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# Hydrothermal processing of fermentation residues in a continuous multistage rig – Operational challenges for liquefaction, salt separation, and catalytic gasification

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## ABSTRACT

Fermentation residues are a waste stream of biomethane production containing substantial amounts of organic matter, and thus representing a primary energy source which is mostly unused. For the first time this feedstock was tested for catalytic gasification in supercritical water ( $T \geq 374$  °C,  $p \geq 22$  MPa) for methane production. The processing steps include hydrothermal liquefaction, salt separation, as well as catalytic gasification over a ruthenium catalyst in supercritical water.

In continuous experiments at a feed rate of  $1 \text{ kg h}^{-1}$  a partial liquefaction and carbonization of some of the solids was observed. Significant amounts of heavy tars were formed. Around 50% of the feed carbon remained in the rig. Furthermore, a homogeneous coke was formed, presumably originating from condensed tars. The mineralization of sulfur and its separation in the salt separator was insufficient, because most of the sulfur was still organically bound after liquefaction.

Desalination was observed at a salt separator set point temperature of 450 °C and 28 MPa; however, some of the salts could not be withdrawn as a concentrated brine. At 430 °C no salt separation took place. Higher temperatures in the salt separator were found to promote tar and coke formation, resulting in conflicting process requirements for efficient biomass liquefaction and desalination. In the salt separator effluent, solid crystals identified as struvite (magnesium ammonium phosphate) were found. This is the first report of struvite formation from a supercritical water biomass conversion process and represents an important finding for producing a fertilizer from the separated salt brine.

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## 1. Introduction

Synthetic natural gas (SNG) from waste biomass has gained importance as a substitute for the decreasing stocks of fossil fuels. One of its advantages is the possibility to distribute it over an existing grid. Biological anaerobic digestion processes are widely applied for the conversion of biomass to biomethane, which is similar to SNG, however, with an incomplete conversion of organic matter. The fermentation residues are used as fertilizers because of their high content in nutrients. Their organic fraction is not used for energy generation. Gasification in supercritical water is a promising method to convert wet biomass efficiently to SNG and to recover nutrient salts. Gasification of the lignocellulose-rich fermentation residues would offer the possibility to exploit also the residual energetic content of the digested biomass.

Processing in sub- and supercritical water has the advantage of a reduced process energy demand compared to low-pressure steam processes. Furthermore, mass transport barriers for gases and organic molecules are lowered as a result of a change in the water's solvent properties upon heating, thus promoting heterogeneous reactions [1].

The general feasibility of gasifying cellulose and lignin under hydrothermal conditions has been demonstrated by different research groups [2–5]. Natural feedstocks containing a broad range of components similar to fermentation residues have been tested for hydrothermal gasification by several authors in a batch [6–9] and in a continuous system [10–14]. Fermentation residues have been continuously gasified at a temperature of 600 °C for hydrogen production [15]. Issues like catalyst deactivation [11,12], incomplete conversion, or reactor plugging caused by inorganic precipitates or by sticky organic substances [12–15] were reported in all these studies.

A process design developed at the Paul Scherrer Institut (PSI) [16] combines salt separation with catalytic gasification in supercritical water, avoiding blockage and catalyst deactivation by salt precipitates on the one hand and allowing for a recovery of nutrients contained in the biomass on the other hand. Schubert [17] and Müller [18] gasified crude glycerol over 2% Ru/C in the continuous test rig KONTI-2, which is a simplified setup of PSI's hydrothermal gasification process. In the study presented here, a feedstock containing solids was tested for the first time in the KONTI-2 rig.

The liquefaction and gasification of fermentation residues in a batch reactor system under the experimental conditions of PSI's catalytic process have already been reported from an earlier study [19]. Full conversion could be obtained in these experiments in the presence of a 2% Ru/C catalyst. At high biomass-to-catalyst ratios the conversion was incomplete, which was explained by poisoning of the catalyst by the sulfur contained in the fermentation residue. In the continuous process, sulfur is assumed to be mineralized and removed in the salt separator before the catalytic bed.

With the optimum process parameters gained from preliminary experiments in the batch reactor, a first continuous gasification experiment in the KONTI-2 rig was done with fermentation residue from the overflow of the second stage of a two-stage digestion plant. It was a test for obtaining a first

assessment of which process steps behaved as expected and which ones needed further study and testing. These steps included:

- Pumping of the fermentation residue with a newly designed pump for constant feeding of biomass containing solids at low flow rates ( $\sim 1 \text{ kg h}^{-1}$ ) and pressures of up to 35 MPa.
- Liquefaction of the fermentation residue in the preheater
- Splitting-off of N, S, P from the biomass and their conversion to inorganic salts in the preheater and the salt separator (i.e. mineralization)
- Enrichment of salts in the brine effluent and depletion of salts in the stream to the catalytic reactor
- Gasification, water-gas shift, and methanation reactions in the catalytic reactor

Further liquefaction experiments without the catalytic reactor were performed to study the liquefaction and salt separation steps individually.

## 2. Experimental

The continuous test rig KONTI-2 (Fig. 1) with a maximum capacity of  $1 \text{ kg h}^{-1}$  was used for the gasification and liquefaction experiments with fermentation residue. The heated zone is divided into three sections: preheater, salt separator, and catalytic reactor. Flushing was accomplished by a preparative HPLC pump (Varian, PrepStar, Solvent Delivery Module SD-1). For the processing of the fermentation residues, a custom made piston pump, in the following referred to as *slurry feeder* (Fig. 1) was used. It consisted of two 316 LN stainless steel cylinders (Schenker, Switzerland) with a working volume of 2.6 l each that were operated by a hydraulic drive (Bosch Rexroth).

For the liquefaction, the biomass was first heated to near-critical conditions in the tubular preheater (SITEC, stainless steel 316 L, length 1.70 m, I.D. 12 mm). In the salt separator (SITEC, titanium grade 5, length 694 mm, I.D. 12 mm), entering from the top via a dip tube (I.D. 1 mm), the preheated feed stream is further heated to supercritical conditions. A detailed description of the salt separator can be found in Refs. [18,20].

Precipitated salts and other particles with a high density are withdrawn at the lowest point of the salt separator and subsequently cooled in a tube-in-tube cooler. Particles are collected in particle trap 1, while the brine containing the redissolved salts is depressurized by a relief valve (Swagelok) after passing filter 1 (pore size 25  $\mu\text{m}$ ). The flow rate is controlled by a mass flow controller (Bronkhorst, Liquiflow). The desalinated biomass leaves the salt separator at the top and is transferred to the reactor (SITEC, stainless steel 1.4435, length 1.40 m, I.D. 12 mm, O.D. 18 mm) via a heated transfer tube. For the gasification experiment, the reactor was filled with 40 g of 2% Ru/C catalyst from the top to half of the reactor length. The remaining part was filled with 2 mm ZrO<sub>2</sub> extrudates as a non-catalytic bed material. For the liquefaction experiments, the reactor was replaced by an unheated stainless steel tube for the reduction of the dead volume. In this case, the effluent is referred to as "back effluent".

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