of 32% hemicellulose, 14% cellulose, and 46% lignin [26]. Le et al. [27] suggested the application of coconut shell activated carbon in wastewater treatment, heavy metal remediation and air purification because of its high density, high purity and dust-free construction.

Brazil is the leading sugarcane (*Saccharum* sp.) producing country with 768 Mt of production in 2013 followed by India (321 Mt) and China (128 Mt) [14]. Due to this enormous sugarcane production, Brazil together with USA produces 90% of the global bioethanol [3]. The worldwide sugarcane production per annum is 1.9 billion tonnes [14], which generates 279 million metric tonnes of residues including bagasse and leaves [28]. The sugarcane bagasse is usually the most abundant lignocellulosic waste in tropical countries [29]. The bagasse contains 32–48% cellulose, 19–24% hemicellulose and 23–32% lignin [20]. At present, sugarcane bagasse is integrated into biorefineries and contributes to the production of fuels, chemicals and electricity [29].

As waste fruit residues are excellent sources of numerous value-added materials such as bioactive components (e.g. phenolics), antioxidants (e.g., vitamins and polyphenols), biosorbents, natural pigments, flavors, aromatic agents and perfume oils, there is minimal literature available on their conversion to biofuels. Choi et al. [30] performed enzymatic hydrolysis and fermentation of waste fruit residues namely orange, lemon, lime, grapefruit, mandarin, apple, banana and pear using *Saccharomyces cerevisiae*. Similarly, Patle and Lal [31] performed acid/enzymatic hydrolysis and fermentation of reducing sugars recovered from apple, pineapple, carrot, mango and sapota residues using *Zymomonas mobilis* and *Candida tropicalis* for ethanol production. However, the acidic nature and bioactive components in waste fruit residues impede the fermentation process requiring additional steps for their exclusion from the fermentation media. For example, orange peels contain peel oil (95% D-limonene) that has antimicrobial activity and inhibits the fermentation process [32]. In such a scenario, a hydrothermal conversion process such as supercritical water gasification (SCWG) could be useful to efficiently transform these fruit wastes into biofuels.

Water above its critical temperature ($T_c > 374$ °C) and critical pressure ($P_c > 22.1$ MPa) is called supercritical water (SCW). SCW has liquid-like densities and gas-like transport properties that make it an ideal solvent for biomass processing and conversion. SCWG has been under intense research for the hydrothermal conversion of lignocellulosic biomass to generate hydrogen-rich gas products [33–36]. Hydrogen (H_2) is a clean energy-dense versatile fuel with the highest energy content (120 MJ/kg) compared to conventional fuels [37]. H_2 can be produced from biomass via thermochemical conversion (e.g., pyrolysis and gasification) and biological conversion (e.g., biophotolysis, photo-fermentation and dark fermentation) [38]. Supercritical CO_2 ($T_c > 31.1$ °C and $P_c > 7.39$ MPa) is another industrial solvent that is primarily used in bioactive chemical extraction from food processing residues and organic wastes [21,39,40]. Due to high carbohydrate and polysaccharide contents in fruit wastes and agro-food residues, their gasification in SCW could potentially have higher yields of H_2. Moreover, SCWG can also eliminate the superfluous expenditures associated with feedstock drying [41,42] and enzymatic pretreatment as otherwise required for biological conversion [3]. However, several parameters that govern SCWG include temperature, pressure, feed