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# Supercritical water gasification of beet residues: From batch to continuous reactor



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## HIGHLIGHTS

- Interest of beet residue gasification (degradation yields and thermodynamics).
- Gasification in a continuous reactor designed for hydrothermal oxidation.
- Comparison between gasification and partial oxidation in a continuous reactor.

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## ABSTRACT

A residue obtained after the distillation of agricultural alcohol called beet residues is gasified in supercritical water to form a mixture of fuel gas. A parametric study and thermodynamic calculations are first proposed in batch reactor. The results show a significant effect of temperature on the overall mass yields. Gasification efficiencies range from 0.60 to 0.90 g g<sup>-1</sup> when temperature increases from 450 to 600 °C. The gas low heating value increases under these conditions from 7.4 to 13.2 MJ kg<sup>-1</sup> of initial dry feedstock. After that, a continuous system designed for hydrothermal oxidation processes has been used. For supercritical water gasification, the reduction of total organic carbon in the liquid effluent output presents a little variation, between 59 and 69%, when the operating conditions are changed. To increase the reaction temperature, supercritical water partial oxidation has been conducted. The highest carbon gasification yield is obtained for the highest equivalent molar ratio, indicating a great interest of partial oxidation. Moreover, the results indicate that this process configuration accepts biomass flow variations without influencing the global efficiency.

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## 1. Introduction

Biomass is the first renewable resource in the world before hydraulic and solar power (Basu and Mettanant, 2009; McKendry, 2002). Hydrothermal biomass gasification is a promising technique for the formation of fuel gases from wet biomass: hydrogen for fuel cells, methane in cogeneration units for the simultaneous production of electricity and heat or the mixture H<sub>2</sub>/CO to produce

synthetic fuel. This technique limits the pre-treatment steps required for various conventional techniques of valorisation, for instance a drying step.

Supercritical water (critical coordinates:  $T_C=374$  °C,  $P_C=22.1$  MPa and  $\rho_C=322$  kg m<sup>-3</sup>) possesses gas like viscosity (better mass transfer) and liquid like density properties (better solvation property). Due to the low value of dielectric constant in the supercritical domain, water becomes completely miscible with many hydrocarbons and gases giving supercritical water a high technological potential (Watanabe et al., 2004). Corrosion issues are also a concern, even without significant addition of an oxidant. Supercritical water gasification is an alternative and complementary technology to “conventional” gasification. It can be particularly relevant for the treatment of wet biomass or organic wastes because it uses biomass water as a reaction medium (Watanabe et al., 2004; Kruse, 2009). The overall reaction is endothermic or slightly exothermic. The first step is the decomposition of the organic matrix. Kinetic works carried out in literature (Lu et al., 2006; Lee et al., 2002; Promdej and Matsumura,

*Abbreviations:* SCWO, supercritical water oxidation; SCWG, supercritical water gasification; SCWPO, supercritical water partial oxidation process; TCD, thermal conductivity detector; TOC, total organic carbon; ER, equivalent molar ratio; LHV, low heating value

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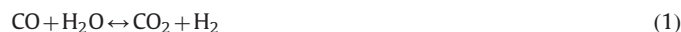
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2011) proposed reaction scheme for glucose as a model compound. At low temperatures and under critical temperature of water ( $T < 374$  °C), the reactions are ionic and intermediate compounds are cyclic compounds. They are recombined to form products with high molecular weights such as tars and chars. Increasing temperature, glucose is first converted into acid by radical mechanisms and then to gases. The gas mixture contains mainly  $H_2$ , CO,  $CO_2$  and  $CH_4$ , adjusted by adapting the operating conditions and / or by using a catalyst (Azadi et al., 2009; Van Rossum et al., 2009; Yanik et al., 2008). Another advantage of this process is to limit gas pollutant emission, due to the low temperature of the process ( $T \leq 700$  °C). Reactions between gases also occur; the main ones are: water gas shift (1) and methanation reactions ((2) and (3)).

Water gas shift reaction:



Methanation reactions:



Concerning the catalytic effects, Antal et al. (1993) show an influence of the reactor wall on the carbon conversion efficiency. The carbon conversion efficiency increases by 0.77 to  $0.9 \text{ g g}^{-1}$  in going from an hastelloy C276 reactor to a corroded hastelloy C276 reactor. Yu et al. (1993) show that the catalytic effect of the wall of the reactors has a significant influence on the conversion yields and composition of gas output. Usually, the volumes of batch reactors used in these studies are very small, with a large ratio surface/volume leading to an enhancement of the catalytic effect. Moreover, the presence of mineral substances or impurities or the addition of catalysts influences the conversion of the raw material (Kruse, 2009; Boukis et al., 2006). The main result is that the alkali salts present in the real biomass increases overall yield of gasification and yield of hydrogen, while that of CO decreases (Yamaguchi et al., 2009): alkali salts catalyse the water gas shift reaction.

As a first objective of this work, in order to derive some knowledge on beet residues gasification and on catalytic effects, a large reactor is chosen in this study, compared with those usually used. A complete experimental study dealing with large variation of process parameters is proposed, on beet residues, glucose and glucose added with catalyst.

As a second objective, research is focused on the implementation of this reaction into a continuous mode, which is a required step prior to large-scale industrialisation. Different types of continuous reactors have been tested at laboratory scale, some of them coming from the concept of gasification processes and others coming from hydrothermal oxidation. A fluidised bed reactor (316L stainless steel, diameter 30 mm, height 915 mm) for biomass gasification in supercritical water has been developed by Lu et al. (2008). It has been designed to avoid plugging problems at temperatures up to 650 °C and pressures up to 30 MPa. Approximately 30 experiments were necessary to achieve the desired experimental conditions, including the aging of the reactor and the mitigation of catalytic activity (passivation). A research team from Twente University in the Netherlands has built and tested a unit called "Process Development Unit". This unit has a capacity of  $5$  to  $30 \text{ L h}^{-1}$  and has been designed for temperatures up to 650 °C and a pressure of 30 MPa. The reactor tube is made of Inconel 825 with an internal diameter of 14 mm and a total length of 15 m. Residence times of 0.5 to 2 min are required to achieve the complete conversion of carbon (Mozaffarian et al., 2004). Research teams from the Karlsruhe centre have built the largest biomass treatment plant by hydrothermal gasification, currently under operation, called VERENA, with an injection flow rate of

$100 \text{ kg h}^{-1}$  (generally up to 20 wt% of dry matter, depending on the nature of the biomass). It was designed to reach 700 °C and 35 MPa. The components exposed to high temperatures are built with a nickel-based alloy (Madenoglu et al., 2011).

Within this context and in order to enhance this approach, the development of continuous supercritical water gasification processes is necessary. In the same conditions of pressure and temperature, another process is developed further than gasification: the hydrothermal oxidation process. The objective of the second part is to study the possibility to adapt a continuous system, already used for oxidation, to biomass gasification. Indeed, many studies have been conducted in the field of supercritical hydrothermal oxidation, offering interesting results to be considered. Two configurations are tested in this work: gasification process and partial oxidation process, in order to increase the medium temperature and to change gas composition. Previous experiments have been conducted on partial oxidation of aqueous wastes (Kipçak and Akgün, 2012) but the two configurations (with or without oxidant) have been scarcely directly compared on the same continuous experimental device.

## 2. Materials and methods

### 2.1. Chemicals products

D-(+)-Glucose (Merck, microcrystalline powder) is used without pre-treatment. Concentrated beet residue comes from agricultural distilleries. It is a high wet product with more than 45 wt% of organic compounds shared between the liquid phase and a solid phase and with a significant content of mineral salts (more than 10 wt%). This biomass can be either filtered, or not, before use. It can also be diluted to adjust the concentration of the solution in the reactor. The mass composition of this biomass is 23.2% of C, 8.4% of H, 53.9% of O, 2.5% of N and 0.1% of S. Table 1 shows the results of different analysis carried out on biomass. Alkaline salts NaCl and KCl used were purchased from Sigma Aldrich. Ultrapure water with resistivity of  $18.2 \text{ M}\Omega$  is used as solvent. The carrier gas ( $N_2$ ) or oxidizing gas ( $N_2/O_2$ : 80/20) are supplied by Air Liquide (France) with a 99% purity.

### 2.2. Batch experiments

The autoclave batch reactor is made of Inconel 625 with  $600 \text{ cm}^3$  volume, manufactured by Top Industries, France, working up to 600 °C and 30 MPa. It is equipped with a stirrer (from 100 to 1500 rpm) that ensures the homogeneity of the mixture. The heating is obtained through heater ceramic collars having an electric power from 1.3 to 2 kW. The cooling is done by a vortex

**Table 1**  
Characteristics of biomass beet residues.

Analysis	Results	Units
Dry matter	58.8	$\text{g g}^{-1}(\%)$
Mineral content	11.4	$\text{g g}^{-1}(\%)$
Organic content	47.4	$\text{g g}^{-1}(\%)$
Total nitrogen	2.4	$\text{g g}^{-1}(\%)$
Ammoniacal nitrogen	0.1	$\text{g g}^{-1}(\%)$
pH	5.8	–
Ratio C/N	9.9	–
Potassium, as $K_2O$	5.9	$\text{g g}^{-1}(\%)$
Sodium, as $Na_2O$	2.6	$\text{g g}^{-1}(\%)$
Density	1.23	–
Moisture content	51.4	$\text{g g}^{-1}(\%)$
Low heating value	14.9	$\text{MJ kg}^{-1}$
High heating value	16.19	$\text{MJ kg}^{-1}$

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