HYDROGEN PRODUCTION BY SCWG TREATMENT OF WASTEWATER FROM AMINO ACID PRODUCTION PROCESS

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Summary

The organic wastewater obtained from an amino acid production process was treated by supercritical water gasification (SCWG) method for achieving water purification and hydrogen production. The SCWG experiments were carried out at temperatures of 600-700 ^{o}C and a pressure of 28 MPa using a continuous-flow reactor packed with Ni/activated charcoal catalyst. Complete gasification of organic compounds in the wastewater was achieved at 665 ^{o}C in the presence of the Ni/AC catalyst. Hydrogen fraction in the gaseous product was over 60 mol%. Salts present in the wastewater feed contributed to the high hydrogen yield.

Keywords

Water Purification and Reclamation, Hydrogen Production, Environmental Reaction Engineering

Introduction

Supercritical water gasification (SCWG) is an emerging technology under development for achieving both environmental cleanup and energy recovery by gasifying aqueous organic matters to combustible gases. The SCWG technology can produce H_2 gas by complete gasification of aqueous organic wastes or wet biomass without drying procedure. A wide range of whole organic materials has been treated in SCWG process. Fundamental SCWG studies with model compounds as a reactant have also been carried out to understand the gasification chemistry. Previous experimental results have suggested that catalytic gasification should be employed in order to achieve complete gasification of concentrated organic matters. Many of salts are demonstrated to catalyze gasification of lignocellulosic wastes or their model compounds in supercritical water, but these alkali catalysts also show a negative effect to corrode reactors made of nickel composite tubing[1]. Activated carbon and activated charcoal are found to be relatively stable under SCWG reaction conditions and to catalyze gasification chemistry[2,3]. Supported nickels are reported as effective catalysts for gasification of lignocellulosic compounds in supercritical water[4-7].

In this work, the effect of Ni/AC catalyst on the extent of gasification and gas product distribution was investigated in the SCWG of the organic wastewater from an amino acid production factory. The results were compared with the SCWG performances with aqueous glucose and valine solutions as model compounds for sugars and amino acids in the wastewater, respectively.

Experimental Section

A continuous-flow reactor was used for the SCWG experiments. 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) when solid catalyst was employed. The feed was delivered into the reactor by a high pressure. The feed was quickly heated to the reaction temperature 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 cooling water jacket was employed in front of the entrance coiled heater to prevent preheating of the reactant flow entering the reactor. An identical cooling water jacket was also installed at the exit of the reactor to quench the product flow to ambient temperature. A back-pressure regulator was used to reduce the pressure of product flow from 28 MPa to atmospheric pressure. The

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reactor effluent was disengaged into gas and liquid products in a gas-liquid separator and the flow rate of each product was measured. For the catalytic experiments, 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.

Results and Discussion

Since the original waste collected at the factory had high organic content near 60 wt%, the waste was diluted with water to have CODs of about 30,000 ppm and then centrifuged at 8,000 rpm for 10 min to remove solid particles prior to the gasification tests.

Table 1. Gasification of the dilute molasses-fermented waste in supercritical water at 28 MPa

Temperature (℃)	600	650	700	625	665
Catalyst	no	no	no	Ni/ AC	Ni/ AC
Feed condition					
COD (gO_2/L)	34	31	31	34	31
pH	5.6	5.6	5.6	5.5	4.8
Feeding rate (g/min)	2.6	2.2	1.8	2.3	1.7
Liquid effluent					
COD dest. (%)	76.0	87.3	96.4	99.5	99.8
pH	7.7	8.6	8.8	8.0	8.4
Gaseous product					
Prod. rate (mL/min)	18.7	47.8	60.4	41.3	81.3
Composition (vol%)					
H_2	38.9	52.7	57.3	58.2	65.3
CO	0.8	1.2	0.6	1.0	0.9
CO_2	46.2	28.4	25.5	31.8	24.4
CH_4	11.5	14.2	14.6	8.6	9.2
C_2H_6	1.7	2.9	1.6	0.4	0.2

Table 1 displays SCWG results for the organic waste without catalyst and with the 16 wt% Ni/AC, respectively. Although a complete conversion of organic compounds in the feed was not realized in the absence of catalysts, H_2 content of the gaseous product was very high compared with that from the valine or glucose gasification (less than 30 vol% at the same conditions). This high concentration of H_2 product was partly attributed to the presence of inorganic materials in the waste feed. It is well known that inorganic materials such as K, Na, Mg, Ca that were present in the molasses-fermented waste catalyze water-gas shift reaction (equation (1)) such that H_2 and CO_2 contents increase while CO content decreases .

$$CO + H_2O \rightarrow H_2 + CO_2 \qquad (1)$$

The Ni/AC catalyst in Table 1 appeared to increase H_2 content much more. The CH_4 content in the absence of catalyst increased with increasing temperature probably by the methanation reaction which was relatively suppressed over the Ni/AC catalyst. C_2- and C_3- hydrocarbons were little formed during the runs with the Ni/AC catalyst. The COD destruction was also enhanced under the catalytic conditions. The pH of the liquid effluents from both the valine and the waste gasifications had a range from 7 to 9, which were high values compared with those from the glucose gasification in supercritical water (pH between 2-5). In this work, a significant amount of ammonia that was expected to be present in the liquid effluents might contribute to the high pH value of the liquid effluents. During the clean-up of the reactor after the gasification runs, a small amount of solid product was found in the preheating zone of the reactor. The solid product was collected, dried and analyzed for volatile compounds, ash, and fixed carbon. The ash content of the solid product was over 50 wt% indicating the precipitation of inorganic compounds contained in the molasses-fermented waste feed during the SCWG run. A significant amount of fixed carbon detected in the solid product must be caused by coking reaction at the preheating region. Consequently, an appropriate method should be developed to remove inorganic portion of the waste during the SCWG run.

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