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Hydrogen Production by Supercritical Water Gasification of Wastewater from Food Waste Treatment Processes

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Abstract

Korean food wastes have high moisture content (more than 85 wt%) and their major treatment processes such as drying or biological fermentations generate concentrated organic wastewater (CODs of about 100,000 mgO_2/L). For obtaining both wastewater treatment and hydrogen production from renewable resources, supercritical water gasification (SCWG) of the organic wastewater was carried out in this work. The effect of catalyst, reaction temperature, and reactor residence time on COD destruction and composition of gas products was examined. As a result, a SCWG of the wastewater over Ni-Y/activated charcoal at 700 ^oC, 28 MPa yielded 99 % COD destruction and hydrogen-rich gas production (45 vol% H_2). A liquid-phase thermal pretreatment to destroy solid particles from the wastewater was proposed for more effective operation of the SCWG system.

1 Introduction

Million tons of food waste are generated annually in Korea. A unique feature of Korean food waste is the high moisture content (more than 85 wt%). Conventional methods to treat the food waste include anaerobic digestion (biomethanation) and dewatering combined with incineration or landfilling. Anaerobic digestion can produce combustible gas consisting exclusively of methane and carbon dioxide at relatively room temperature and pressure conditions. A critical disadvantage of the anaerobic digestion (biomethanation) is that this technology generates high organic content process water as a byproduct. The wastewater should be re-treated before it is released to nature. Dewatering is one of commercialized methods to treat food waste in Korea due to the process simplicity. However dewatering process also generates organic wastewater as byproduct, which has higher organic content (CODs of about 100,000 mgO_2/L) than the wastewater from biomethanation.

In this work, supercritical water gasification (SCWG) technology is examined to convert the organics in the wastewater from food waste treatment processes to hydrogen-rich gas. The SCWG technology is known to produce hydrogen-rich gas by complete gasification of aqueous organic wastes or wet biomass under appropriate reaction conditions. A wide range of whole organic wastes has been treated by the SCWG processes, including sewage sludge [1,2], agricultural wastes such as potato wastes [3], tannery wastes [4], alcohol distillery wastewater [5], and polyvinyl alcohol-contaminated wastewater [6]. Most efforts of those studies have been focused on obtaining optimal reaction conditions for complete destruction of organics in water and hydrogen production. More fundamental SCWG studies with model compounds as a reactant have also been carried out to understand the gasification chemistry [7-12].

2 Experimental Apparatus and Methods

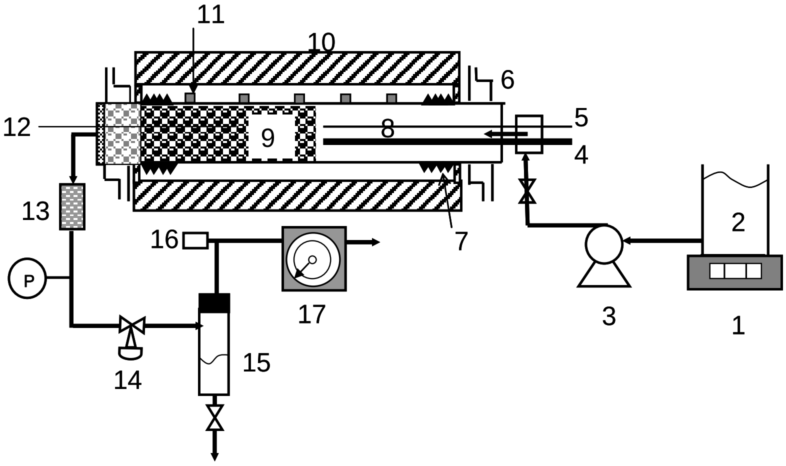


Figure 1: **A schematic diagram of the SCWG system (1, digital balance; 2, feed reservoir; 3, high pressure pump; 4, rod heater; 5, annulus thermocouple; 6, heat exchanger; 7, coiled heater; 8, preheating zone of the reactor; 9, packed-bed of the reactor; 10, furnace; 11, thermocouple mounted on the reactor wall; 12, thermocouple inside the reactor; 13, filter; 14, back-pressure regulator; 15, gas-liquid separator; 16, gas sample outlet; 17, gas flow meter).**

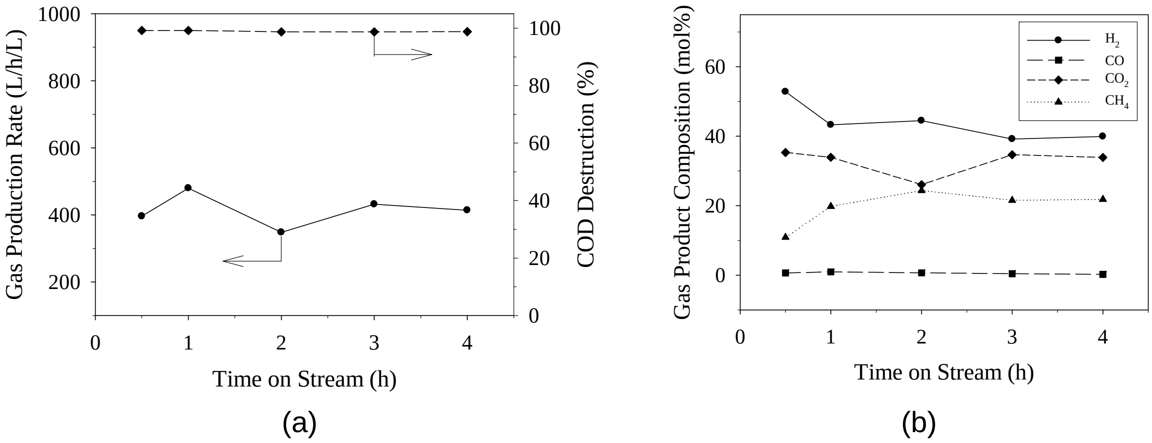
A schematic diagram of the apparatus used in this experiment is shown in Figure 1. The reactor was made of a Hastelloy C-276 tubing with 9.53 mm o.d., 6.22 mm i.d. and 293 mm total length. The reactor consisted of packed-bed of catalyst zone (5.6 cm^3) and reactant preheating zone (3.3 cm^3). The wastewater feeds were delivered into the reactor by a high pressure pump (Waters model 515) and quickly heated to the reaction temperature in the preheating zone by the combination of a coiled heater in the entrance region of the reactor and a rod heater present in the preheating zone of the reactor. Reactor was maintained at a desired temperature by a furnace and another coiled heater in the exit region of the reactor. Reaction temperature was measured by a type K thermocouple installed inside the packed-bed of catalyst. A back-pressure regulator (Tescom model 26-1762-24) was used to reduce the pressure of product flow from 28 MPa to atmospheric pressure. The reactor effluent was disengaged into gas and liquid products in a gas-liquid separator. The flow rate of gas effluent was measured by a wet test meter (Sinagawa model W-NK-0.5A). Liquid product was collected at the bottom of the separator to measure its flow rate. For the catalytic experiments, purified sand was first packed in the cold zone of the downstream of the reactor and then catalyst was consecutively packed in the heating section (about 5.6 cm^3) of the reactor.

Since the original wastewater obtained from the dewatering process of food waste contained significant amounts of solid particles, it was first sieved to less than 0.5 mm to remove big particles and then undertaken thermal treatment at 200 ^oC and 10 MPa to decompose the remaining solid to organic compounds dissolved in water. The product from the hydro-thermal treatment was quenched and its liquid-phase portion was separated to be used as a feed solution for SCWG process. This hydro-thermal treatment of the organic wastewater generated gaseous product to a negligible extent and its amount was not measured in this work. Activated charcoal (Sigma C3014) in 0.42-0.83 mm size was used as a catalyst or a support for nickel catalyst. The activated charcoal contains about 6wt% ash and has a BET surface area of 920 m^2/g. A Ni-Y/AC catalyst was formulated by an incipient wetness method. The weight ratio between Ni and Y per 1g AC support was 0.25:0.0 for the Ni/AC and 0.25:0.10 for the Ni-Y/AC. Nickel(Ⅱ) nitrate hexahydrate (Aldrich No. 203874) and yttrium(Ⅲ) nitrate tetrahydrate (Aldrich No. 217239) were used as precursors. The catalyst was calcined in a nitrogen flow at 500 °C for 3 h, and reduced at 400 °C for more than 10 h under the flow of hydrogen gas.

Compositional analysis of the gaseous products were accomplished with a gas chromatograph (Donam Instruments model DS 6200) using a mixture of 8 % hydrogen in helium as a carrier gas. A thermal conductivity detector was employed for the detection of hydrogen, carbon monoxide, carbon dioxide, and methane, and a flame ionization detector for light hydrocarbons. An 80/100 mesh carbosphere molecular sieve packed column was used. Liquid effluent was analyzed for COD (by closed reflux titrimetric method), and pH (using a pH meter; Orion model 290A).

3 Results and Discussion

The COD value of the original wastewater obtained during dewatering food waste was about 100,000 mgO_2/L and reduced 40 wt% during the pretreatments (sieving and hydrothermal treatment). Figure 2 (a) shows gas production rate and COD destruction as a function of gasification time on stream during the SCWG of the pretreated feed solution at 700 °C, 28 MPa, and 12^{-1} LHSV with Ni-Y/AC catalyst. The gas production rate ranged from 400 to 500 L/h per reactor volume and COD destruction was 99 wt%. The feed solution has pH of 3.3 but the liquid effluent has pH over 7.0. The complete destruction of organic compounds to hydrogen-rich gas was believed to be caused by the catalytic role of the Ni-Y/AC and salts such as NaCl present in the feed solution. Figure 2 (b) shows the content of major constituents in the gaseous product.



(a) (b)

Figure 2: Gasification of pretreated wastewater from the dewatering of food waste in supercritical water at 700 °C, 28 MPa, and 12^{-1} LHSV with Ni-Y/AC catalyst.

The hydrogen content was initially 53 vol% and slightly decreased with time on stream. The methane showed quite different pattern. Carbon monoxide was produced in very small amount, indicating that the water-gas shift reaction was catalyzed in the reaction conditions.

Table 1 displays more experimental data obtained by the SCWGs of the wastewater from the food waste dewatering process. It is evident the presence of salts in the feed solution, which catalyzed the water-gas shift reaction. Activated charcoal (AC) significantly enhanced COD destruction but did not appear to catalyze the water-gas shift mechanism. The formulated Ni-Y/AC catalyst seems to activate hydrogen formation reactions. A bench-scale SCWG reactor (0.2L working volume) has been constructed for the study of system development at our laboratory. It is hoped to report more experimental results on the SCWG treatments of food waste deriven wastewater using the bench-scale reactor in the near future.

Table 1: Effect of temperature and catalyst on the SCWG of the wastewater from food waste processes at 28 MPa and 12^{-1} LHSV.

Reaction conditions				
Catalyst	no	no	AC	Ni-Y/AC
Temperature (^oC)	550	620	600	700
Feed solution				
COD (mgO_2/L)	54,840	54,840	57,600	59,520
TS (%)	3.2	3.2	3.0	<0.1
pH	3.3	3.3	3.7	3.1
Gaseous product				
Production rate (L/h/L)	349	434	523	420
HHV ($kcal/Nm^3$)	2,943	4,157	3,687	3,735
Composition (vol%)				
H_2	33.5	34.1	38.3	43.9
CO	1.5	0.8	1.3	0.6
CO_2	48.0	37.2	37.2	32.8
CH_4	13.9	22.3	19.8	19.7
Liquid effluent				
COD destruction (%)	77	90	99	99
pH	7.2	7.4	7.3	7.6

Acknowledgements

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