



Pressure and time effect over semi-continuous gasification of zootechnical sludge near critical condition of water for green chemicals production



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HIGHLIGHTS

- Near critical condition of water.
- Thermodynamic evaluations for the production of green chemicals.
- Operative condition effect on the SCWG process.

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ABSTRACT

Aim of the paper is the analysis of experimental data from digestate from buffalo sewage gasification carried out at high pressure, close water critical condition. Experiments were performed in a semi-continuous reactor, by loading the biomass, continuously feeding the pressurised water and removing the gas product from the reaction vessel. At a fixed value of temperature (310 °C), two pressure levels were investigated across the water critical pressure (110 bar and 320 bar). According to the expectation, from the treatment of this type of biomass a liquid fraction, containing some components that can be used as chemicals for the “green industries”, was obtained. Aldehydes and carboxylic acids were the main product obtained and the liquid phase composition was revealed to be sensitive to the pressure level, since a more concentrated product was obtained at lower pressure level. In addition, a reaction pathways is proposed coherently to the observed evolution of the liquid phase composition.

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1. Introduction

The hydrothermal processes are defined as chemical–physical processes performed at high temperature (200–600 °C) and pressure (50–400 bar), generally close to water critical point [1]. When this characteristic thermodynamic point is overcome, a real super-critical water gasification process (SCWG) takes place but, also in case of lower temperature or pressure but close to water critical point, some valuable products can be obtained [2]. Compared to the traditional gasification, these processes have considerable advantages, especially when the matrices to be treated (biomass/waste) show a high moisture content (>70%), very common

occurrence when dealing with real biomasses. The adoption of high pressure in hydrothermal processes can lead to significant gains, if compared to the traditional treatments [3], for three main reasons:

1. Not pre-drying stage (high energy consuming step) is requested in order to reduce the moisture content of biomasses. Under these operative conditions, the water acts is involved in the gasification reaction, being also able to solubilise organic compounds such as tars which otherwise should be removed outstream as in conventional gasification processes.
2. Raw materials containing lignocellulosic fraction, fatty acids and proteins can be processed through hydrothermal processes, obtaining different bio-products such as biogas, methane, hydrogen, biocrude oil, biodiesel. In addition, under controlled

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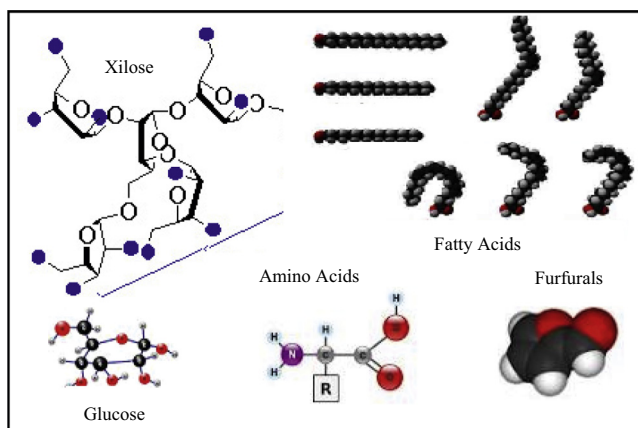


Fig. 1. Reaction intermediate near water critical conditions.

conditions, several intermediate compounds as shown in Fig. 1 can be obtained.

- In these conditions the mass transfer across the phases is eliminated and therefore a higher reaction rate beyond to more effective separations and purifications. Furthermore, the products resulting from hydrothermal processes are completely sterilized avoiding the formation of pathogenic organisms such as toxins, bacteria and viruses.

Different studies [4,5] have demonstrated that, in high pressure processes, even under critical water pressure, the carbohydrates in biomass are rapidly hydrolyzed into monosaccharides and also that the rapidly isomerises glucose into fructose. Fructose is rapidly degraded through isomerization reactions, dehydration, defragmentation, rearrangement and recombination. The spectrum of products is very complex and includes phenols, furans, acids and aldehydes which can then be converted into gaseous products (in supercritical conditions) or liquid/solid (in subcritical conditions). On the other hand, the study of the glucose and fructose decomposition as model substrate, represents the first step for the development understanding these complex reaction mechanisms [6,7]. Referring to the valuable compounds mentioned above, the main component obtained from this process is the Hydro-Methyl Furfural (HMF) that can be converted to 2,5-dimethylfuran (DMF) which is a liquid biofuel with a greater energy content bioethanol. Oxidation of HMF gives 2,5-furandicarboxylic acid which has been proposed as a replacement for terephthalic acid in the production of polyesters. It can also be converted to gamma-valerolactone, 2,5-furandicarboxylic acid or 2,5-bis(hydroxymethyl)furan [8]. Furfurals are used as solvents in the petrochemical industry or in the solid resins production but they can also be added in the act in the solvents production. Also acetic acid is a common chemical reactant industrially used in the production of polyethylene terephthalate, the most diffused material for plastic bottles.

Cellulose acetate can be used to produce supports for photographic applications, the polyvinyl acetate used in the glues for wood, and in many synthetic fibres. The other carboxylic acid, formic acid, has different applications, although the most common one is related to the salts forming formates, used in the textile, paper, rubber, plastic and in the tanning of leather, but also as artificial flavorings and perfumes. The tridrossibenzene is a phenol used as active compound in the pharmaceutical industry.

In this area experimental data from digestate from buffalo sewage gasification are carried out at high pressure in order to produce liquid fraction containing some components that can be used as chemicals for the “green industries” such as syngas that could be used for the energy support for the same process.

2. Materials and methods

Gasification test were performed by modifying and experimental set up described elsewhere [9].

The tested biomass was digestate from buffalo sewage that was pre-conditioned by anaerobic treatment for about 20 days, after a filtration trough a 3 mm mesh.

The system operates in semi-continuous conditions, by loading the volume of 275 ml of digestate into the autoclave-reactor model Limbo li (Büchi, Switzerland). Whilst 2 ml/min of high pressure water were feed trough an AGP-1 Gradient Pump (Dionex, USA) to reach the constant pressure inside the reactor. After the transient period, need to achieve the operating pressure and temperature (about 120 min), a gas stream was continuously extracted from the reactor.

During each run, the temperature was fixed at 310 °C, whilst the effect of pressure was investigated by performing test at two different pressure levels: 110 and 320 bar. Internal pressure was controlled by using an on-off valve (Model 462007/4000, Buchi). The gas stream leaving the reactor was sent to a single stage condenser, working at atmospheric pressure and 0 °C. This separation stage removed the condensable fraction from the gas stream. Both phases were analysed: the gas phase was investigated using a GC (Hewlett Packard 6890) equipped with a TDC detector.

The liquid fraction was analysed using an on-line GC HP 6890 (Hewlett Packard, USA) equipped with a TDC detector. For aldehydes, determination an optimised analytical method based on HPLC model 1100 equipped with DAD detector and Phenomenex Idro RP 80 column was used (Agilent, USA), whilst sugar and carboxylic acids amount was measured via another optimised analytical technique by using a HPCL (Dionex, USA) equipped with NUCLEOGEL ION 300 OA. In order to gain information about the reaction time, the condensate composition was also analysed as a function of the reaction time. At the end on the test, the composition of the residual liquid fraction in the reactor was also analysed.

The chromatograms show several peaks, each corresponding to a specific molecule. Since a complete series of analytical standard was not available and in order to make a quantitative evaluation of the compounds, each chromatogram was analysed by grouping molecules that possess similar response factors with known ones. The quantitative data was expressed as the sum of the quantities of individual peaks at any portion of the chromatogram, in the text this “class” of compound is identified by the prefix “as”.

3. Results and discussion

The digestate from buffalo sewage, after the pre-conditioning and the filtration stage, showed the total solid residue, as well as the relative amount of fixed and volatile solids, as reported in Table 1.

The pH of the substrate was stable around 7.4 and, in this condition, neither hydroxides nor carbonates were detected but exclusively bi-carbonate. The titration with H₂SO₄ (0.1 N) revealed an alkalinity of about 3.65 g CaCO₃/l. Liquid chromatographic characterisation of the sample, reported in Table 2, clearly indicated that carboxylic acids (as acetic acid) predominates over aldehydic species and furfuryl alcohol.

Table 1
Digestate residue solids analysis after pre-treatment.

Solid residue (wt%) 0.75	
Fixed solids (wt%)	Volatile solids (wt%)
45	55

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