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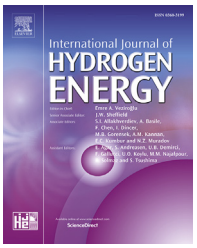

Sustainable hydrogen production options from food wastes

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ABSTRACT

In this study, two thermochemical processes, namely steam gasification and supercritical water gasification (SCWG), were comparatively studied to produce hydrogen from food wastes containing about 90% water. The SCWG experiments were performed at 400 and 450 °C in presence of catalyst (Trona, K_2CO_3 and seaweed ash). The maximum hydrogen yield was obtained at 450 °C in presence of K_2CO_3 catalyst. In second process, hydrothermal carbonization was used to convert food wastes into a high-quality solid fuel (hydrochar) that was further gasified in a dual-bed reactor in presence of steam. The steam gasification of hydrochar was carried out with and without catalysts (iron–ceria catalyst and dolomite). The maximum hydrogen yield obtained from steam gasification process was 28.08 mmol/g dry waste, about 7.7 times of that from SCWG. This study proposed a new concept for hydrogen production from wet biomass, combination of hydrothermal carbonization following steam gasification.

Introduction

Biomass gasification is one of the green hydrogen production methods as the biomass is CO_2 neutral, environmentally clean and well spread all over the world. A number of studies have been published regarding hydrogen production from biomass via different processes. Biomass based hydrogen production technologies can be divided into two general categories: thermochemical and biochemical processes. Biological processes are the steam reforming of gas produced by fermentation, and the direct biological production of hydrogen via the coupled dark and photo fermentation [1]. In thermochemical process, steam gasification is a promising technology, which produces H_2 and CH_4 in higher amounts. But the main problem of conventional steam gasification is the impurities like char and tar. Therefore, purification operations are needed to achieve the required quality standard. Extensive studies have been reported on the tar elimination in steam gasification of biomass. In order to enhance hydrogen production by tar elimination, many catalysts have been studied for steam gasification of biomass [2]. Moreover, the most important drawback of steam gasification is that it becomes very inefficient for a high moisture biomass, due to the necessity of energy intensive drying process. So, for the biomass with high moisture content (up to 90%), biochemical processes or supercritical water gasification are preferable. A major

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limitation of biochemical processes is that they are very slow with a relatively low efficiency and often the case, an additional step for steam reforming of methane is required. On the other hand, gasification in supercritical water media (above 374 °C and 22.1 MPa) is a novel method for conversion of biomass into gaseous product, consisting of mainly CO_2, H_2 and CH_4. The main advantage of supercritical water gasification is the high gasification efficiency and low levels of char and tars [3]. Above the critical point, water exhibited unique properties such as low viscosity, high diffusivity and low dielectric constant. Due to lower the dielectric constant and the number of hydrogen bonds than those of ambient water, supercritical water acts as organic solvent which is effective in dissolving many organic compounds and gases and thus providing the homogeneity in reaction media [4]. Moreover, water does not only behave like solvent, it is also a reactant producing H_2 in SCWG conditions, the conversion of CO with water into H_2 and CO_2 [5].

Supercritical water gasification (SCWG) has received extensive worldwide attention, many studies on SCWG of both model compounds such as cellulose and lignin [6], humic acid [7], glucose [8] and lactose [9] and real biomass such as black liquor [10], horse manure [11], fruit wastes [12], chicken manure [13], algae [5,14] or sewage sludge [15] etc. were conducted. There are some recent reviews [16–18] about the research studies carried out in the last decades. There are two approaches for SCWG of biomass in terms of operating temperature; low temperature SCWG (between 374 °C –550 °C) and high temperature SCWG (between 550 °C –700 °C) [19]. Due to high activation energy of gasification reactions producing H_2, catalysis is necessary for future development of low temperature SCWG technology [18]. The various catalysts have been evaluated to increase H_2 yield with high gasification efficiency. Both homogenous alkali catalysts such as K_2CO_3, NaOH, KOH, $CaCO_3$, Na_2CO_3, $KHCO_3$ and heterogeneous transition metal catalysts mainly as Ni, Pd, Co, Mo and Zn have been tested in previous studies [20–22]. Among them, alkali salts are cost-effective catalysts and enhance water gas shift reaction, providing high H_2 yields [5,18].

Besides SCWG, steam gasification of the hydrochar derived from biomass via hydrothermal carbonization as a pretreatment process may be another option for hydrogen production from the biomass with high moisture content. Hydrothermal carbonization (HTC) occurs in aqueous medium at low temperatures ranging from 160 to 270 °C under autogenic pressure. Because of this, HTC is an especially promising technology for conversion of feedstock having high water content (up to 80%) into a coal-like product, called hydrochar. A number of studies have been performed on hydrothermal carbonization covering a wide range of wastes with high water content, such as grape pomace [23], orange pomace [24], poultry litter [25], sewage sludge [26], olive mill wastewater [27], digestate [28], etc.

Despite the great interest arisen by HTC processes, a few study has been concerned the suitability of HTC as upgrading pretreatment for subsequent biomass steam gasification [15,29]. Gai et al. [15] investigated the steam gasification of hydrochar derived from HTC of sewage sludge. They observed that steam gasification of sewage sludge derived hydrochar resulted in a higher hydrogen yield and energy efficiency than direct steam gasification of sewage sludge. In another study, Álvarez-Murillo reported that hydrochar of olive stone provided improved gasification characteristics [29].

The huge amount of food wastes are being generated over the world and it is an important issue, directly linked with environmental, economic and social impacts. However, they can be considered as a plentiful resource for hydrogen production. In this study, hydrogen production from food wastes was studied. Because food waste is a wet feedstock, hydrothermal processes were chosen as gasification and pretreatment methods. Differently from the studies in the literature, the objective of this study was to investigate the two processes, comparatively, for hydrogen production: (1) supercritical water gasification and (2) conventional steam gasification of the hydrochar derived from food wastes. To the best of the authors' known, the gasification processes have not been investigated with food wastes so far.

Materials and methods

Material

Food wastes (containing 88.6 wt % water) were collected from main hall of Izmir Municipality and then smashed into slurry in a blender. The slurry was stored at −30 °C until use. The hydrochar was obtained by hydrothermal carbonization (HTC) of food wastes. A 150 g slurry of food wastes was loaded into the reactor (V = 500 mL) and sealed. The reactor was heated to 200 °C and kept for 1 h. Resulting hydrochars and aqueous phases were separated by filtration and were oven dried at 105 °C for 24 h. For HTC, process conditions were selected taking into account the mass yield (43.0 wt %) and energy yield (55.9%). The dried hydrochar was ground and passed through a 0.20-mm mesh for steam gasification experiments. The properties of food wastes and their hydrochar are given in Table 1.

In supercritical water gasification experiments, Trona ($Na_2CO_3 \cdot NaCO_3 \cdot 2H_2O$), K_2CO_3 and seaweed ash were used as catalyst. Seaweed ash was obtained by burning seaweed at

Table 1 – Properties of food waste.

	Food waste	Hydrochar
Solid content (as received, wt%)	11.4	–
pH	3.6	–
Proximate analysis (dry, wt%)		
Volatile matter	61.1	46.1
Fixed carbon	33.1	50.7
Ash	5.8	3.2
Elemental Analysis (dry, wt%)		
C	46.7	62.1
H	5.2	5.1
N	2.2	2.5
S	0.2	<0.1
GCV (MJ/kg)	19.0	24.7
Inorganic content (dry, wt%)		
Na	0.01	0.01
K	2.67	1.43
Ca	0.63	0.99
Fe	0.05	0.11

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