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Hydrothermal catalytic gasification of fermentation residues from a biogas plant



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ABSTRACT

Biogas plants, increasing in number, produce a stream of fermentation residue with high organic content, providing an energy source which is by now mostly unused. We tested this biomass as a potential feedstock for catalytic gasification in supercritical water ($T \geq 374$ °C, $p \geq 22$ MPa) for methane production using a batch reactor system. The coke formation tendency during the heat-up phase was evaluated as well as the cleavage of biomass-bound sulfur with respect to its removal from the process as a salt. We found that sulfur is not sufficiently released from the biomass during heating up to a temperature of 410 °C. Addition of alkali salts improved the liquefaction of fermentation residues with a low content of minerals, probably by buffering the pH. We found a deactivation of the carbon-supported ruthenium catalyst at low catalyst-to-biomass loadings, which we attribute to sulfur poisoning and fouling in accordance with the composition of the fermentation residue. A temperature of 400 °C was found to maximize the methane yield. A residence time dependent biomass to catalyst ratio of $0.45 \text{ g g}^{-1} \text{ h}^{-1}$ was found to result in nearly full conversion with the Ru/C catalyst. A Ru/ZrO₂ catalyst, tested under similar conditions, was less active.

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1. Introduction

Due to the increasing demand for energy and the finiteness of fossil energy carriers, biomass has gained widespread attention as a renewable energy source. Wet biomass has an enormous potential, especially because in many cases these streams are waste products, therefore avoiding competition between fuel and power generation and food production. Anaerobic biological digestion to methane is already a widely applied method for recovering energy from sewage sludge and manure; however, incomplete conversion as well as the slow rate of conversion of a biological process are major drawbacks. Gasification in supercritical water is a promising method to convert biomass efficiently and with a high rate. It requires

the feedstock to be a pumpable fluid, which is, however, not the case for many wet organic waste streams such as grocery wastes. Therefore, a combination of biological digestion with hydrothermal gasification offers advantages for both processes. In this case, biological digestion can be regarded as a pretreatment step for the biomass, during which easily digestible components such as starch and proteins are degraded, reducing the solid content of the biomass and increasing the pumpability. The external energy input to anaerobic digestion is low. The residual digested sludge contains biologically persistent components such as lignin and cellulose, which have been successfully subjected to hydrothermal gasification by different groups [1–4]. In that way, the complementary advantages of both processes are

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combined to yield a maximum efficiency of biomass into fuel conversion. Fermentation residues and other feedstocks containing a broad range of components similar to fermentation residues have been tested for hydrothermal gasification by several authors in a batch [5–7] and in a continuous system [8–11]. Fermentation residues have been continuously gasified at a temperature of 600 °C for hydrogen production [12].

In hydrothermal gasification, including processes operated both in sub- and in supercritical water, the properties of water are advantageous for degrading large biomass molecules to smaller ones [13]. The rate of hydrolysis is greatly enhanced due to the increased ion product of water at subcritical conditions [14]. At supercritical conditions, the good solubility for organic molecules and gases lowers mass transport limitations, and the poor solubility for salts can be utilized for recovering salts in a concentrated form [15–17]. Furthermore, supercritical water conditions were found to suppress coke formation [18,19].

Gasification of wet biomass in low temperature supercritical water (<500 °C) has the advantage of a reduced process energy demand because the specific enthalpy of the water at these conditions is significantly lower than the one of superheated steam at low pressure and the same temperature. Methane, which is the thermodynamically favored product at low temperatures, can be distributed over an already existing gas pipeline system. However, an efficient conversion of biomass at low temperatures requires the use of a catalyst.

In this study, the residue of an anaerobic digestion plant converting grocery wastes into biogas was evaluated regarding its suitability for a further degradation to methane via catalytic gasification in low temperature supercritical water with a combined nutrient salt recovery [20].

Parametric experiments were performed in a batch reactor system in order to screen for the optimum conditions with regard to a future test in a continuous gasification system. The influence of different parameters was tested independently. Some of the experimental conditions were chosen to simulate the preheating section of the continuous process, i.e. by applying subcritical temperatures with no catalyst present. Other experiments corresponded to the conditions prevailing in the salt separator and the catalytic reactor, respectively. Regarding the preheater, the coke formation tendency of the feedstock and the influence of different alkali compounds on it were studied. Regarding the salt separator, we focused on the separation of biomass-bound sulfur. Sulfur is known to have a poisoning effect on the catalyst and therefore needs to be separated before the catalytic reactor in a continuous system [21–23]. For the reactor, two different supported ruthenium catalysts were tested, and the reaction temperature was varied. The influence of reaction time at supercritical conditions was also investigated. This parameter cannot be transferred directly to a continuous system because of the different hydrodynamic situation. By monitoring the time dependent pressure changes, the effective reaction time was determined. Using this effective reaction time, a proposal was made for correlating the reactivity in the batch system to the expected one in a continuous fixed-bed system. Ruthenium was used as catalyst because it has a good activity and selectivity towards methane production as well as a good stability in the hydrothermal environment [24–26].

2. Experimental

2.1. Compositional analysis of the fermentation residue

Water content and loss on ignition (also reported as “residue on ignition” or “minerals”) were determined following standardized procedures [27,28]. For elemental composition analysis, the fermentation residue was first digested by *aqua regia* using a microwave oven (Multiwave 4000, Anton Paar) and then analyzed with ICP-OES (Cirros, Spectro). Additionally, the dry matter (DM) was analyzed with a CHONS-analyzer (LECO). Sulfate was determined by ion chromatography (Dionex Summit), equipped with a Metrosept A Supp 5 analytical anion separation column (Metrohm), an ASRS 300 anion suppressor (Dionex), and an ED 50 electrochemical detector (Dionex) in the conductivity mode. As mobile phase, a mixture of 1 mmol L⁻¹ NaHCO₃ and 3.2 mmol L⁻¹ Na₂CO₃ was used.

For the analysis of macromolecules, a method adapted from fodder analysis was applied [29]. The method comprises a stepwise extraction and gravimetric determination of the following components: substances soluble in a neutral detergent solution, substances soluble in an acid detergent solution (hemicelluloses), substances soluble in 72% (wt/wt) sulfuric acid (cellulose), acid insoluble substances (lignin and acid insoluble ash). The extraction was performed in specific filter bags F57 for Fiber with a pore diameter of 25 μm, purchased from Ankom Technology, USA. The extraction solutions were purchased from the same company. The fermentation residue was wet sieved over a 250 μm sieve and dried prior to extraction. This was done in order to remove particles of small size, which would otherwise pass the pores of the filter bag and thus lead to an overestimation of soluble substances. The particle size distribution was determined as a slurry with a particle size analyzer (CILAS 1190 wet, detection range 0.04–2500 μm).

2.2. Liquefaction and gasification experiments

The gasification experiments were conducted in a 316 stainless steel reactor (HiP, USA) with an inner volume of 52.5 mL. The reactor was flushed with argon before the experiment. For the experiments with catalyst, the reactor was pressurized with 4 MPa of argon in order to reduce evaporation of water during the heat-up phase. Since the presence of argon was found to have no significant influence on the product composition, the heat-up experiments were performed without argon. In this case, the reactor was evacuated before the experiment. The reactor was heated in a preheated fluidized sand bath. A thermocouple in contact with the reactor contents was used to monitor the effective reaction temperature. A stainless steel capillary was attached to the reactor, connecting the reaction chamber with the monitoring section containing a pressure sensor and a valve for withdrawal of gaseous reaction products after the experiment. The monitoring section with a total volume of ca. 2 mL was not heated. The reaction was quenched by immersing the hot reactor in a cold-water bath.

The fermentation residue was used as received but was not previously dried in order to avoid loss of volatile compounds. For maintaining a stable quality of the fresh fermentation residue, it was stored in a refrigerator. Only for the heat-up

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